

BUILDING MATERIALS

PROPERTIES, PERFORMANCE AND APPLICATIONS

Donald N. Cornejo

Jason L. Haro

Editors



Materials Science and Technologies Series

NOVA

Materials Science and Technologies Series

BUILDING MATERIALS: PROPERTIES, PERFORMANCE AND APPLICATIONS

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BUILDING MATERIALS: PROPERTIES, PERFORMANCE AND APPLICATIONS

DONALD N. CORNEJO
AND
JASON L. HARO
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PREFACE

Building material is any material which is used for a construction purpose. Apart from naturally occurring materials, many man-made products are in use. The manufacture of building materials is an established industry in many countries and the use of these materials is typically segmented into specific specialty trades, such as carpentry, plumbing, roofing and insulation work. This new book presents a wide variety of research on issues facing the building industry today. A study on the use of syntactic foams as a building material is presented. The acoustic performance of building materials with respect to their insulative properties is also analyzed. Other topics include the performance of building stones in relation to salt weathering, the behavior of building materials submitted to fire, the problem of microbe invasion into building materials and a study to develop a series of experimental methods to determine the moisture transport and storage properties of building materials.

Chapter 1 - Syntactic foams as building materials are studied. Various manufacturing parameters contributing to syntactic foam composition in relation with the 'pre-mould' method were identified and inter-related. An equation based on lattice unit cell models with the minimum inter-microsphere distance concept for a relation between volume expansion rate of bulk microspheres in aqueous starch and microsphere size was derived and successfully used to predict experimental data. A simple method for estimation of syntactic foam density prior to completion of manufacture was suggested. Shrinkage of syntactic foam precursor was discussed in relation with different stages such as slurry, dough and solid. Also, the 'post-mould' buoyancy method involving mixing starch particles and ceramic hollow microspheres in water is discussed in relation with composition and properties. It was found that starch particles tend to adhere to hollow microspheres during mixing, forming agglomerations. A transition in the formation of mixture volumes in water was found to take place at a calculated relative density value of 1 for an agglomerate consisting of multiple starch particles and one microsphere. A Simple Cubic cell model for the starch-microsphere inter-distance was adopted to quantitatively explain various effects on starch content in agglomeration such as hollow microsphere size, initial bulk volume of hollow microspheres and water volume. Further, the following were found for syntactic foams: (a) volume fraction of starch in foam is of linear relation with starch content in binder for a given experimental data range and (b) shrinkage of syntactic foam precursor is relatively high for small hollow microspheres with high starch content. Compressive failure behaviour and mechanical properties of the manufactured foams were evaluated. Not much difference in failure behaviour or in mechanical properties between the two different (pre- and post-mould)

methods was found for a given binder content in syntactic foam. Compressive failure of all syntactic foams was of shear on plane inclined 45° to compressive loading direction. Failure surfaces of most syntactic foams were characterised by debonded microspheres. Compressive strength and modulus of syntactic foams were found to be dependant mainly on binder content but independent of microsphere size. Some conditions of relativity arising from properties of constituents leading to the rule of mixtures relationships for compressive strength and to understanding of compressive/transitional failure behaviour were developed. The developed relationships based on the rule of mixtures were partially verified.

Novel sandwich composites made of syntactic foam core and paper skin were developed. Interface bonding between syntactic foam core and paper skin was controlled by varying starch content. Two different microsphere size groups were employed for syntactic foam core manufacturing. Properties of skin paper with starch adhesive on were found to be affected by drying time of starch adhesive. Skin paper contributed to increase up to 40% in estimated flexural strength over syntactic foams, depending on starch content in adhesive between syntactic foam core and paper skin. Small microsphere size group for syntactic foam core was found to be advantageous in strengthening of sandwich composites for a given starch content in adhesive. This finding was in agreement with calculated values of estimated shear stress at interface between paper skin and foam core. Failure process of the sandwich composites was discussed in relation with load-deflection curves. Hygroscopic behaviour of syntactic foam panels was investigated. Moisture content in syntactic foam was measured to be high for high starch content in syntactic foam panels. No significant moisture effect on flexural strength syntactic foam panels after being subjected to moisture about two months was found. However, substantial decrease in flexural modulus was found for syntactic foam panels made of large microspheres although not much moisture effect was found on that of small microspheres.

Chapter 2 - Soluble salts are one of the main decay agents of building materials, affecting both natural and man-made products applied in old and new constructions, endangering cultural significant structures and thwarting the performance of materials in new buildings. Salts could promote erosive decay (provoking loss of material, mainly by physical action but there are also references to chemical attack) and could also contribute to the formation of coatings, such as the (in)famous "black crusts". The present review will be focused on the response to salt pollution microscopic of macroscopic features of natural building stones, considering predictions of theoretical models, results of simulation experiments and field observations. Several types of rocks (igneous, sedimentary, metamorphic) will be considered, in order to gain information on the influence of textural, mineral-chemical and structural aspects, such as grain size, mineralogical composition (specially relevant to understand chemical susceptibility), presence of heterogeneities, natural anisotropy surfaces (such as bedding) and previous weathering state of the stones (weathering state when extracted from the quarry, before application, an aspect that is particularly relevant for igneous rocks, specially granites, since it affects properties, such as porosity and capillary rise kinetics, that control migration of salt solutions and influence the crystallization position of soluble salts). It is hoped that this review will contribute to identify susceptible geological features that affect the performance of building stones in relation to salt weathering and, in this way, contribute to the discussion on the basis for recommendations about selection of building stone, in relation to foreseeable salt contamination conditions.

“In my beginning is my end.” T. S. Eliot in *East Coker*, N.º 2 of *Four Quartets*. A digital copy can be found <http://www.tristan.icom43.net/quartets/coker.html>.

“The nitre!” I said; “see, it increases. It hangs like moss upon the vaults.”. Edgar Allen Poe in *The Cask of Amontillado*. A digital copy can be found in <http://www.gutenberg.org/dirs/etext97/1epoe10h.htm>.

Chapter 3 - In this chapter, the Boltzmann Transport Equations (BTE) is used to formulate the transport laws for equilibrium and irreversible thermodynamics and these BTE equations are suitable for analyzing system performance that are associated with systems ranging from macro to micro dimensions. In this regard, particular attention is paid to analyze the energetic processes in adsorption phenomena as well as in semiconductors from the view point of irreversible thermodynamics. The continuity equations for (i) gaseous flow at adsorption surface, and (ii) electrons, holes and phonons movements in the semiconductor structures are studied. The energy and entropy balances equations of (i) the adsorption system for macro cooling, and (ii) the thermoelectric device for micro cooling are derived that lead to expressions for entropy generation and system's bottlenecks. The BTE equation is applied to model the adsorption cooling processes for single-stage, multi-stage and multi-bed systems, and the simulated results are compared with experimental data. This chapter also presents a thermodynamic framework for the estimation of the minimum driving heat source temperature of an advanced adsorption cooling device from the rigor of Boltzmann distribution function. From this thermodynamic analysis, an interesting and useful finding has been established that it is possible to develop an adsorption cooling device as a green and sustainable technology that operates with a driving heat source temperature of near ambient. Moreover, the Onsager relations are applied to model the thermoelectric transport equations and, after coupling with Gibbs law and BTE, the temperature-entropy flux derivations are further developed and presented the energetic performances of thermoelectric cooling systems.

Chapter 4 - Microbes – including bacteria, fungi, algae and lichen – are successful invaders of all types of building materials in indoor and outdoor environment on modern and historic buildings. With respect to the numerous problems caused by biogenic spoilage and deterioration of building materials our contribution will present (a) the most important groups of chemoheterotrophic and chemolithotrophic bacteria, cyanobacteria, fungi and lichens occurring on rock, plaster, mortar, paint coatings, plaster board and other building materials; (b) the mechanisms and destruction phenomena caused by microbes ranging from mere esthetical spoilage to significant material losses (c) the environmental factors – humidity, ventilation, nutrient availability - enhancing or inhibiting microbial growth, (d) the state of the art methods for detection and analysis of biodeteriorative organisms and processes especially highlighting the molecular techniques as e.g. genetic fingerprinting of microbial communities and single microbial species (DGGE, RFLP) or quantification of microbes in materials by real time PCR, (e) possible strategies for antimicrobial treatments and preventive measures with focus on pros and cons of hydrophobic treatments, nano-technology based paint coatings and novel disinfectants. The contribution will aim to researchers in the fields of material sciences and building physics as well as to practitioner of building industries, thus descriptions on microbiology and molecular techniques will be given on a high quality but generally understandable level.

Chapter 5 - Moisture accumulation within the material of a building envelope can lead to poor thermal performance of the envelope, degradation of organic materials, metal corrosion

and structure deterioration (Künzel, 1995; Pel, 1995; Qin et al. 2007, 2008a). In addition to the building's construction damage, moisture migrating through building envelopes can also lead to poor interior air quality as high ambient moisture levels result in microbial growth, which may seriously affect human health and be a cause of allergy and respiratory symptoms. Also, human perception of air quality and the transport of volatile and semi-volatile organic compounds through building materials depend largely on the relative humidity. Therefore, the investigation of heat and moisture transfer in porous building materials is important not only for the characterization of behavior in connection with durability, waterproofing and thermal performance, but also building energy efficiency and avoiding health risk due to the growth of microorganisms.

Chapter 6 - Acoustic comfort is increasingly necessary in view of rising levels of noise pollution, especially in medium-sized towns and large cities. According to the WHO, noise pollution today is the type of pollution that affects the largest number of people in the world, second only to air and water pollution. Urban growth, along with the ever increasing number of circulating vehicles, greatly contributes to the higher levels of urban noise emission. Inhabitants of large cities all around the globe complain about noise, reporting irritability, rising blood pressure, headaches, sleep disorders, stress, etc. Considering that traffic and neighborhood noises (neighbors, construction work, religious buildings, commercial, cultural, and leisure activities) disturb people in their homes, it is conceivable that the sound insulation provided by façades and walls are inadequate, resulting in poor acoustic comfort. This chapter analyzes the acoustic performance of building materials with respect to their insulative properties. This performance is evaluated through *in situ* measurements of sound insulation, or alternatively, by computational simulation. This alternative is presented through real case studies in homes. The values found are compared with the limits set by International Standards for acoustic comfort. Techniques for measuring parameters that characterize building materials for acoustic comfort are presented and discussed. This chapter therefore offers an overview of building acoustics and acoustic performance of materials. The advantages and disadvantages of each of these approaches are discussed, as are technical standards in different countries.

Chapter 7 - The strict correlation between indoor radon exposure and potential health hazard to occupants is well known. The indoor radon concentrations mainly depend on radon exhalation from surrounding soil, but also on exhalation from building materials and radon in domestic water supply. The radon emanating from building materials achieves a larger relevance in some areas of the world, where rocks enriched in radon precursors, are used in construction industry, either as cut-stone or in a granular form to prepare cements. The parameter that better expresses the indoor accumulation of radon released by geological materials is the radon exhalation rate. With a view to this, it is very important to study factors that influence the phenomenon and to standardise the experimental procedure to measure radon exhalation rates. An experimental set-up to measure simultaneously ^{222}Rn and ^{220}Rn release from building material is presented. The method makes use of a continuous monitor equipped with a solid-state alpha detector, in-line connected to a small accumulation chamber. Parameters controlling exhalation rates are discussed: temperature, air mixing, humidity and particle size. Guidelines for a standard experimental protocol are advanced and a tentative classification of building materials is proposed on the basis of radon exhalation rates required to reach legal indoor radon action levels.

Chapter 8 - The behavior of building materials submitted to fire points out the important role of water content. The experimental results show in some cases that a significant plateau appears at a given temperature (around 100 °C). The specificity of this study is to presents a coupled hydro-thermal model based on the mechanics of partially saturated porous media. Such a model is used to simulate a thermal loading up to 1100 °C applied on a thin wall. The effect of phase-change phenomenon is taken into account. The model can also takes into account the effect of vapor pressure on the position of plateau. A parametric study is achieved illustrating the influence of: initial water content, intrinsic permeability and the form of isotherm sorption curve on the hydro-thermal response of thin wall. Compared to the experimental curves obtained in Scientific Center and Technical of Building (CSTB France), the predicted results for the phase-change phenomenon by the hydro-thermal model are in accordance with the experimental observations.

Chapter 9 - While recycling of low added-value residual materials constitutes a present day challenge in many engineering branches, attention has been given to cost-effective building materials with similar constructive features as those presented by materials traditionally employed in civil engineering. Bearing in mind their properties and performance, this chapter addresses prospective applications of some elected agroindustrial residues or by-products as non-conventional building materials as means to reduce dwelling costs.

Such is the case concerning blast furnace slag (BFS), a glassy granulated material regarded as a by-product from pig-iron manufacturing. Besides some form of activation, BFS requires grinding to fineness similar to commercial ordinary Portland cement (OPC) in order to be utilized as hydraulic binder. BFS hydration occurs very slowly at ambient temperatures while chemical or thermal activation (singly or in tandem) is required to promote acceptable dissolution rates. Fibrous wastes originated from sisal and banana agroindustry as well as from eucalyptus cellulose pulp mills have been evaluated as raw materials for reinforcement of alternative cementitious matrices, based on ground BFS.

Production and appropriation of cellulose pulps from collected residues can considerably increase the reinforcement capacity by means of vegetable fibers. Composites are prepared in a slurry dewatering process followed by pressing and cure under saturated-air condition. Exposition of such components to external weathering leads to a significant long-term decay of mechanical properties while micro-structural analysis has identified degradation mechanisms of fibers as well as their mineralization. Nevertheless, these materials can be used indoors and their physical and mechanical properties are discussed aiming at achieving panel products suitable for housing construction whereas results obtained thus far have pointed to their potential as cost-effective building materials.

Phosphogypsum rejected from phosphate fertilizer industries is another by-product with little economic value. Phosphogypsum may replace ordinary gypsum provided that radiological concerns about its handling are properly overcome as it exhales radon-222, a gaseous radionuclide whose indoor concentration should be limited and monitored. Some phosphogypsum properties of interest (e.g., bulk density, consistency, setting time, free and crystallization water content, and modulus of rupture) have indicated its large-scale exploitation as surrogate building material.

Chapter 10 - Structural concrete made with recycled aggregates from construction and demolition waste is an eco-efficient solution to reduce both the production of waste and the depletion of natural non-renewable materials. Even though this material shows great potential as an alternative to conventional concrete (made with primary aggregates), its large-scale use

has been hampered by lack of regulation and technical documentation. Furthermore, some production procedures hinder the use of recycled aggregates under normal waste collection conditions.

In this Chapter, the specific problems of preparing concrete with recycled aggregates are addressed and the properties of recycled aggregates *versus* primary (natural stone) aggregates are compared.

A general methodology to predict the long-term performance (in terms of both mechanical properties and durability) of concrete made with recycled aggregates using the corresponding performance of equivalent conventional concrete (reference concrete) is proposed and validated. The approach employed includes an international literature review and a summation of experimental campaigns monitored / supervised by the author.

This methodology allows the early estimation of the properties of concrete made with recycled aggregates based on the properties of the aggregates mix and of young concrete, which can be used both by the structural designer and the contractor, thus effectively removing a barrier to the widespread use of this material.

Chapter 1

SYNTACTIC FOAMS AS BUILDING MATERIALS CONSISTING OF INORGANIC HOLLOW MICROSPHERES AND STARCH BINDER

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ABSTRACT

Syntactic foams as building materials are studied. Various manufacturing parameters contributing to syntactic foam composition in relation with the 'pre-mould' method were identified and inter-related. An equation based on lattice unit cell models with the minimum inter-microsphere distance concept for a relation between volume expansion rate of bulk microspheres in aqueous starch and microsphere size was derived and successfully used to predict experimental data. A simple method for estimation of syntactic foam density prior to completion of manufacture was suggested. Shrinkage of syntactic foam precursor was discussed in relation with different stages such as slurry, dough and solid. Also, the 'post-mould' buoyancy method involving mixing starch particles and ceramic hollow microspheres in water is discussed in relation with composition and properties. It was found that starch particles tend to adhere to hollow microspheres during mixing, forming agglomerations. A transition in the formation of mixture volumes in water was found to take place at a calculated relative density value of 1 for an agglomerate consisting of multiple starch particles and one microsphere. A Simple Cubic cell model for the starch-microsphere inter-distance was adopted to quantitatively explain various effects on starch content in agglomeration such as hollow microsphere size, initial bulk volume of hollow microspheres and water volume. Further, the following were found for syntactic foams: (a) volume fraction of starch in foam is of

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linear relation with starch content in binder for a given experimental data range and (b) shrinkage of syntactic foam precursor is relatively high for small hollow microspheres with high starch content. Compressive failure behaviour and mechanical properties of the manufactured foams were evaluated. Not much difference in failure behaviour or in mechanical properties between the two different (pre- and post-mould) methods was found for a given binder content in syntactic foam. Compressive failure of all syntactic foams was of shear on plane inclined 45° to compressive loading direction. Failure surfaces of most syntactic foams were characterised by debonded microspheres. Compressive strength and modulus of syntactic foams were found to be dependant mainly on binder content but independent of microsphere size. Some conditions of relativity arising from properties of constituents leading to the rule of mixtures relationships for compressive strength and to understanding of compressive/transitional failure behaviour were developed. The developed relationships based on the rule of mixtures were partially verified.

Novel sandwich composites made of syntactic foam core and paper skin were developed. Interface bonding between syntactic foam core and paper skin was controlled by varying starch content. Two different microsphere size groups were employed for syntactic foam core manufacturing. Properties of skin paper with starch adhesive on were found to be affected by drying time of starch adhesive. Skin paper contributed to increase up to 40% in estimated flexural strength over syntactic foams, depending on starch content in adhesive between syntactic foam core and paper skin. Small microsphere size group for syntactic foam core was found to be advantageous in strengthening of sandwich composites for a given starch content in adhesive. This finding was in agreement with calculated values of estimated shear stress at interface between paper skin and foam core. Failure process of the sandwich composites was discussed in relation with load-deflection curves. Hygroscopic behaviour of syntactic foam panels was investigated. Moisture content in syntactic foam was measured to be high for high starch content in syntactic foam panels. No significant moisture effect on flexural strength syntactic foam panels after being subjected to moisture about two months was found. However, substantial decrease in flexural modulus was found for syntactic foam panels made of large microspheres although not much moisture effect was found on that of small microspheres.

1. INTRODUCTION

Syntactic foams are made of pre-formed hollow microspheres (or called microballoons or microbubbles) and binder. They can be used in various structural components including sandwich composites [1, 2] and in areas where low densities are required e.g. undersea/marine equipment for deep ocean current-metering, anti-submarine warfare [3-7]. When they are used as core materials for sandwich composites, they contribute to increase in specific stiffness. They further contribute to not only the reduction in damage and but also the prevention of failure of composite systems by inducing their own damage when used for protective structural components [8]. Their other uses include products in aerospace and automotive industries [9]. The syntactic foams in the past, however, have been relatively heavy compared to the traditional expandable foams, limiting their applications.

A wide range of different types of syntactic foams can be made by selecting different materials and consolidating techniques for binder and hollow microspheres. The consolidating techniques include coating microspheres [10], rotational moulding [11], extrusion [12, 13] and ones that use inorganic binder solution and firing [14], dry resin

powder for sintering [15-18], compaction [19, 20], liquid resin as binder [21] for in situ reaction injection moulding, and buoyancy [8, 22, 23]. The last method (buoyancy) has recently been demonstrated to be capable of control of a wide range of binder contents at low costs, widening applicability of syntactic foams. It allows us to use starch as binder for manufacturing syntactic foams. Starch has some advantages over other binders such as epoxies, phenolics, etc. It is readily available, environmentally friendly, and an inexpensive renewable polymeric binder. Also, low cost hollow microspheres (known as cenospheres) are available as part of fly ash when generated as by-product from a coal-fired power station. Otherwise, they would have been pollutants. For example, the production of flyash as pollutant is expected to be over 140 million tonnes in 2020 in India and waiting to be utilized [24]. Therefore, syntactic foams as new building materials made of such inorganic hollow microspheres and starch binder have begun to attract interests for applications in interior cladding of buildings for which traditionally gypsum boards [25] have been dominantly used.

Compressive failure behaviour of syntactic foams has been studied by many researchers. Narkis et al [10, 15] found that failure of syntactic foams with a low concentration of resin is mainly by disintegration under compression. It was reported, however, that a high density syntactic foam containing under compression failed with formation of 45° shear plane [26, 27]. Recently Kim and Oh [28], and Gupta et al [29] have also reported that failure mode of a syntactic foam with relatively high concentration of resin under uniform compression was by shear on inclined planes. Gupta et al [29, 30] highlighted that the shear failure mechanism is affected by specimen aspect ratio. Kim and Plubrai [8] studied low density (0.11 - 0.15 g/cc) glass/epoxy syntactic foams and found that compressive failure was of 'layered crushing'. Factors affecting the compressive failure behaviour, thus, may include various properties of constituents.

Sandwich composite is a form for application of syntactic foam and may be adopted for various products in building industry. It is meant to be light and stiff for structural components subjected to flexural loads. Various types of sandwich composite can be made by selecting different constituent materials for core and skin. For the selection of constituent materials, factors such as properties and cost may be considered. In building industry, material cost is a driving force in selecting materials when large quantities of materials are required. In applications for interior walls and ceilings, material weight is an important consideration for installation and performance. There have been efforts to reduce the material density in such applications by forming gas bubbles in the case of gypsum [31] but without much success compared to syntactic foams. The mechanical performance of sandwich composites consisting of syntactic foam (for core) and paper (for skin) is generally affected by (a) bonding condition between core and skins requiring consideration of parameters such as microsphere size, (b) starch permeation into paper and (c) starch concentration which are not normally considered in other types of sandwich composites [1, 27, 32, 33]. Such parameters would be potentially important in continuous mass production for optimization when starch is used.

In this chapter, the principles of manufacturing syntactic foams made of cenospheres and starch are introduced, and various recent research findings for

- a) properties of constituent materials for syntactic foams,
- b) mechanical behaviour of syntactic foams, and

- c) behaviour of sandwich panel made of cenospheres and starch for core and paper for skin

are discussed.

2. CONSTITUENT MATERIALS FOR SYNTACTIC FOAMS

2.1. Hollow Microspheres

Ceramic hollow microspheres (composed of silica 55-60%, alumina 36-40%, iron oxide 0.4-0.5% and titanium dioxide 1.4-1.6%) supplied by Enviro-spheres Pty Ltd, Australia were used. Four different size groups (or commercial grades), SL75, SL150, SL300 and SL500, were employed. Scanning electron microscope (SEM) images of hollow microspheres are given in Figure 1.

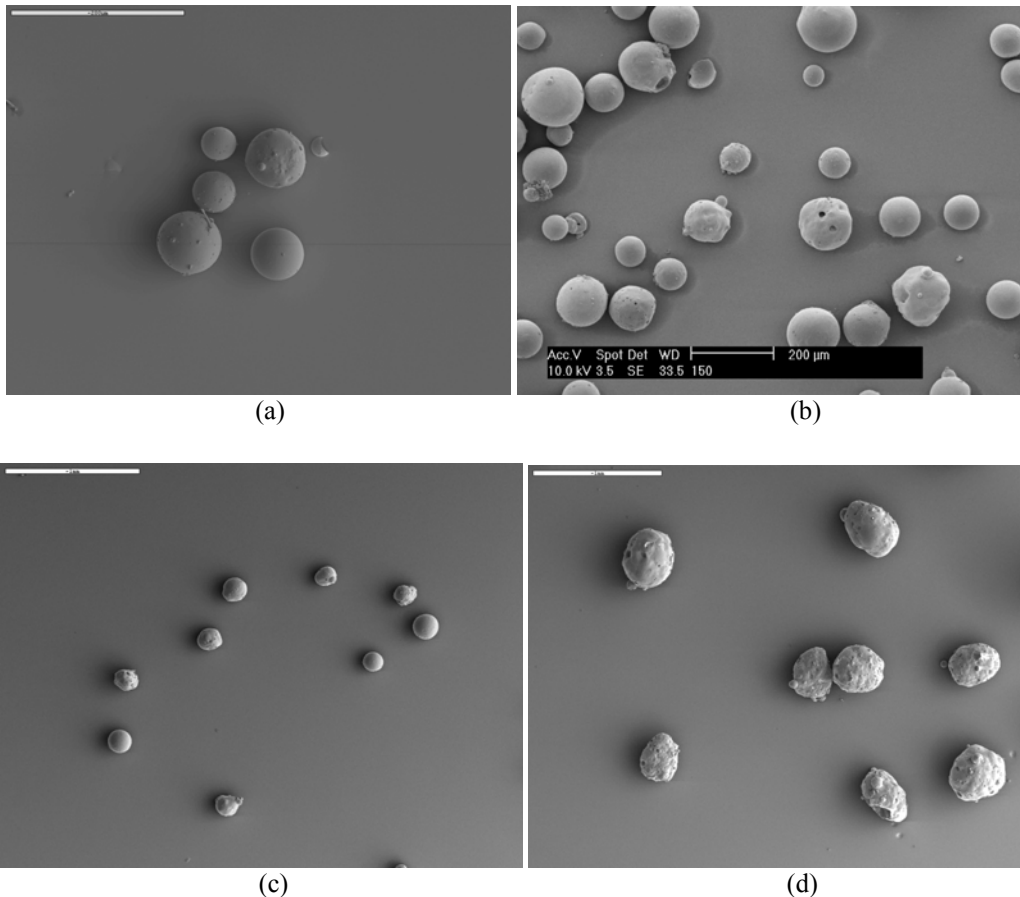


Figure 1. SEM images of hollow microspheres: (a) SL75 (the scale bar represents 200 µm); (b) SL150 (the scale bar represents 200 µm); (c) SL300 (the scale bar represents 1 mm); and (d) SL500 (the scale bar represents 1 mm).

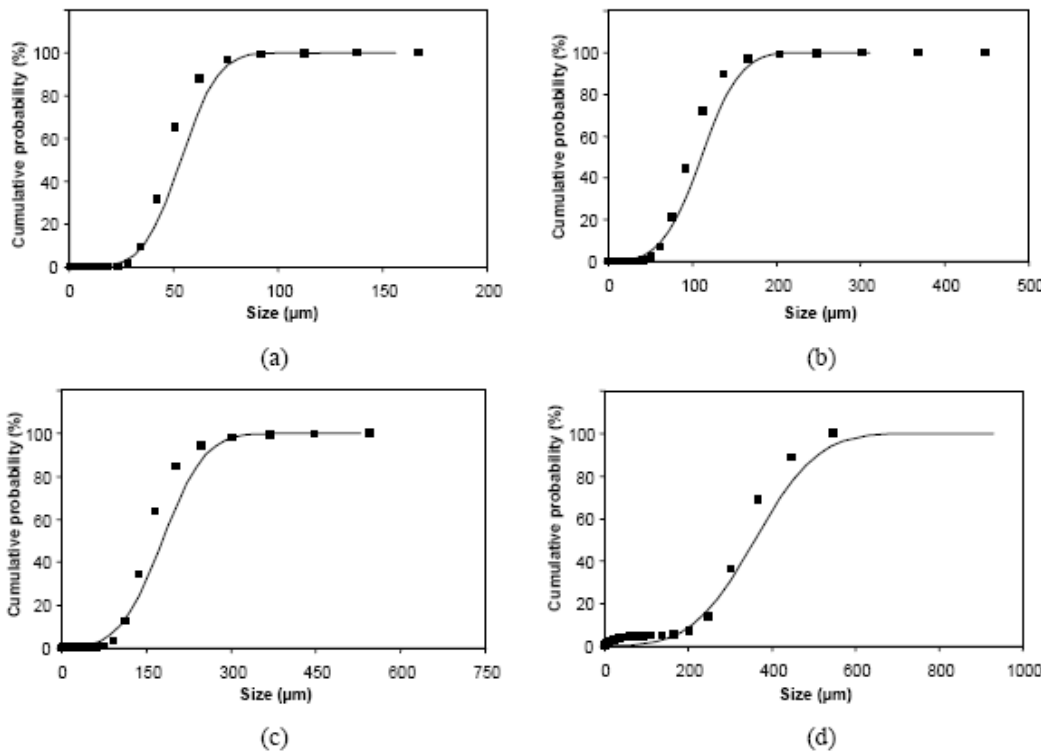


Figure 2. Size distributions of different hollow microsphere size groups with the cumulative Gaussian distribution curves: (a) SL75; (b) SL150; (c) SL300; and (d) SL500.

Table 1. Particle and bulk densities of hollow microspheres employed

Hollow microspheres	Particle density (g/cc)	Bulk density (g/cc)
SL75	0.68	0.39
SL150	0.73	0.42
SL300	0.80	0.43
SL500	0.89	0.36

Microsphere sizes were measured using a Malvern 2600C laser particle size analyser and were found to be of approximately Gaussian distribution as shown in Figure 2. Particle densities and bulk densities of the four hollow microsphere groups were also measured using a Beckman Air Comparison Pycnometer (Model 930, Fullerton, California) and a measuring cylinder (capacity 250cc) respectively. Three hundred taps were conducted for each bulk density measurement. An average of five measurements was taken for each size group and all values are listed in Table 1.

2.2. Starch as Binder

Potato starch (Tung Chun Soy and Canning Company, Hong Kong) was used as binder for hollow microspheres. Particle density of the potato starch was measured using a Beckman

Air Comparison Pycnometer (Model 930) and an average of three measurements was found to be 1.50g/cc. Bulk density was also measured using a measuring cylinder with a tapping device (300 taps were conducted) and an average of five measurements was found to be 0.85g/cc. Figure 3 shows SEM images of starch particles employed. A gelatinization temperature range for starch was measured to be 64-69°C.

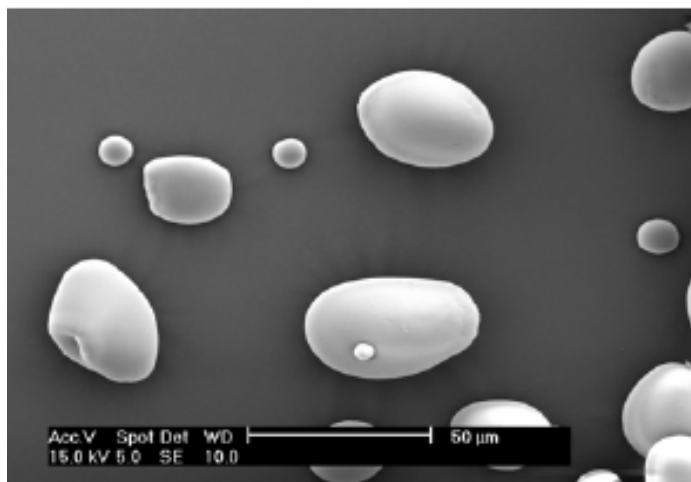


Figure 3. SEM image of potato starch granules prior to gelatinization.

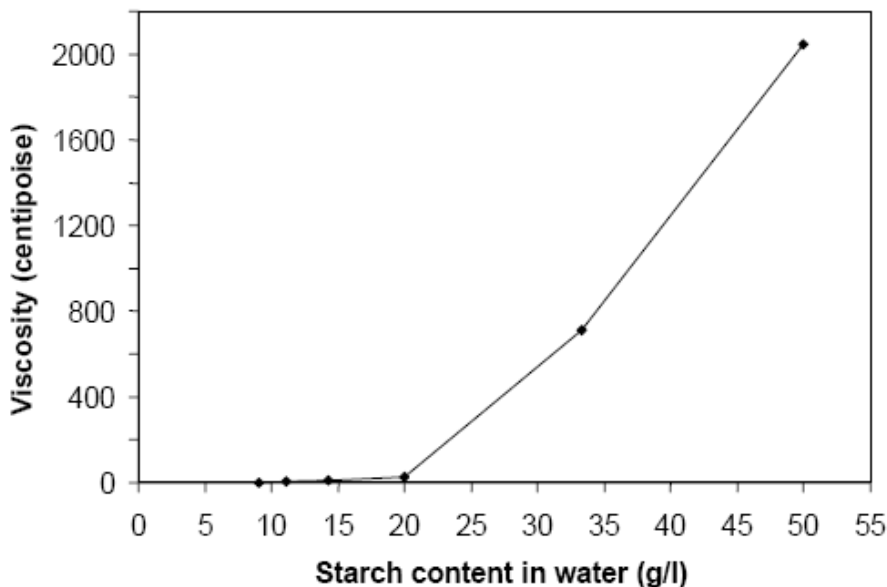


Figure 4. Viscosity of binder consisting of gelatinized starch and water as a function of starch content in water.

Viscosities of binder consisting of various contents of gelatinized starch in water were measured at 25°C using a Cannon-Fenske Routine viscometer (for low viscosities) and a

Brookfield Synchro-Lectric viscometer (LVF 18705) (for high viscosities). Results are shown in Figure 4.

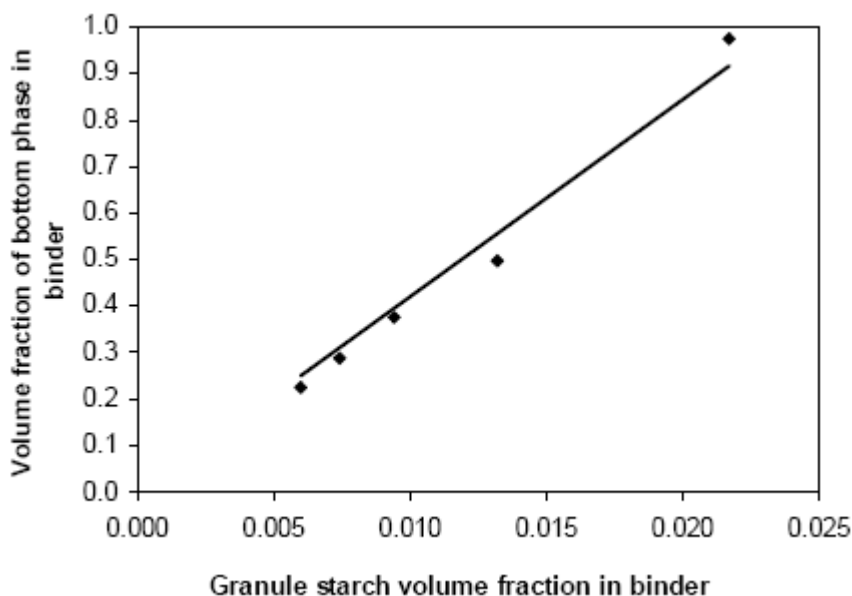


Figure 5. Volume fraction of gelatinized starch sediment (bottom phase) measured in a cylinder without microspheres versus initial granule starch volume fraction. Correlation coefficient of the best fit line with a forced intercept at zero is 0.988.

Volume fraction of starch sediment without using microspheres (SSWMS) (only two phases in this case formed – see Figure 6) measured in a measuring cylinder versus initial granule starch content prior to gelatinization is shown in Figure 5. As expected, the gelatinized starch sediment is approximately proportional to starch content as the high correlation coefficient of 0.988 with a forced intercept at zero indicates. The slope (= 42) may be used to quantify starch expansion as a result of gelatinization swelling.

It is noted that the volume fraction of bottom phase of gelatinized starch approaches a value of 1 (Figure 5) at a volume fraction of initial granule starch of about 0.022 corresponding to a viscosity of 715 centipoise (Figure 4) at which viscosity increases rapidly. Also, it was experienced that, when starch content is higher than 0.022, moulding of mixture consisting of microspheres and binder was difficult. Thus, the point (a volume fraction of 1), at which no phase separation would occur, appears to be a critical point that may be used as the practical limit of workability range for moulding.

3. THE PRINCIPLES OF THE BUOYANCY METHOD FOR MANUFACTURING SYNTACTIC FOAMS

The basic principles for manufacturing of syntactic foams containing starch as binder are based on the buoyancy of hollow microspheres in aqueous starch binder. The starch binder can be diluted for the purpose of controlling binder content in syntactic foam. When

microspheres are dispersed in binder as a result of stirring/tumbling, the mixing container is left until microspheres float to the surface and starch settles down, forming three phases i.e. top phase consisting of microspheres and binder, middle phase of water, and bottom phase of starch/microspheres and water as shown in Figure 6. The top phase is to be used for moulding. Gelatinization of starch in the mixture can be conducted at two different points in time. One is prior to the addition of hollow microspheres to water-starch mixture and the other after moulding, which will be referred to as pre- and post-mould methods respectively. More details are available in references [22, 23].

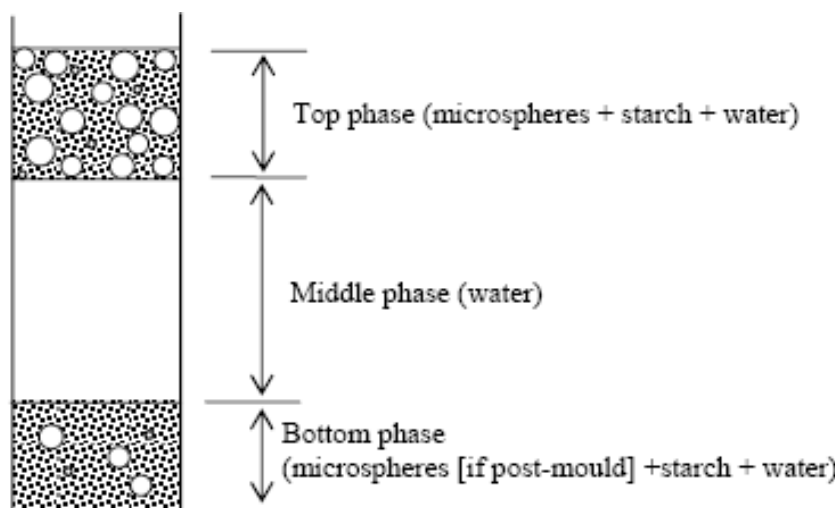


Figure 6. Schematic of phase separation.

4. BEHAVIOUR OF HOLLOW MICROSPHERES IN AQUEOUS GELATINIZED STARCH

It is useful to understand microsphere behaviour in aqueous starch binder during manufacturing for the microstructure formation and properties of syntactic foams consisting of microspheres and starch. The starch is a heterogeneous material consisting mainly of amylose and amylopectin [34]. When uncooked starch in water is heated above a critical temperature called gelatinization temperature, it swells to many times their original volume and starts to act as a binder for hollow microspheres. The properties of syntactic foams are largely dependant upon starch content so that starch content control is important.

4.1. Lattice Models for Microsphere Dispersion in Aqueous Gelatinized Starch

Microspheres in aqueous gelatinized starch in the top phase (Figure 6) can be modeled using the lattice points for expected microsphere positions and mean sized balls for microsphere size variation. The simple cubic (SC) unit cell, face centred cubic (FCC) unit cell, and body centred cubic (BCC) unit cell for the lattice are can be used for the modeling as

shown in Figure 7. The top phase volume (Figure 6) is always larger than the initial bulk volume of microspheres in air (IBVMS) in the case of pre-mould method as a result of expansion caused by starch binder between microspheres.

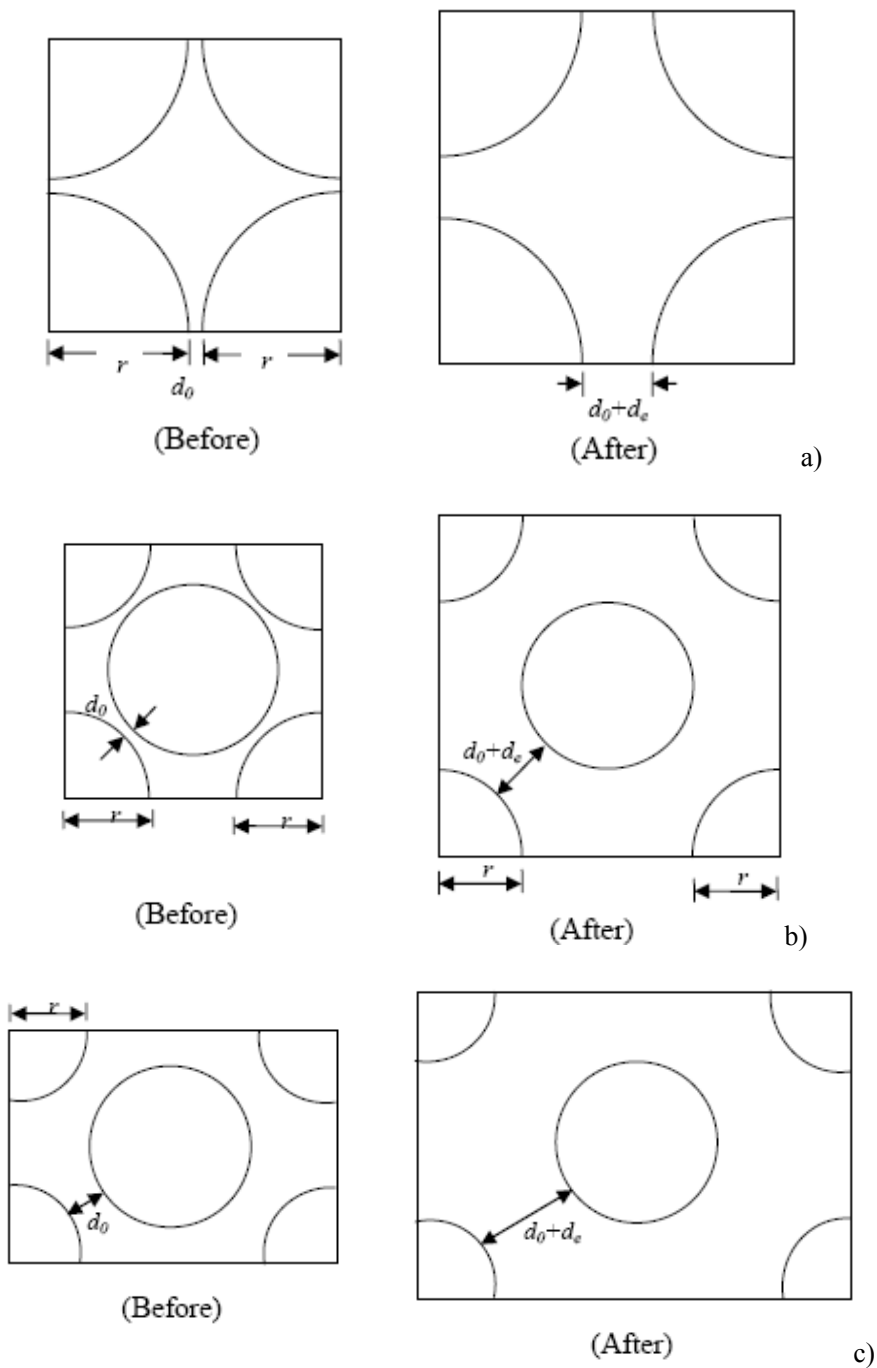


Figure 7. Mono-sized microsphere models before and after expansion of bulk microspheres: (a) front view of simple cubic (SC) unit cell; (b) front view of face centred cubic (FCC) unit cell; and (c) diagonal cross section view of body centred cubic (BCC) unit cell.

The volume expansion rate (VER) of IBVMS in the top phase is defined as

$$VER = (\text{Top phase volume}) / \text{IBVMS} \quad (1).$$

The VER based on the three models (independent of model type) was derived by calculating volumes for spheres before and after expansion to be

$$VER = \left(1 + \frac{d_e}{2r + d_0} \right)^3, \quad (2)$$

where r is the radius of microsphere, d_0 is the initial *MID*, and $(d_0 + d_e)$ is the *MID* after expansion. For a practical microsphere dispersion in the top phase, equivalent values for d_0 and d_e can be found. The d_0 , when $d_e = 0$, in Equation (2) was calculated for each microsphere size group using the packing factor (= [microsphere bulk density]/[microsphere particle density]) of bulk microspheres for a given mean radius of microspheres and given in Table 2.

Table 2. Packing factors and d_0 values of bulk microspheres for different microsphere size groups

Hollow microspheres	Packing factor of bulk microspheres	d_0 for SC (μm)	d_0 for FCC(μm)	d_0 for BCC(μm)
SL75	0.57	-1.49	4.87	3.24
SL150	0.58	-3.40	9.72	6.37
SL300	0.54	-1.82	19.77	14.25
SL500	0.40	33.76	81.91	69.59

4.2. Numerical Calculation of Minimum Inter-Microsphere Distance

A minimum inter-microsphere distance (MID), when microspheres are dispersed in the top phase, may be an indicator of the volume expansion of IBVMS. (The MID is a surface-to-surface distance.) A computer program was written in MATLAB 6.5 to produce 3D computer models for random dispersion of microspheres and to find a MID for a given volume fraction of microspheres. Microspheres with random sizes but with Gaussian distribution as measured for microspheres (See Figure 2) were randomly positioned in 3D space as shown in Figure 8 for examples. Mean radii corresponding to experimental values, 26.72, 55.27, 89.09, and 179.73 μm were nominated for SL75, SL150, SL300, and SL500 respectively, with respective standard deviations of 7.06, 18.2, 29.95, and 58.83 μm . 3D model space size for dispersion of microspheres was varied depending on microsphere size to reduce the computer running time. Thus, a virtual box with dimensions of 500 x 500 x 500 μm was used for SL75, a virtual box with dimensions of 1000 x 1000 x 1000 μm for both SL150 and SL300, and a virtual box with dimensions of 2000 x 2000 x 2000 μm for SL500.

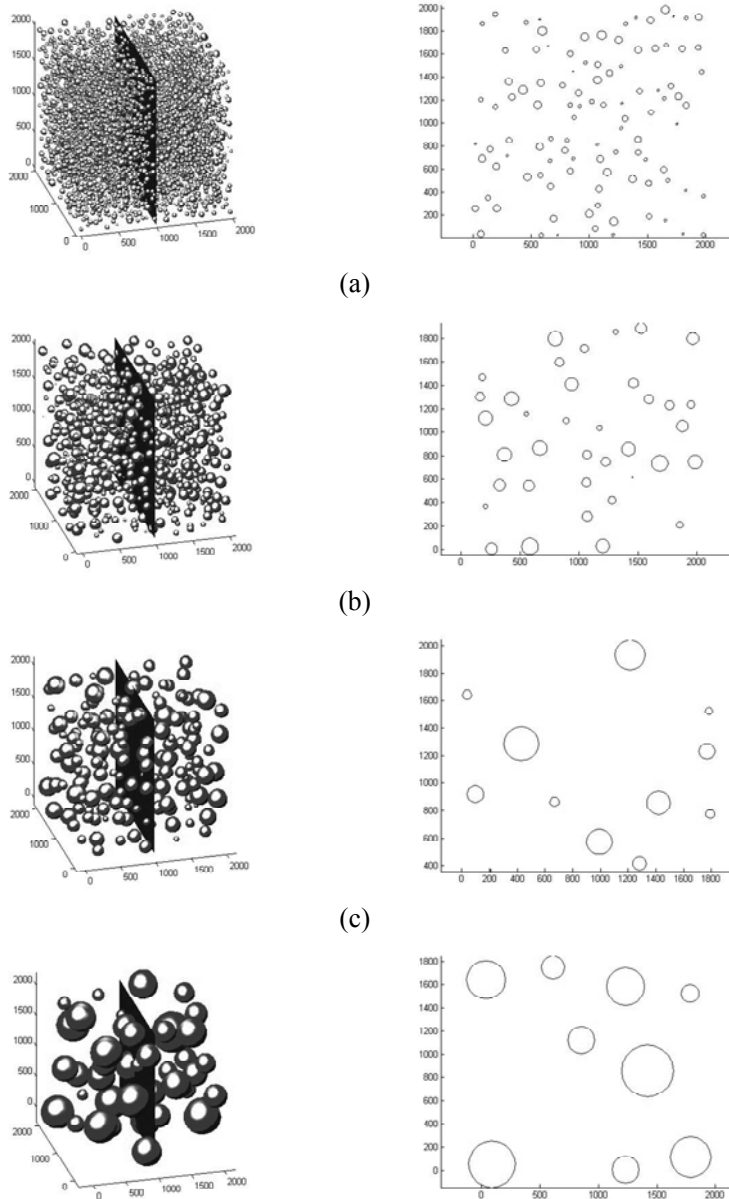


Figure 8. Some examples of 3D models with cross sections used for a manufacturing condition with an initial microsphere bulk volume of 30cc and a water/starch mass ratio of 110/1: (a) SL75, volume fraction of microspheres = 0.09, MID = 40 μm ; (b) SL150, volume fraction of microspheres = 0.1, MID = 80 μm ; (c) SL300, volume fraction of microspheres = 0.12, MID = 140 μm ; and (d) SL500, volume fraction of microspheres = 0.18, MID = 190 μm . All scale units for the images are in μm .

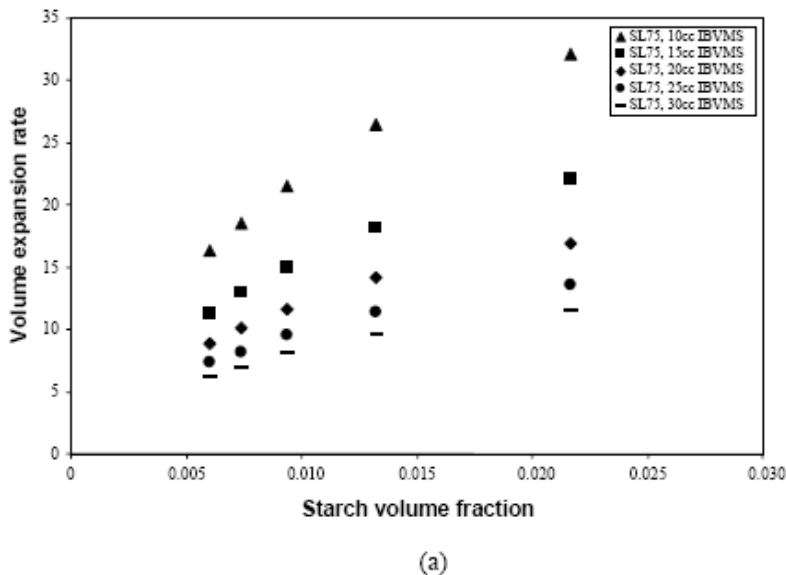
The 3D computer models (Figure 8) were created by rejecting microspheres which are closer to existing microspheres than those with a nominated MID and otherwise accepting microspheres until a nominated volume fraction of microspheres is reached. A total number of trials with microspheres for a given MID was 20,000 at which a total number of accepted microspheres in a box is identical with that at 15,000th microsphere. Iteration was conducted to find a MID corresponding to a volume fraction of microspheres experimentally given and was ended when

$$\frac{|v_{ms} \text{ from experiment} - \text{Calculated } v_{ms}|}{v_{ms} \text{ from experiment}} \leq 0.048 \quad (3)$$

where v_{ms} is the volume fraction of microspheres.

4.3. Comparison between Theoretical and Experimental Results for VER for IBVMS

Experimental VER of IBVMS in the top phase after tumbling/stirring is plotted in Figure 9 as a function of starch content in binder. It is surprisingly high particularly for small sized microspheres (SL75) to be $VER > 30$ and is also high for high starch content and low IBVMS. The effect of IBVMS on the expansion rate seems to be due to the buoyant force because the smaller the IBVMS, the lower the buoyant force, giving smaller squeezing force and hence larger inter-microsphere distances. Also, it is a truism that the volume expansion is caused by distance increase between microspheres. Once microspheres are wetted with binder, their distances between microspheres would be affected by various factors such as starch content, IBVMS, etc.



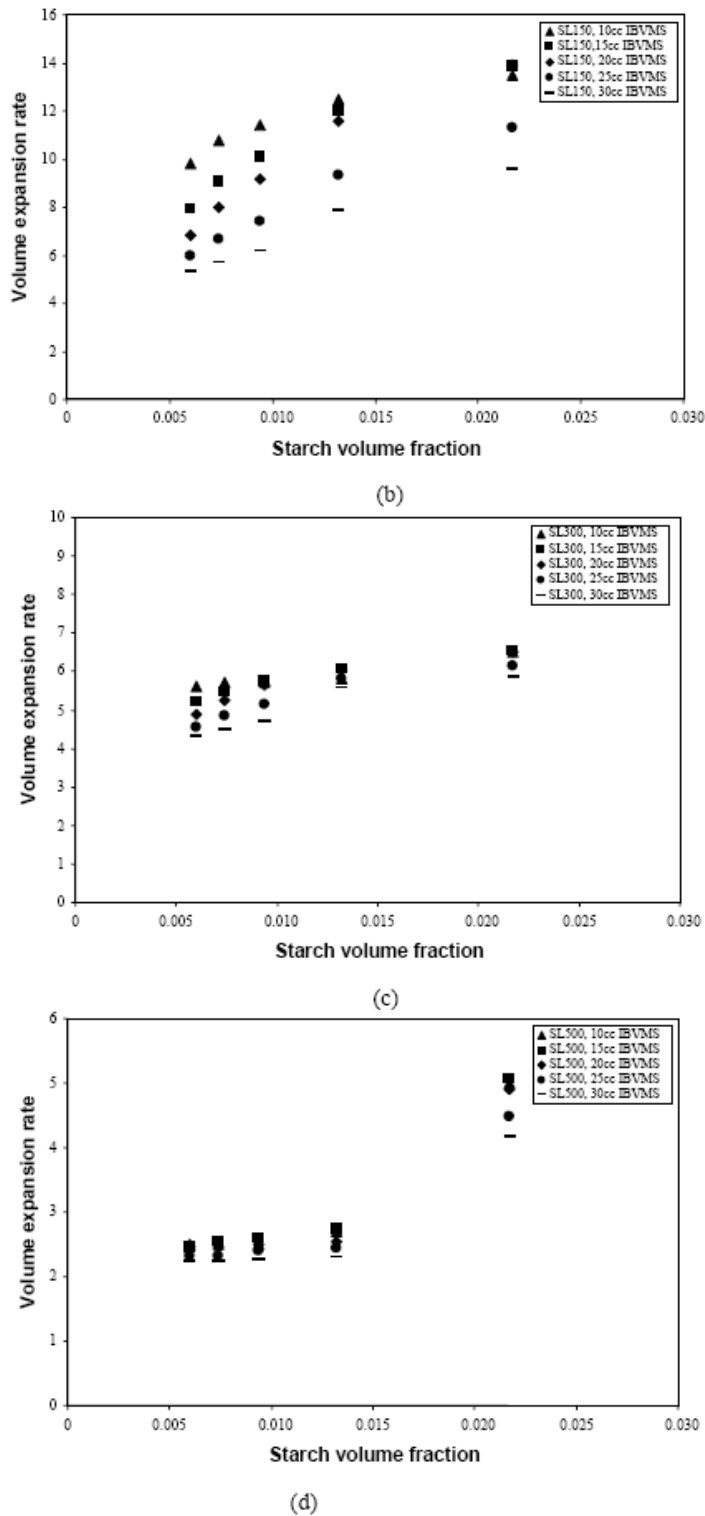


Figure 9. Volume expansion rate (VER) (= top phase volume / IBVMS) after tumbling/stirring as a function of initial granule starch volume fraction in binder: (a) SL75, (b) SL150, (c) SL300, and (d) SL500.

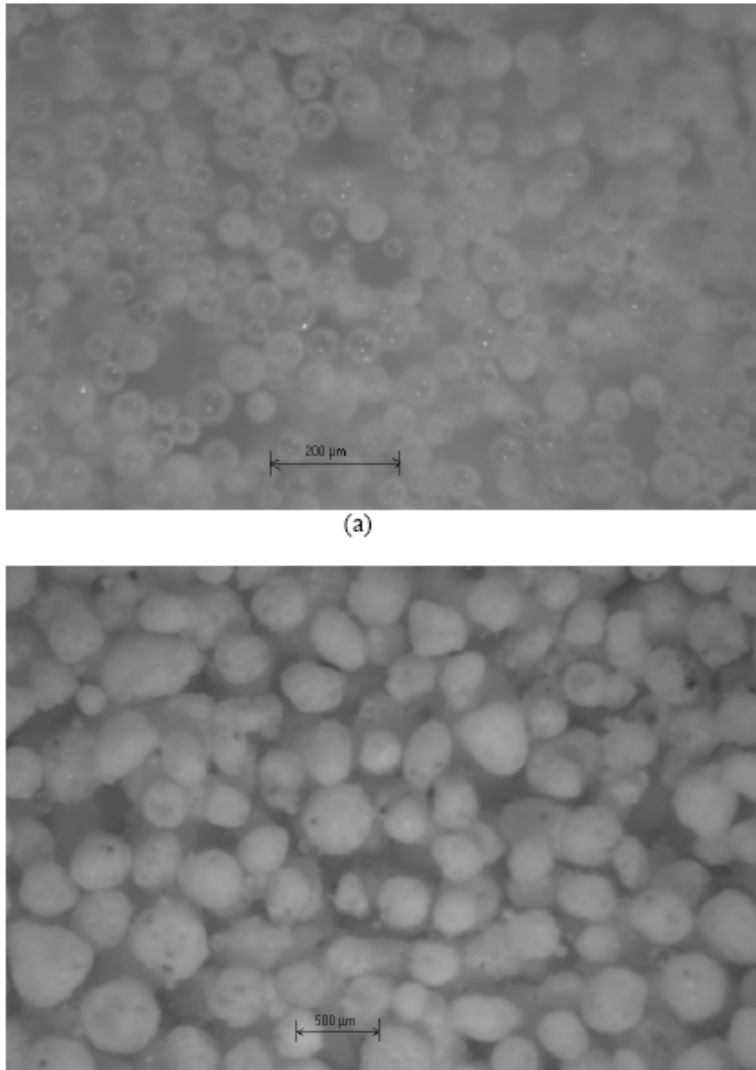


Figure 10. Surface images of the top phase consisting of gelatinized starch as binder and microspheres for a mass ratio of water/starch of 70/1 (or a volume fraction of granule starch in binder of 0.0094): (a) SL75; and (b) SL500.

Surfaces of top phases of SL75 and SL500 were viewed under an optical microscope as shown in Figure 10. Some distances between microspheres are vaguely seen in SL75 and are obvious in SL500. It was assumed that a MID exists in the top phase for a given manufacturing condition. Also, the top phase can be assumed as being formed through random positioning of microspheres after the tumbling/stirring. The numerical calculations conducted were on the basis of these two assumptions. The experimental VER versus numerically calculated MID ($= d_0 + d_e$) is shown in Figure 11 with theoretical curves generated according to Equation (2). The theoretical curves based on BCC and FCC models appear to be in a good agreement with data. Meanwhile, SC model appears to be in a relatively poor agreement with data compared to the other models and has unrealistic values for d_0 being negative as listed in Table 2. The predictions based on the lattice models would be useful for

practical design of mixing containers, syntactic foam composition estimation (to be further discussed below) for different microsphere sizes and eventually for optimization of manufacturing system.

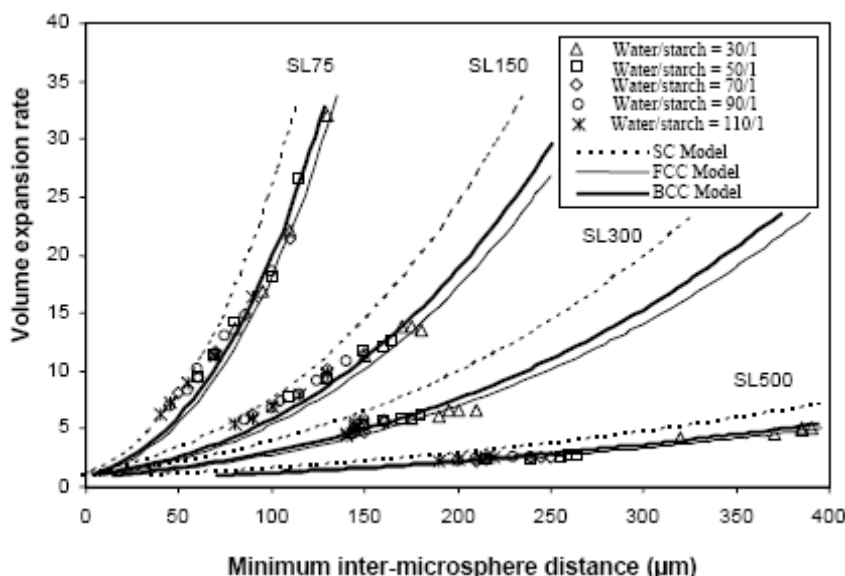


Figure 11. Experimental volume expansion rate (VER) versus numerically calculated minimum inter-microsphere distances ($MID = d_0 + d_e$) in comparison with theoretical curves generated according to Equation (2). The initial bulk volumes of microspheres (10cc, 15cc, 20cc, 25cc and 30cc) for each water/starch ratio are seen such that the higher VER the lower IBVMS.

4.4. Starch Concentration between Microspheres and Syntactic Foam Density Estimation

Starch concentration in binder trapped in the top phase (BTTP) between microspheres can be found using a volume rate (VR) defined as

$$VR = \frac{\text{Volume of SSTTP}}{\text{Volume of BTTP}} \quad (4)$$

where SSTTP is the starch sediment lost to the top phase due to microspheres. It is illustrated in relation with SSWMS (starch sediment without microspheres) in Figure 12. The top phase after mixing consists of microspheres and binder. The binder trapped between microspheres in the top phase further consists of starch and water. The bottom phase in Figure 12 is shown for two different cases together i.e. one with microspheres and the other without microspheres. VR values are given in Table 3. Each mean value of VR was obtained from 5 different IBVMS's (10cc, 15cc, 20cc, 25cc, and 30cc) for a given microsphere size group and starch content in binder. VR's are seen to be not much dependant on IBVMS as the low standard deviations indicate.

Also, VR appears to decrease as the volume fraction of SSWMS in binder decreases, indicating that starch concentration in BTTP decreases with decreasing viscosity of binder.

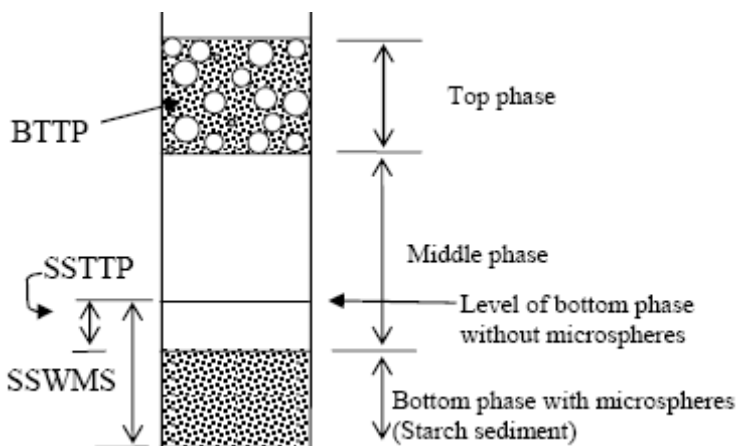


Figure 12. Schematic of various components after phase separations with/without microspheres in mixture for pre-mould method. The 'level of bottom phase without microspheres' is for only two phases.

Table 3. Mean VR (=SSTTP/BTTP) for various microsphere size groups. Each set of mean and standard deviation was obtained from 5 different initial bulk volumes of microspheres (IBVMS's - 10cc, 15cc, 20cc, 25cc, and 30cc)

VR	Standard deviation	Volume fraction of SSWMS in binder	Mean radius of microspheres (μm)
1.21	0.017	0.98	26.72 (SL75)
1.26	0.213		55.27 (SL150)
1.82	0.067		89.09 (SL300)
1.17	0.266		179.73 (SL500)
0.75	0.013	0.50	26.72 (SL75)
0.83	0.056		55.27 (SL150)
0.83	0.080		89.09 (SL300)
0.78	0.174		179.73 (SL500)
0.69	0.018	0.37	26.72 (SL75)
0.80	0.055		55.27 (SL150)
0.73	0.058		89.09 (SL300)
0.35	0.173		179.73 (SL500)
0.61	0.015	0.29	26.72 (SL75)
0.69	0.027		55.27 (SL150)
0.58	0.038		89.09 (SL300)
0.20	0.031		179.73 (SL500)
0.55	0.018	0.23	26.72 (SL75)
0.62	0.006		55.27 (SL150)
0.52	0.038		89.09 (SL300)
0.11	0.025		179.73 (SL500)

Table 4. Syntactic foams manufactured using pre-mould process

Microsphere grade	Water / starch mass ratio	Fraction of starch in binder		Fraction of starch in foam		Fraction of microspheres in foam		Volume fraction of void between microspheres in foam (v_i)	Volume ratio of foam / bulk microspheres (r_i)	Foam density (g/cc)
		Mass (m_b)	Volume (v_b)	Mass (m_s)	Volume (v_s)	Mass (m_m)	Volume (v_m)			
SL75	30/1	0.0323	0.0217	0.1935	0.0491	0.807	0.451	0.50	1.27	0.38
	50/1	0.0196	0.0132	0.1611	0.0400	0.839	0.460	0.50	1.25	0.37
	70/1	0.0141	0.0094	0.1228	0.0295	0.877	0.465	0.51	1.23	0.36
	90/1	0.0110	0.0074	0.0876	0.0203	0.912	0.465	0.51	1.23	0.35
	110/1	0.0090	0.0060	0.0602	0.0137	0.940	0.471	0.52	1.22	0.34
SL150	30/1	0.0323	0.0217	0.1525	0.0411	0.848	0.469	0.49	1.23	0.40
	50/1	0.0196	0.0132	0.1197	0.0317	0.880	0.479	0.49	1.20	0.39
	70/1	0.0141	0.0094	0.0942	0.0243	0.906	0.481	0.49	1.20	0.39
	90/1	0.0110	0.0074	0.0672	0.0170	0.933	0.486	0.50	1.19	0.38
	110/1	0.0090	0.0060	0.0530	0.0132	0.947	0.486	0.50	1.19	0.37
SL300	30/1	0.0323	0.0217	0.1349	0.0391	0.865	0.470	0.49	1.15	0.44
	50/1	0.0196	0.0132	0.1071	0.0301	0.893	0.471	0.50	1.14	0.43
	70/1	0.0141	0.0094	0.0876	0.0241	0.912	0.471	0.50	1.14	0.41
	90/1	0.0110	0.0074	0.0566	0.0151	0.943	0.471	0.51	1.14	0.40
	110/1	0.0090	0.0060	0.0421	0.0111	0.958	0.474	0.52	1.14	0.40
SL500	30/1	0.0323	0.0217	0.1289	0.0317	0.871	0.361	0.61	1.11	0.37
	50/1	0.0196	0.0132	0.0809	0.0189	0.919	0.363	0.62	1.10	0.35
	70/1	0.0141	0.0094	0.0494	0.0112	0.951	0.363	0.63	1.10	0.34
	90/1	0.0110	0.0074	0.0347	0.0078	0.965	0.363	0.63	1.10	0.33
	110/1	0.0090	0.0060	0.0196	0.0043	0.980	0.365	0.63	1.09	0.33

The quantities of SSTTP and IBVMS may be used for foam density calculation prior to manufacturing if the final volume of foam is equal to IBVMS. There is some difference, though, between the final volume of foam and IBVMS as listed in Table 4 with other measurements for manufactured syntactic foams. It shows the volume ratio of foam/bulk microspheres in a range of 1.1 -1.3 and the larger the microsphere size the lower the ratio. Thus, the VR would provide useful estimation for the foam density within some error range.

4.5. Shrinkage after Moulding and Composition

Shrinkage of microsphere-binder mixture prior to the final foam formation for SL150 after moulding is measured in percentage of initial volume for different mass ratios of water/starch in binder (50/1, 70/1 and 90/1) and given in Figure 13 (a) as a function of drying time. Density change due to drying for the same moulded mixture is also given in Figure 13 (b) with different stages being defined earlier for dough and solid. Also, two different stages are seen in Figure 13 (a) i.e. shrinkage rapidly occurs at an early stage until about 120 min for all water/starch mass ratios and then reaches a plateau value at a later stage - this was found for all other microsphere size groups. The transition between the two stages of shrinkage (Figure 13 (a)) corresponds with a transition from dough to solid shown in Figure 13 (b). It can be deduced that positions of microspheres in a moulded mixture stabilize at the transition (in Figure 13(a)) after the large shrinkage, making water evaporation difficult as a result of reduction of inter-microsphere distances. Subsequently, the moulded mixture goes into the

stage of solid at which forming is difficult. In practical manufacturing, a two-step process viz moulding first and then forming at a point prior to the transition between dough and solid would be suggested for foam dimensional control.

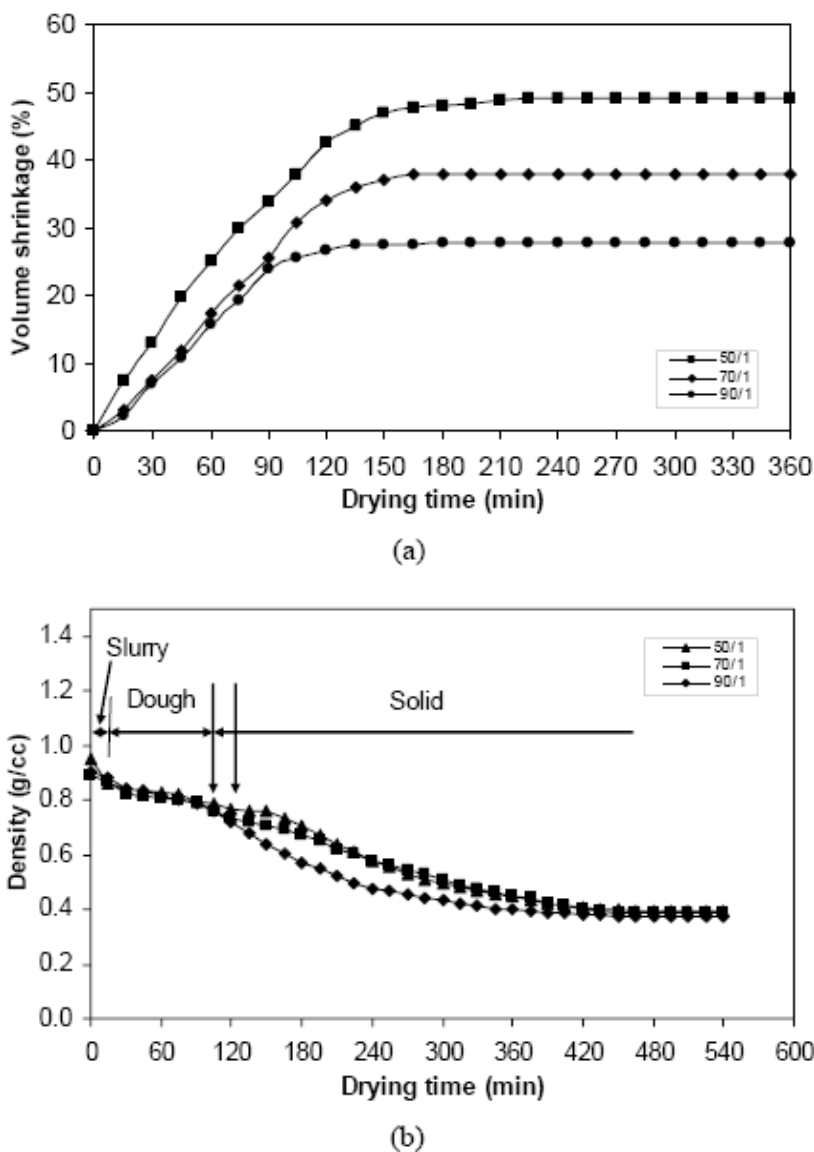


Figure 13. Shrinkage and density measurements for SL150 after moulding for mass ratios of water/starch in binder – 50/1, 70/1 and 90/1: (a) shrinkage of microsphere-binder mixture in percentage of initial volume versus drying time; and (b) density of the microsphere-binder mixture versus drying time. The double arrows between dough and solid in '(b)' are to indicate a range affected by water/starch ratio – the higher starch content the longer dry time.

Some example images of polished cross sections for manufactured syntactic foam microstructures after embedding in an epoxy are shown in Figure 14. Voids between microspheres are not identifiable due to the preparation technique but other quantities as given in Table 4 are comparable with the images.

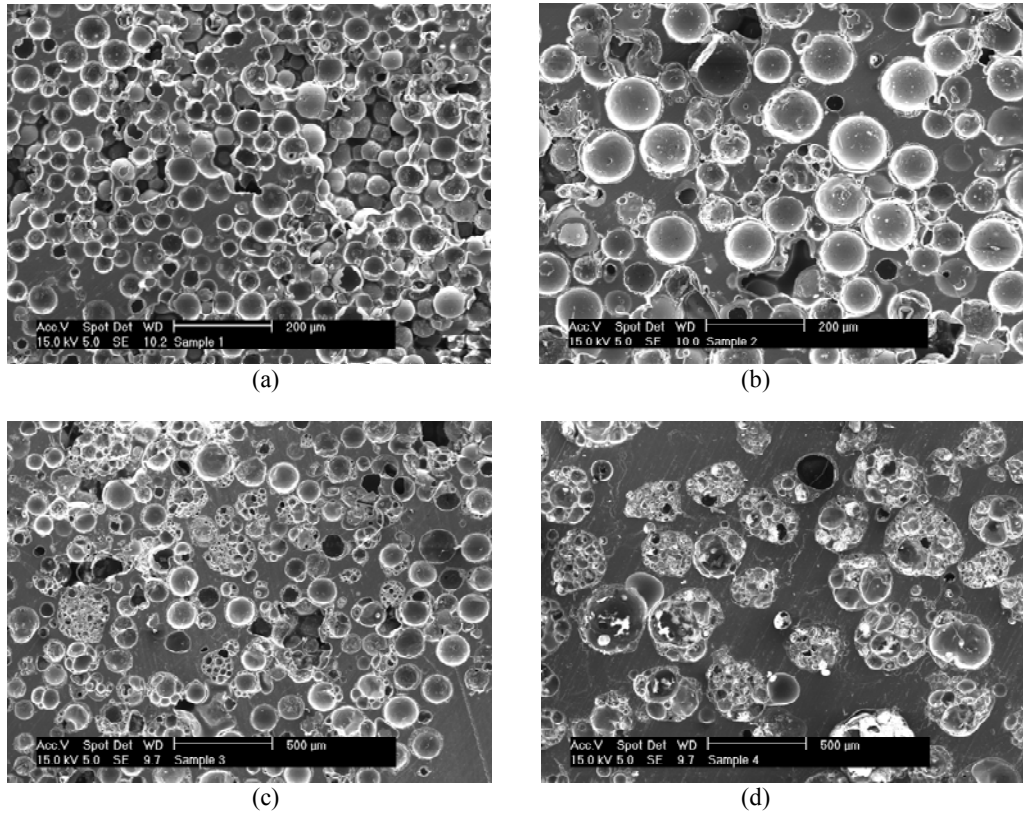


Figure 14. SEM images of the polished cross-sections of syntactic foams made of: (a) SL75; (b) SL150; (c) SL300; and (d) SL500 for a water/starch mass ratio of 70/1 in binder. Samples were prepared by embedding in an epoxy.

Volume fractions of microspheres (v_{ms}), binder (starch) (v_b) and voids (v_v) in Table 4 were measured using:

$$v_v = 1 - (v_{ms} + v_b) = 1 - \rho_{sy} \left(\frac{m_{ms}}{\rho_{ms}} + \frac{m_b}{\rho_b} \right) \quad (5)$$

$$v_{ms} = \rho_{sy} \frac{m_{ms}}{\rho_{ms}} \quad (6)$$

and

$$v_b = \rho_{sy} \frac{m_b}{\rho_b} \quad (7)$$

where ρ is the density, m is the mass fraction, and subscripts (sy , ms and b) denote syntactic foam, microsphere and binder (starch), respectively.

5. INTERACTION BETWEEN STARCH PARTICLES AND HOLLOW MICROSPHERES IN AQUEOUS ENVIRONMENT

Composition of syntactic foam manufactured with the post-mould method is affected by interaction between starch particles and microspheres in water prior to being gelatinized after moulding.

To characterize volume change in water of hollow microsphere and starch particles, the bulk volume expansion rate (BVER) in water versus bulk volume in air is given in Figure 15. The BVER is defined as

$$\text{BVER} = \frac{\text{Bulk volume in water}}{\text{Bulk volume in air}}. \quad (8)$$

The bulk volume of microspheres in water was measured from top phase volume (TPV) without starch and the bulk volume of starch particles in water from sediment volume without microspheres. The VER appears approximately 1.2 and approximately independent of bulk volume variation in air. In addition, a long term VER of starch particles is given in Figure 16 where VER is seen to be constant for the first three days and to slightly increase afterwards.

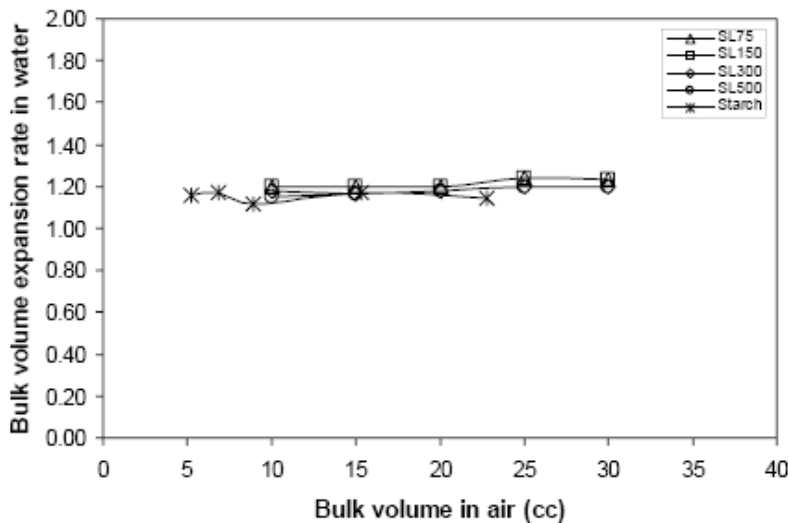


Figure 15. Bulk volume expansion rate (BVER) (= bulk volume in water / bulk volume in air) versus bulk volume in air of hollow microspheres and starch particles.

The total of top and bottom phase volumes (Figure 6) after mixing microspheres and starch particles together in water depends upon the mixture ratio. The total volume change ratio after mixing in water (TVCRAM) defined as

$$\text{TVCRAM} = \frac{\text{Top and bottom phase volumes after mixing}}{\text{Microsphere and starch bulk volumes in water before mixing}} \quad (9)$$

is given as a function of starch volume fraction before mixing (SVFBM) defined as

$$\text{SVFBM} = \frac{\text{Starch bulk volume in water before mixing}}{\text{Microsphere and starch bulk volumes in water before mixing}} \quad (10)$$

in Figure 17 for SL75 and SL300. It appears to be dependant upon microsphere size as well. As the microsphere mean size decreases, TVCRAM generally increases. This indicates that large gaps between microspheres and starch particles exist for small microspheres (SL75). Also, the maximum TVCRAM occurs at a starch volume fraction as indicated with filled and open arrows respectively for SL75 and SL300. (The position of the arrow will be further discussed below.) Further, the TVCRAM does not appear to be much affected by initial bulk volume of microspheres (IBVMS).

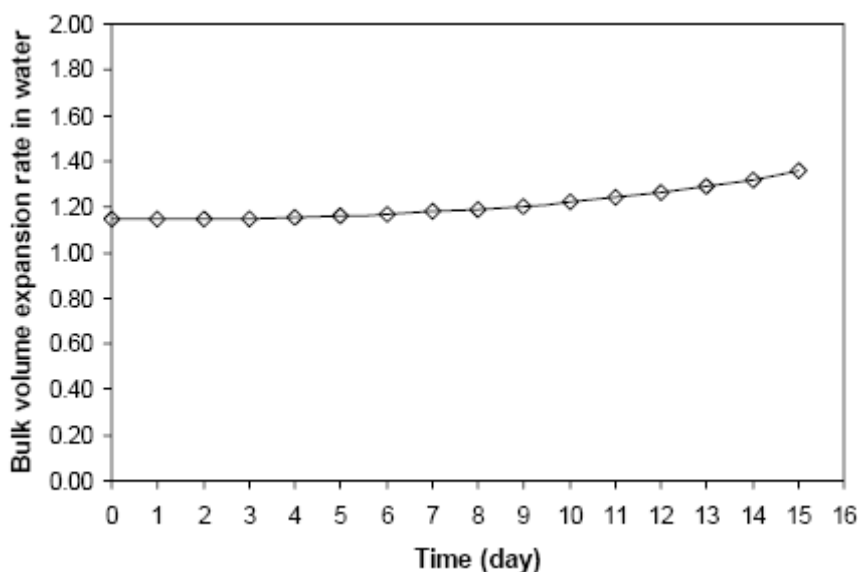


Figure 16. Long term bulk volume expansion rate (BVER) (= bulk volume in water / bulk volume in air) of starch particles in water as a function of time (number of days) elapsed.

During the phase separation after tumbling of the aqueous mixture, it can be observed that the starch particles tend to settle to form sediment while microspheres tend to float (due to their density differences). Also, there is some interaction between microspheres and starch particles. Some starch particles are carried by microspheres to form the top phase, while some microspheres are carried by starch particles to form the bottom phase. To quantify this phase separation phenomenon, bottom phase volume fraction after mixing (BPVFAM) defined as

$$\text{BPVFAM} = \frac{\text{Bottom phase volume after mixing}}{\text{Top and bottom phase volumes after mixing}} \quad (11)$$

is plotted as a function of SVFBM for SL75 and SL300, and shown in Figure 18.

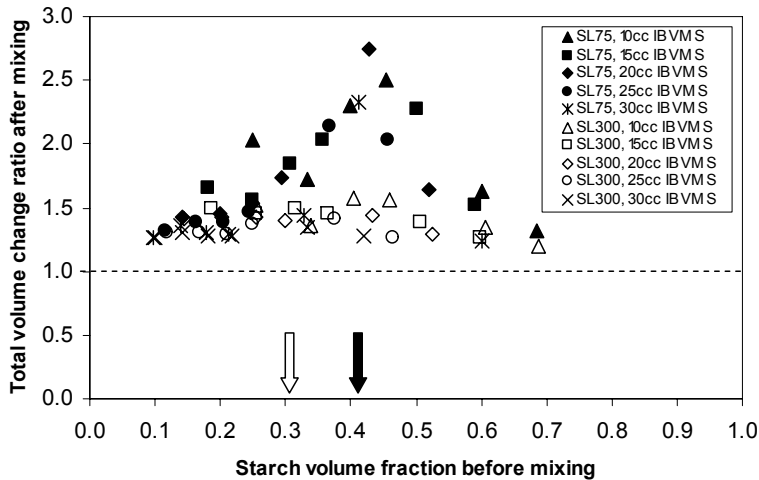


Figure 17. Total volume change ratio after mixing (TVCRAM) as a function of SVFBM.

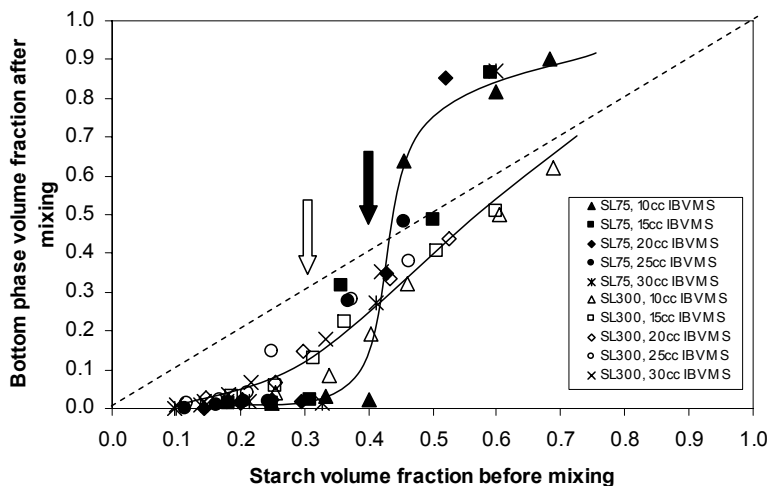


Figure 18. Bottom phase volume fraction after mixing (BPVFAM) as a function of SVFBM.

If there were no such interaction between microspheres and starch particles, all the data points would have been on the dashed line shown in Figure 18 and $BPVFAM = SVFBM$. Data points under the dashed line indicate that starch particles are trapped in the top phase but those above the dashed line indicate that microspheres are trapped in the bottom phase. However, those that are close or on the dashed line do not necessarily mean that separation was complete. Thus, those data points close to the dashed line provide only a necessary condition (not sufficient condition) for the case where no interaction between microspheres and starch particles exists. Further, a physical transition (not graphical) in each size group is seen to occur at the similar starch volume fraction to that for TVCRAM (Figure 17) as indicated with filled and open arrows for SL75 and SL300 respectively.

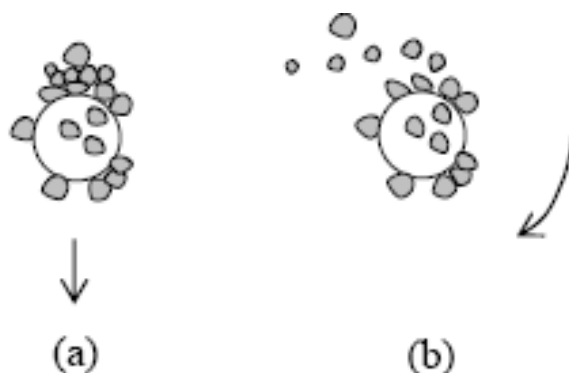


Figure 19. Schematic representation of observation for starch particles on a microsphere in water: (a) translational motion; and (b) rotational motion.

It was learnt from direct microscopic observations that the starch particles tend to adhere to microspheres. When a microsphere settles, starch particles that already adhered to the microsphere do not easily separate from the microsphere. However, starch particles settled on top of other starch particles that are already adhered to a microsphere readily separated when the microsphere motion changed from translational motion to rotational motion as illustrated in Figure 19. This indicates that the attractive force between a starch particle and a microsphere is stronger than that between starch particles. Agglomerations are hence formed by starch particles acting as glue between microspheres. The buoyancy of each agglomerate depends upon composition – the more starch particles the heavier the agglomerate. The volume fraction of starch particles in an agglomerate consisting of one microsphere and multiple starch particles required to yield a relative density of 1.0 (VFSRD) was calculated to be 0.41 and 0.31 for SL75 and SL300 respectively. For these calculations, the mean diameter of microspheres was used and it was assumed that starch particles are spherical. Those calculated values are compared with the transitional points indicated by arrows in Figure 17 and Figure 18. It is important to note that the values of VFSRD correspond to the transitional points. Thus, the VFSRD appears a good indicator for both the maximum TVCRAM and the transitional points.

The use of the VFSRD as the transitional point indicator can be explained in statistical terms. The phase separation is likely to be a stochastic process. When the volume fraction of starch is lower than VFSRD, the density of an agglomeration is likely to be less than 1, allowing it to float to form the top phase. When a density of an agglomeration is higher than 1, it will settle to form the bottom phase. The abruptness of the transition (Figure 18) for small microspheres can be explained as follows. It is a truism that smaller starch-microsphere inter-distance will allow more starch particle-microsphere collisions. As the microsphere size of a given microsphere bulk volume decreases in a given space, the number of microspheres increases but starch-microsphere distances decrease. As a result, agglomeration will occur more rapidly for small microspheres and will produce larger agglomerates. Consequently, few individual particles or/and small agglomerates are formed when small microspheres are used. Such individual particles or/and small sized agglomerates are the ones that causes smoothness of the transition because their densities are not much affected and tend to follow the dashed line in Figure 18.

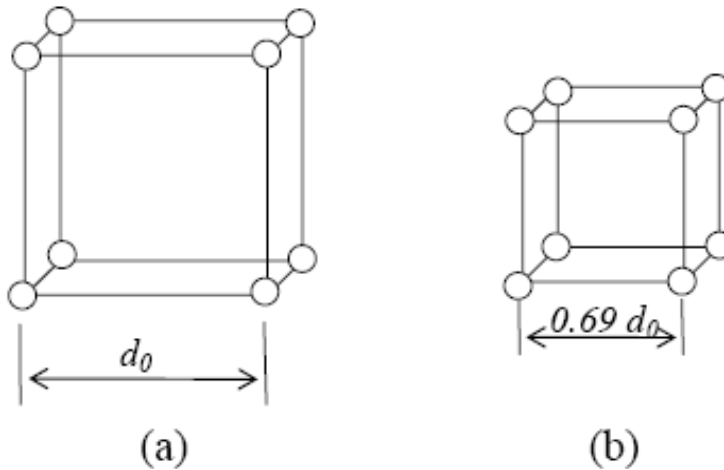


Figure 20. Simple Cubic cell model: (a) initial distance d_0 , (b) after three times microsphere bulk volume increase in a given space.

One could expect some effect of IBVMS on the transitional behaviour (Figure 18) because starch-microsphere distance can be affected by it since starch-microsphere inter-distance is relatively small for a large IBVMS. The inter-particle distance (d) can be readily estimated using a Simple Cubic unit cell model with an initial distance (d_0) (Figure 20 (a)). The distance (d) here is for center to center for simplicity by ignoring sphere size in a large space. When IBVMS increases from 10cc to 30cc for example, particle numbers in a representative section, 1000 become 3000 in a given space and $d = 0.69 d_0$ (31% decrease) as illustrated in (Figure 20). For a microsphere size effect, the same model may be used. When SL300 microspheres are replaced with an equivalent volume of SL75 microspheres (70% decrease in mean size), particle numbers 1000 become approximately 37,066 and $d = 0.30 d_0$ (70% decrease). Therefore, the IBVMS effect on the inter-particle distance appears not as significant as microsphere size as seen in Figure 17 and Figure 18. Further, a follow-up experiment was conducted to see the effect of water volume in the mixture (using a starch volume fraction of 0.4 and a water volume range of 90 – 400cc in the same measuring cylinder) given that the more water volume the longer inter-particle distances. However, no noticeable effect was found on the scales in Figure 17 or Figure 18. The water volume effect seems be offset by the effect of particle traveling distance, given that the longer the traveling distances the higher the chance of collision between starch particles and, hence, the higher chance for forming agglomerations.

Starch particle volume fractions (= starch particle volume / TPV) in the top phase (SVFTP) for a constant IBVMS of 30cc are showed in Figure 21. It can be estimated using manufactured foams and

SVFTP

$$= [\text{IBVMS}/\text{TPV}] \times [\text{Foam volume}/\text{IBVMS}] \times [\text{Starch volume in foam}/\text{Foam volume}]$$

where the Starch volume in foam is

$$[\text{Foam mass} - \{\text{Foam volume} / (\text{Foam volume} / \text{Microsphere bulk volume})\} \times \text{Microsphere bulk density}] / [\text{Starch particle density}].$$

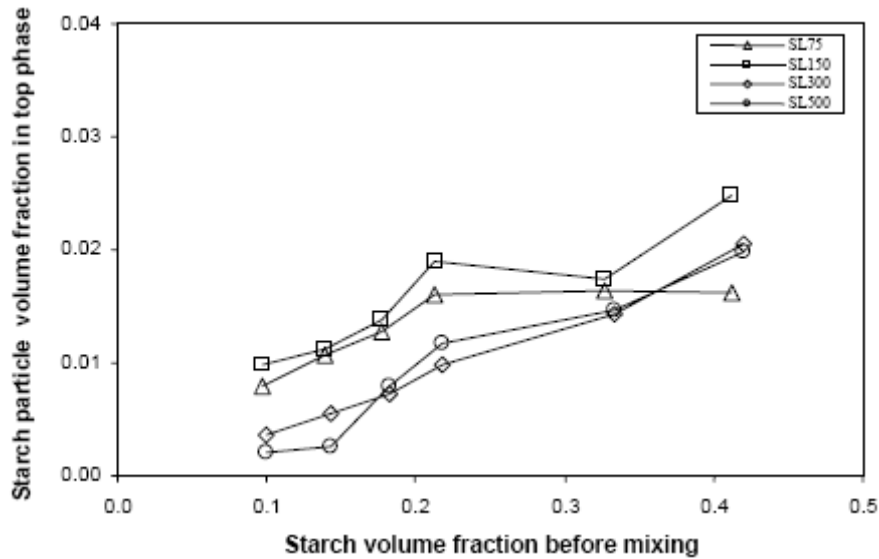


Figure 21. Starch particle volume fraction in the top phase (SVFTP) after phase separation versus starch volume fraction before mixing (SVFBM) for an IBVMS of 30cc.

Table 5. Syntactic foams manufactured using post-mould process

Microsphere grade	Water / starch mass ratio	Fraction of starch in binder		Fraction of starch in foam		Fraction of microspheres in foam		Volume fraction of void in foam (v_v)	Volume ratio of foam / bulk microspheres (r_i)	Foam density (g/cc)
		Mass (m_b)	Volume (v_b)	Mass (m_s)	Volume (v_s)	Mass (m_m)	Volume (v_m)			
SL75	20/1	0.0476	0.0323	0.1639	0.0398	0.836	0.448	0.51	1.28	0.36
	30/1	0.0323	0.0217	0.1197	0.0283	0.880	0.460	0.51	1.25	0.36
	50/1	0.0196	0.0132	0.0809	0.0187	0.919	0.468	0.51	1.23	0.35
	70/1	0.0141	0.0094	0.0602	0.0137	0.940	0.471	0.52	1.22	0.34
	90/1	0.0110	0.0074	0.0421	0.0094	0.958	0.471	0.52	1.22	0.33
	110/1	0.0090	0.0060	0.0272	0.0060	0.973	0.474	0.52	1.21	0.33
SL150	20/1	0.0476	0.0323	0.1166	0.0310	0.883	0.482	0.49	1.19	0.40
	30/1	0.0323	0.0217	0.0909	0.0236	0.909	0.486	0.49	1.19	0.39
	50/1	0.0196	0.0132	0.0706	0.0181	0.929	0.489	0.49	1.18	0.38
	70/1	0.0141	0.0094	0.0530	0.0134	0.947	0.493	0.49	1.17	0.38
	90/1	0.0110	0.0074	0.0310	0.0077	0.969	0.496	0.50	1.16	0.37
	110/1	0.0090	0.0060	0.0234	0.0058	0.977	0.496	0.50	1.16	0.37
SL300	20/1	0.0476	0.0323	0.1007	0.0281	0.899	0.470	0.50	1.15	0.42
	30/1	0.0323	0.0217	0.0775	0.0211	0.923	0.472	0.51	1.14	0.41
	50/1	0.0196	0.0132	0.0421	0.0111	0.958	0.474	0.52	1.14	0.40
	70/1	0.0141	0.0094	0.0272	0.0071	0.973	0.474	0.52	1.14	0.39
	90/1	0.0110	0.0074	0.0196	0.0051	0.980	0.476	0.52	1.13	0.39
	110/1	0.0090	0.0060	0.0119	0.0031	0.988	0.477	0.52	1.13	0.39
SL500	20/1	0.0476	0.0323	0.0975	0.0233	0.903	0.364	0.61	1.10	0.36
	30/1	0.0323	0.0217	0.0775	0.0182	0.923	0.364	0.62	1.10	0.35
	50/1	0.0196	0.0132	0.0385	0.0087	0.962	0.365	0.63	1.09	0.34
	70/1	0.0141	0.0094	0.0196	0.0043	0.980	0.365	0.63	1.09	0.33
	90/1	0.0110	0.0074	0.0119	0.0026	0.988	0.366	0.63	1.09	0.33
	110/1	0.0090	0.0060	0.0119	0.0026	0.988	0.366	0.63	1.09	0.33

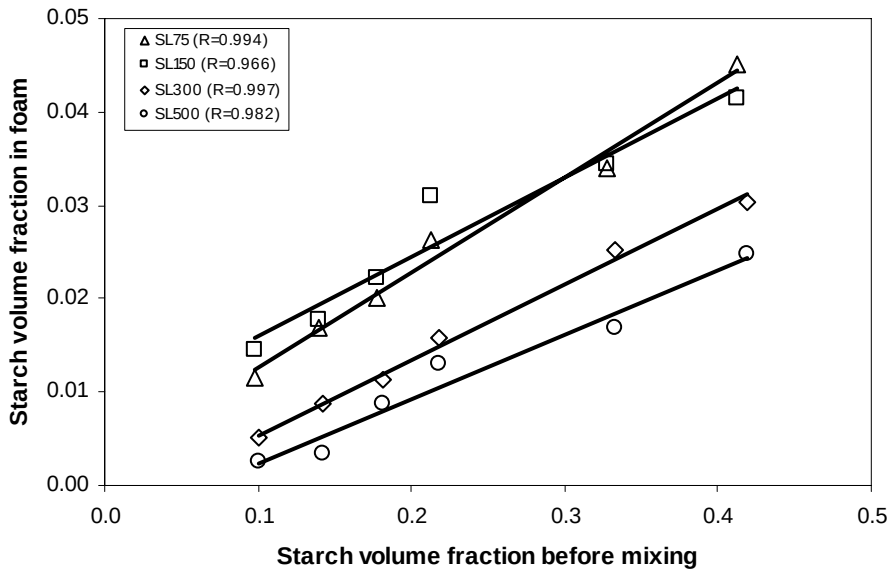


Figure 22. Starch volume fraction in foam (SVFF) versus starch volume fraction before mixing (SVFBM) for an IBVMS of 30cc. Correlation coefficient (R) is given for each microsphere size group.

In general, the SVFTP tends to be high for small microspheres, indicating small microspheres carry more starch particles perhaps due to small inter-particle distances as discussed above. Other characteristics of manufactured foams such as volume fractions of voids, volume ratios of foam/bulk microspheres, and densities are listed in Table 5.

Starch volume fraction in foam (SVFF) manufactured for various microsphere size groups but a constant IBVMS of 30cc are given as a function of SVFBM in Figure 22. They increase in the given range of SVFBM's linearly with increasing SVFBM with high correlation coefficients, 0.994, 0.966, 0.997, and 0.982 for SL75, SL150, SL300, and SL500 respectively. Both SVFTP and SVFF would be expected to be affected by the transitional point (or VFMSRD point) but the linearity of the foam density (Figure 22) in particular does not appear to be much affected. Probable reasons are that the transitions of SL300 is relatively smooth (Figure 18) and the transitional points of SL75 and SL150 are around the high ends of the range of SVFBM (Figure 22).

6. MECHANICAL BEHAVIOUR OF SYNTACTIC FOAMS

6.1. Transitions in Mechanical Behaviour

It is important to identify transitions in mechanical behaviour for understanding failure of syntactic foams and for developing relationships based on the rule of mixtures for various properties. In general, syntactic foam is of ternary system. A ternary system diagram for microspheres, binder and voids (between microspheres) is given Figure 23. The location of point *A* on the voids-microspheres axis depends on the way of packing microspheres without binder and size distribution of microspheres. Point *B* on the microsphere-binder axis indicates a volume ratio of binder to microspheres when the void fraction is zero.

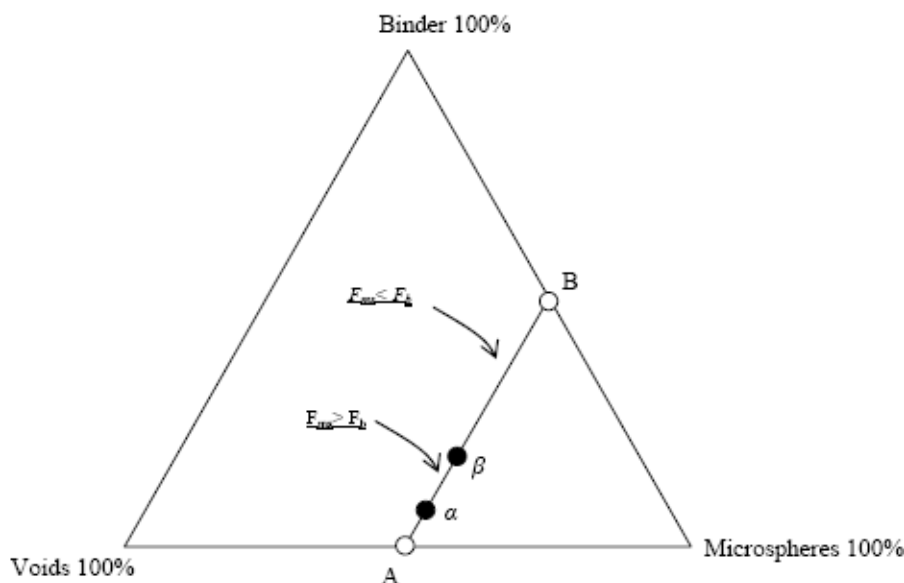


Figure 23. Transitional points and various conditions under compression on the diagram of ternary system.

When the void volume fraction decreases and simultaneously the binder volume fraction increases, the composition of the volume fractions of three constituents follows the line from *A* to *B*. The slope of line *A-B* depends on volume fraction ratio of three constituents. It is in parallel with the voids-binder axis when an amount of decreased void volume is replaced by the same amount of binder volume for a constant microsphere volume fraction; it is higher than that of the voids-binder axis when voids are replaced by binder whose volume is higher than that of voids; or it is otherwise lower.

Compressive mechanical behaviour of syntactic foams is dependant upon properties and volume fractions of constituents, and geometry of microspheres such as ratio of microsphere diameter to wall thickness. Position *A* is the point at which no structural strength exists in the absence of binder. However, as the binder is added, the syntactic foam begins to have a structural strength but the strength is not sufficient until it reaches a certain point α . Thus, syntactic foams in the range between point *A* and point α are not structurally useful and thus failure mode is mainly of gross disintegration as addressed in the literature [8, 10]. As binder content increases past the point α , syntactic foams become useful for structural applications and further their mechanical behaviour is affected by various conditions arising from relative properties of constituents and relativity between load carrying capacities of constituents.

6.2. Relative Conditions and Rules of Mixtures

The compressive (uni-axial) load carrying capacity of syntactic foam (F_{sy}) is divided into two parts i.e. one for microspheres and the other for binder so that

$$F_{sy} = F_{ms} + F_b \quad (12)$$

where F_{ms} is the load carrying capacity of microspheres and F_b is the load carrying capacity of binder.

As the volume fractions of constituents vary, two cases are possible i.e. $F_{ms} > F_b$ and $F_{ms} < F_b$.

The first case [$F_{ms} > F_b$] takes place when binder content is low so that microspheres take up more load up to a point β than binder (Figure 23). However, as the binder content increases, the second case ($F_{ms} < F_b$) occurs in region β -B so that β is a transitional point between the two cases or a point where $F_{ms} = F_b$.

In the first case of [$F_{ms} > F_b$], bonding strength (σ_{bond}) between microspheres (or shear strength of binder depending on failure mechanism) in relation with shear strength of microspheres (σ_{ms}^s) can be considered. Two different conditions are possible i.e. $\sigma_{ms}^s < \sigma_{bond}$ and $\sigma_{ms}^s > \sigma_{bond}$ as will be discussed below.

When the condition of [$F_{ms} > F_b$ and $\sigma_{ms}^s < \sigma_{bond}$] takes place, a possible failure mode under the condition is of shear as illustrated in Figure 24. In this case, shear stress of binder ($\sigma_b^{s'}$) does not reach the shear strength of binder (σ_b^s) at the time microspheres fail due to its premature failure caused by insufficient binder so that $\sigma_b^{s'} < \sigma_b^s$ as illustrated in Figure 25(a). Shear failure surface of this syntactic foam would consist of shear failed broken microspheres and binder areas which are proportional to respective volume fractions (v_{ms} and v_b). Therefore, the rule of mixtures relationship for shear strength of syntactic foam (σ_{sy}^s) can be obtained for a constant void fraction, $v_v (= 1 - v_{ms} - v_v)$, as

$$\sigma_{sy}^s = \sigma_b^{s'} v_b + \sigma_{ms}^s v_{ms} \quad (13).$$

Also, Equation (13) is graphically shown in Figure 25 (b) and compressive strength of syntactic foam (σ_{sy}^c) is given by

$$\sigma_{sy}^c = 2\sigma_{sy}^s = 2\sigma_b^{s'} v_b + 2\sigma_{ms}^s v_{ms} \quad (\text{for } \theta = 45^\circ) \quad (14).$$

when the shear strains of binder and microspheres (γ_b and γ_{ms} respectively) are equal at fracture (if iso-strain condition applies), the shear stress of binder at the premature failure ($\sigma_b^{s'}$) can be related with microsphere shear strain at fracture (γ_{ms}^*):

$$\sigma_b^{s'} = G_b \gamma_{ms}^* \quad (15)$$

where G_b is the shear modulus of binder.

When the condition of [$F_{ms} > F_b$ and $\sigma_{ms}^s > \sigma_{bond}$] takes place, however, microspheres do not fail but debonding between microspheres occurs. Once debonding occurred, binder alone is not capable of further resisting to an increasing compressive load, resulting in total failure of syntactic foam.

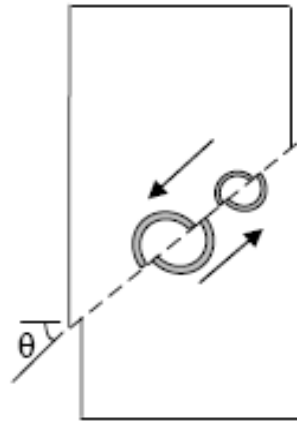


Figure 24. Shear failure of syntactic foams. Binder carries load after microspheres fail.

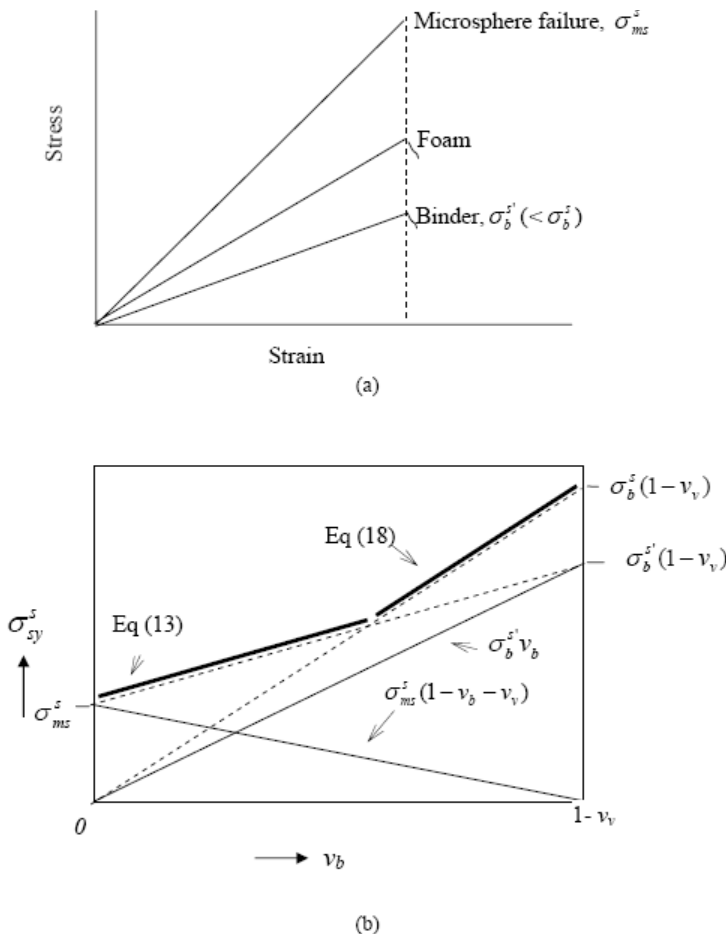


Figure 25. (a) Stress and strain at failure for $[F_{ms} > F_b \text{ and } \sigma_{ms}^s < \sigma_{bond}^s]$. (b) Rule of mixtures for shear failure conditions $[F_{ms} > F_b \text{ and } \sigma_{ms}^s < \sigma_{bond}^s]$ and $[F_{ms} < F_b, \sigma_{ms}^s < \sigma_b^s \text{ and } \gamma_{ms}^* < \gamma_b^*]$ at a constant void fraction (v_v).

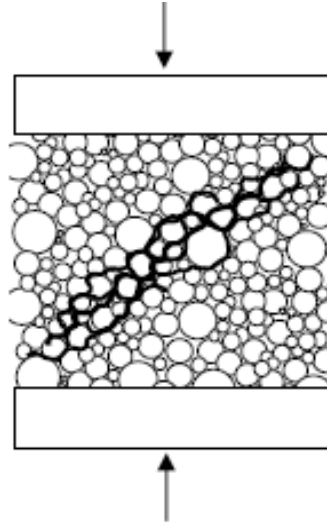


Figure 26. Shear failure of syntactic foams. Debonding area is indicated by thick lines. (Binder and voids are not shown).

Thus, fracture surfaces of syntactic foams consist of mainly unbroken microspheres as will be seen later (Figure 32). The compressive strength (σ_{sy}^c) of syntactic foams, therefore, is mainly dependant upon bond strength (σ_{bond}) particularly for a low binder content (generally dependant upon σ_{bond} and/or σ_b^s) but independent of strength of microspheres. When shear failure occurs as illustrated in Figure 26, shear strength of syntactic foam (σ_{sy}^s) depends on debonding area (A_{bond}) which is larger than an ideally straight cut area of binder (A_{ideal}) inclined 45° to compressive loading direction. The A_{ideal} is proportional to volume fraction of binder (v_b). Thus, it is not unreasonable to assume that debonding/shear area is proportional to volume fraction of binder (v_b) to develop a rule of mixtures relationship for syntactic foam shear strength (σ_{sy}^s) given by

$$\sigma_{sy}^s = C' \sigma_{bond} v_b \quad (16)$$

or

$$\sigma_{sy}^c = C \sigma_{bond} v_b \quad (17)$$

where C' and C are proportional constants. Equation (16) is illustrated in Figure 27.

In the second case of [$F_{ms} < F_b$] where volume fraction of binder is relatively high, the relativity between σ_{ms}^s and σ_{bond} is no longer of major issue in the development of a rule of mixtures relationship for compressive/shear strength of syntactic foam because binder alone is capable of carrying load irrespective of bonding state even after failure of microspheres.

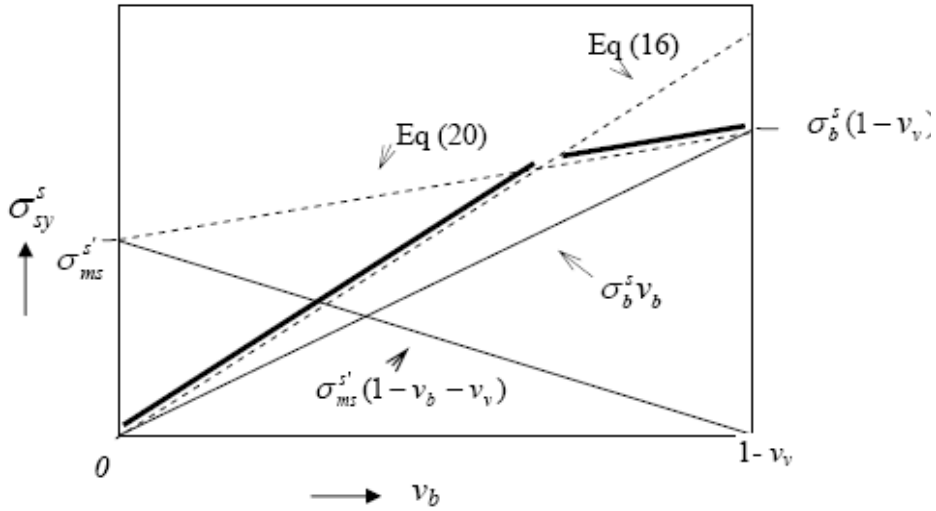


Figure 27. Rule of mixtures for shear failure conditions $[F_{ms} > F_b \text{ and } \sigma_{ms}^s > \sigma_{bond}^s]$ and $[F_{ms} < F_b, \sigma_{ms}^s > \sigma_b^s \text{ and } \gamma_{ms}^* > \gamma_b^*]$ at a constant void fraction (v_v).

Thus, relativity between shear fracture stresses (σ_{ms}^s and σ_b^s respectively for microspheres and binder) and strains (γ_{ms}^* and γ_b^* respectively for microspheres and binder) appears to be appropriate to be considered for imposition of conditions (see below).

When the condition of $[F_{ms} < F_b, \sigma_{ms}^s < \sigma_b^s \text{ and } \gamma_{ms}^* < \gamma_b^*]$ takes place, microspheres fail prematurely on shear plane (if shear failure occurs) and then binder takes over the loading up to a point at which binder fails. In this case, the more microspheres the lower shear strength of syntactic foam for a given void volume fraction (v_v). The shear strength of syntactic foam (σ_{sy}^s) depends on remaining binder so that

$$\sigma_{sy}^s = \sigma_b^s v_b = \sigma_b^s (1 - v_{ms} - v_v) \quad (18)$$

or compressive strength of syntactic foam (σ_{sy}^c) is

$$\begin{aligned} \sigma_{sy}^c &= \frac{\sigma_b^s A_b^s / \sin \theta}{A_{sy}^c} \\ &= 2\sigma_b^s v_b \text{ (if } \theta = 45^\circ) \end{aligned} \quad (19)$$

where A_b^s is the shear area of binder, A_{sy}^s is the shear area of syntactic foam, and A_{sy}^c is the normal compressive area of syntactic foam. Equation (18) is illustrated by thick and dashed

lines in relation with Equation (13) in Figure 25 (b), indicating a transition which can be found by equating Equations (13) and (18).

When the condition of $[F_{ms} < F_b, \sigma_{ms}^s < \sigma_b^s \text{ and } \gamma_{ms}^* > \gamma_b^*]$ takes place, microspheres do not fail until binder fails but they fail immediately as the binder fails on shear plane (if shear failure occurs) so that microspheres do not reach its shear strength (σ_{ms}^s) and failure stress ($\sigma_{ms}^{s'}$) is lower than σ_{ms}^s . The syntactic foam strength is found

$$\sigma_{sy}^s = \sigma_b^s v_b + \sigma_{ms}^{s'} v_{ms} \quad (20)$$

or

$$\sigma_{sy}^c = 2\sigma_b^s v_b + 2\sigma_{ms}^{s'} v_{ms} \quad (21)$$

Equation (20) is illustrated by thick and dashed lines in relation with Equation (13) in Figure 28 (b), indicating a transition which can be found by equating Equations (13) and (20).

When the condition of $[F_{ms} < F_b, \sigma_{ms}^s > \sigma_b^s \text{ and } \gamma_{ms}^* > \gamma_b^*]$ takes place, binder fails on the shear plane first (if shear failure occurs) and immediately would be followed by microsphere detachment from binder, and microspheres alone are not capable of carrying further load. Therefore, microspheres also contribute to the compressive strength of syntactic foam (σ_{sy}^c) but at a stress ($\sigma_{ms}^{s'}$) lower than its shear strength (σ_{ms}^s) so that the syntactic foam strength is found according to Equations (20) and (21).

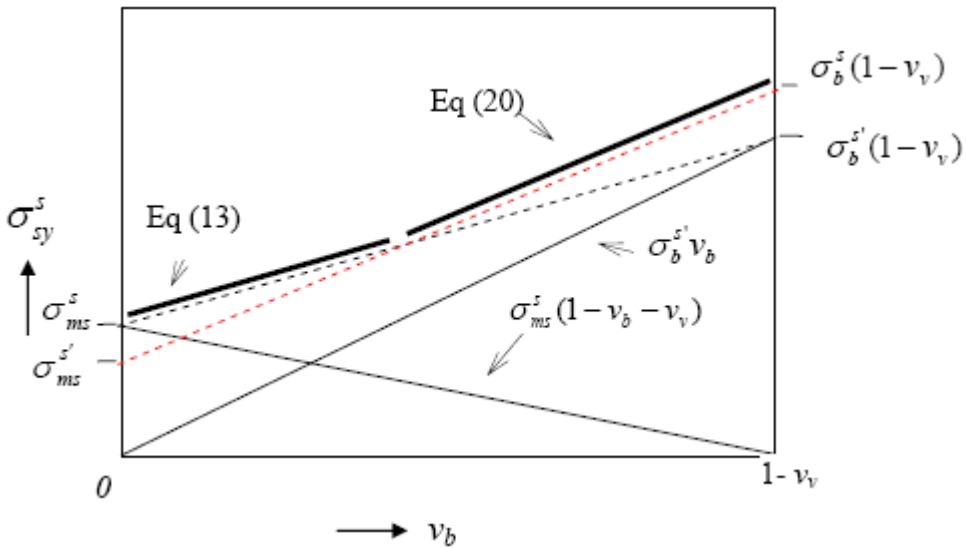


Figure 28. Rule of mixtures for shear failure conditions $[F_{ms} > F_b \text{ and } \sigma_{ms}^s < \sigma_{bond}]$ and $[F_{ms} < F_b, \sigma_{ms}^s < \sigma_b^s \text{ and } \gamma_{ms}^* > \gamma_b^*]$ at a constant void fraction (v_v).

For a constant v_b , Equation (20) is illustrated in relation with Equation (16) by a thick line in Figure 27, indicating that a transition occurs depending on volume fraction of binder for a constant void fraction. The transition can be found by equating Equations (16) and (20).

Given $\sigma_{ms}^{s'} < \sigma_{ms}^s$, $\sigma_{ms}^{s'} = G_{ms} \gamma_b^*$ where G_{ms} is the shear modulus of microspheres (if iso-strain condition applies).

When the condition of [$F_{ms} < F_b$, $\sigma_{ms}^s > \sigma_b^s$ and $\gamma_{ms}^* < \gamma_b^*$] takes place, the iso-strain failure would unlikely take place because microsphere geometry.

Some example failure surfaces for $F_{ms} < F_b$, are found in the literature [20, 29]. The rule of mixtures equations above are summarized in Table 6.

Table 6. Summary for rules of mixtures

$F_{ms} > F_b$		
$\sigma_{ms}^s < \sigma_{bond}$		$\sigma_{ms}^s > \sigma_{bond}$
$\sigma_{sy}^s = \sigma_b^{s'} v_b + \sigma_{ms}^s v_{ms}$ Equation (13) or $\sigma_{sy}^c = 2\sigma_b^{s'} v_b + 2\sigma_{ms}^s v_{ms}$ Equation (14) $G_{sy} = G_b v_b + G_{ms} v_{ms}$ Equation (22)		$\sigma_{sy}^s = C' \sigma_{bond} v_b$ Equation (16) or $\sigma_{sy}^c = C \sigma_{bond} v_b$ Equation (17) $G_{sy} = C' G_b v_b$ Equation (24)

$F_{ms} < F_b$		
$\sigma_{ms}^s < \sigma_b^s$		$\sigma_{ms}^s > \sigma_b^s$
$\gamma_{ms}^* < \gamma_b^*$	$\gamma_{ms}^* > \gamma_b^*$	$\gamma_{ms}^* > \gamma_b^*$
$\sigma_{sy}^s = \sigma_b^s v_b$ Equation (18) or $\sigma_{sy}^c = 2\sigma_b^s v_b$ Equation (19) $G_{sy} = G_b v_b + G_{ms} v_{ms}$ Equation (22)	$\sigma_{sy}^s = \sigma_b^s v_b + \sigma_{ms}^{s'} v_{ms}$ Equation (20) or $\sigma_{sy}^c = 2\sigma_b^s v_b + 2\sigma_{ms}^{s'} v_{ms}$ Equation (21) $G_{sy} = G_b v_b + G_{ms} v_{ms}$ Equation (22)	$\sigma_{sy}^s = \sigma_b^s v_b + \sigma_{ms}^{s'} v_{ms}$ Equation (20) or $\sigma_{sy}^c = 2\sigma_b^s v_b + 2\sigma_{ms}^{s'} v_{ms}$ Equation (21) $G_{sy} = G_b v_b + G_{ms} v_{ms}$ Equation (22)

Elastic modulus may be derived using the rule of equations for compressive strength above if iso-shear condition is imposed.

When the condition of [$F_{ms} > F_b$ and $\sigma_{ms}^s < \sigma_{bond}$] takes place, both microspheres and binder contribute to syntactic foam shear modulus (G_{sy}) at the beginning of deformation.

Thus, both sides of Equation (13) are divided by syntactic foam shear strain (γ_{sy}) or binder shear strain (γ_b) or microsphere shear strain (γ_{ms}), given $\gamma_{sy} = \gamma_b = \gamma_{ms}$, so that

$$G_{sy} = G_b v_b + G_{ms} v_{ms} \quad (22)$$

where G_b is the binder shear modulus and G_{ms} is an average microsphere shear modulus due to random shear positions on each microsphere. Also syntactic foam shear modulus (G_{sy}) may be converted into syntactic foam compressive modulus (E_{sy}) using [36]

$$E_{sy} = 2(1 + \nu) G_{sy} \quad (23)$$

where ν is the Poisson's ratio which is often approximately zero for some foams.

Similarly, Equation (22) can be applicable for other conditions such as [$F_{ms} < F_b$, $\sigma_{ms}^s < \sigma_b^s$ and $\gamma_{ms}^* < \gamma_b^*$] and [$F_{ms} < F_b$, $\sigma_{ms}^s > \sigma_b^s$ and $\gamma_{ms}^* > \gamma_b^*$].

For the condition [$F_{ms} > F_b$, $\sigma_{ms}^s > \sigma_{bond}^s$], shear modulus of syntactic foam is obtained from Equation (16):

$$G_{sy} = C' G_b v_b \quad (24)$$

or if $\nu = 0$,

$$E_{sy} = C' G_b v_b / 2 \quad (25).$$

The binder elastic modulus in Equation (25) is dependant upon the binder structure between microspheres. Thus, generally the binder would be microscopically subjected to combined compressive, shear and tensile stresses but macroscopically in shear in the current case. Also, when microspheres are rigid and they would be in translational/rotational motion under loading and the syntactic foam modulus in the absence of binder is zero like dry powder qualifying Equation (25) for a boundary condition (see point A in Figure 23).

6.3. Mechanical Properties and Failure Behaviour

Volume fractions for syntactic foams as functions of volume fraction of starch in binder prior to drying are given for the failure behaviour study in Figure 29.

Given that high starch contents lead to high density and expensive syntactic foams, the current manufacturing method appears useful allowing us to achieve small volume fractions of starch in syntactic foams. Volume fraction of microspheres in foam (Figure 29(a)) is seen to be not much affected by starch content in binder (= water + starch before drying) and this trend becomes more prominent for SL500 irrespective of gelatinization timing (e.g. pre- or post-mould gel).

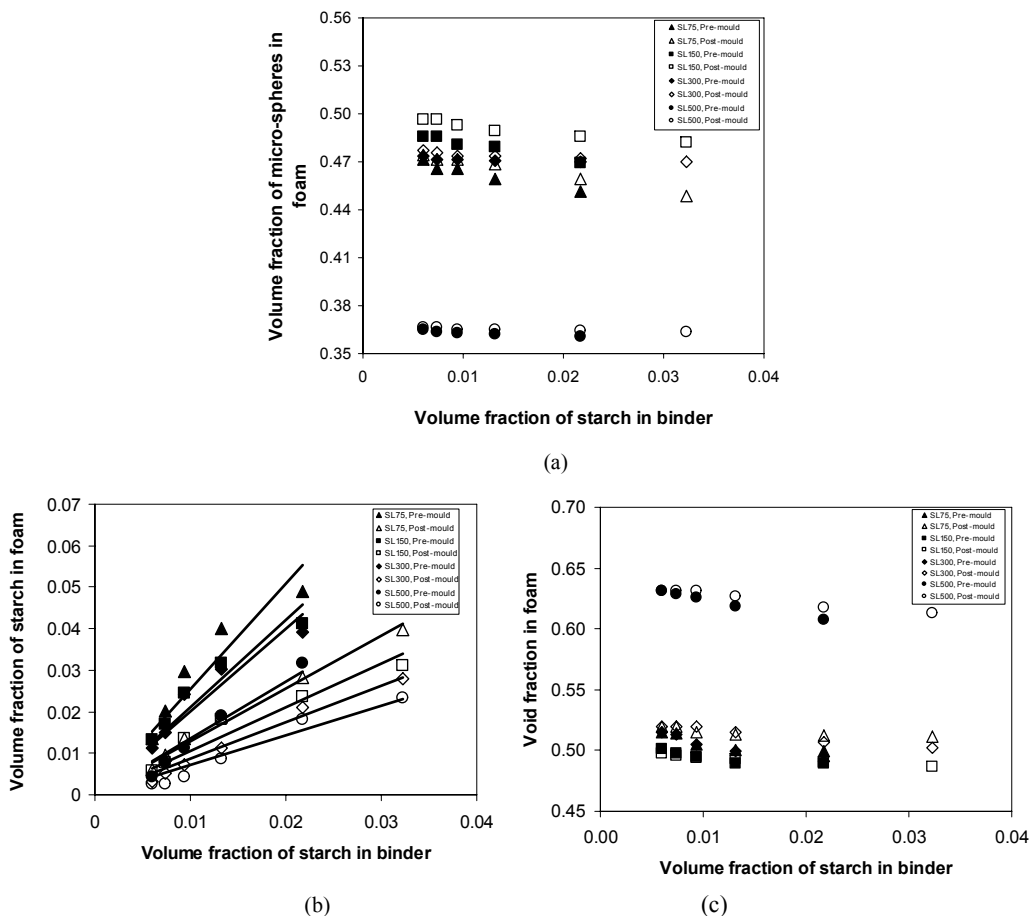


Figure 29. Various volume fractions for foams manufactured as a function of volume fraction of starch in binder prior to drying: (a) volume fraction of microspheres in dried foam; (b) volume fraction of starch in dried foam (correlation coefficients with a forced intercept at zero for SL75 pre = 0.928, SL150 pre = 0.939, SL300 pre = 0.938, SL500 pre = 0.970; SL75 post = 0.993, SL150 post = 0.956, SL300 post = 0.987, SL500 post = 0.969); and (c) void fraction in dried foams.

The reason for this is that the amount of starch contained in SL500 is relatively small as seen in Figure 29(b). Volume fraction of microspheres for SL500 is found to be particularly low compared to others. This appears to be related to an approximately constant high void fraction in SL500 as shown in Figure 29(c). Volume fraction of starch in foam (Figure 29(b)) is highly proportional to starch content in binder with high correlation coefficients as given in the caption of Figure 29(b). Also it increases as microsphere size becomes small and is high for pre-mould method.

General features of stress-strain curves resulted from mechanical testing for all microsphere size groups were found to be similar to each other. Some typical stress-strain curves represented by SL300 foams are given in Figure 30 in which various starch contents for both pre- and post-mould methods are shown.

The maximum stresses (or compressive strengths) generally appear to be followed by the negative slopes and then plateau regions in the case of low starch contents (or low strengths). In the case of high starch contents, however, the low negative slopes tend to be accompanied by some undulation.

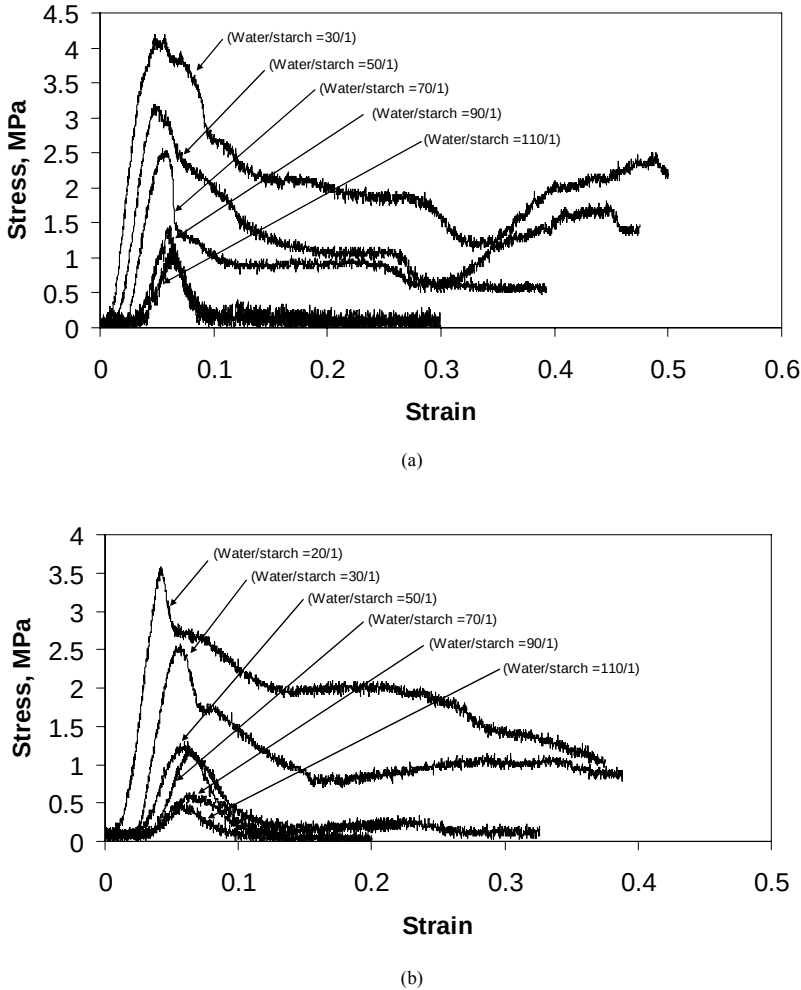


Figure 30. Typical stress-strain curves (SL300) with mass ratios of water to starch : (a) pre-mould method; and (b) post-mould method. The mass ratios of water to starch given here correspond with volume fractions of starch in binder in Figure 29 respectively.

It was difficult to define a densification stage in a curve. This seems to be due to shear failure mechanism of relatively high aspect ratio of compressive specimens, which will be discussed below because, once shear failure at the maximum stress occurred, sliding of fracture surfaces rather than densification is possible.

It was observed that compressive failure of all the foams is generally either by shear on planes inclined approximately 45° to the loading direction (Figure 31(a) and (c)) or of ‘cup and cone’ type with vertical splitting (Figure 31(b) and (d)).

Some SEM images for specimens with various starch contents in foams (prepared with a constant mass ratio of water to starch, 70/1) and various size groups are shown in Figure 32. Not many broken microspheres are seen on fracture surfaces of low binder contents, indicating that microspheres were mainly debonded and hence the failures were governed under the condition of $[F_{ms} > F_b \text{ and } \sigma_{ms}^s > \sigma_{bond}]$.

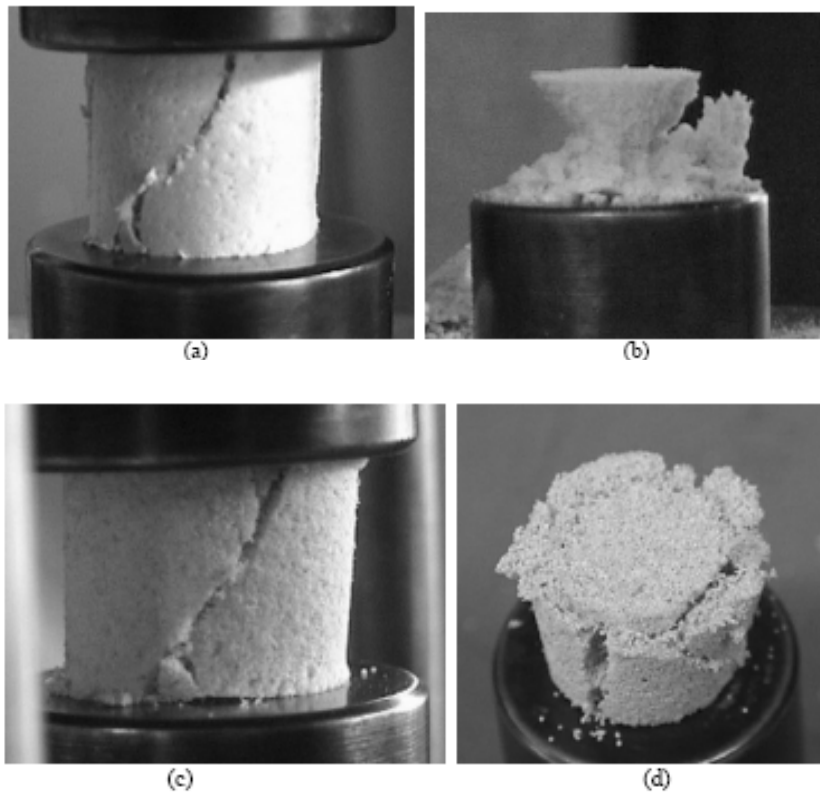


Figure 31. Some examples of failure mode showing shear on planes inclined about 45° to the loading direction or 'cup and cone' type: (a) SL75, pre-mould gel, mass ratio of water to starch =110/1; (b) SL150, pre-mould gel, mass ratio of water to starch =110/1; (c) SL300, pre-mould gel, mass ratio of water to starch =110/1; and (d) SL500, post-mould gel, mass ratio of water to starch =30/1.

In some other specimens of SL300 containing highest binder contents for both pre- and post-mould methods (prepared with a mass ratio of water to starch, 30/1), however, many broken microspheres were found on fracture surfaces, indicating the condition of $[F_{ms} > F_b \text{ and } \sigma_{ms}^s > \sigma_{bond}]$ was terminated but it is possible that the condition of $[F_{ms} > F_b \text{ and } \sigma_{ms}^s < \sigma_{bond}]$ commenced due to increased binder content.

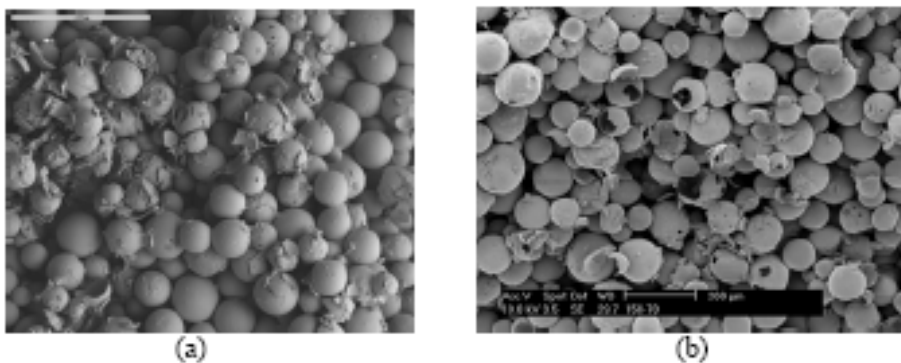


Figure 32. (Continued).

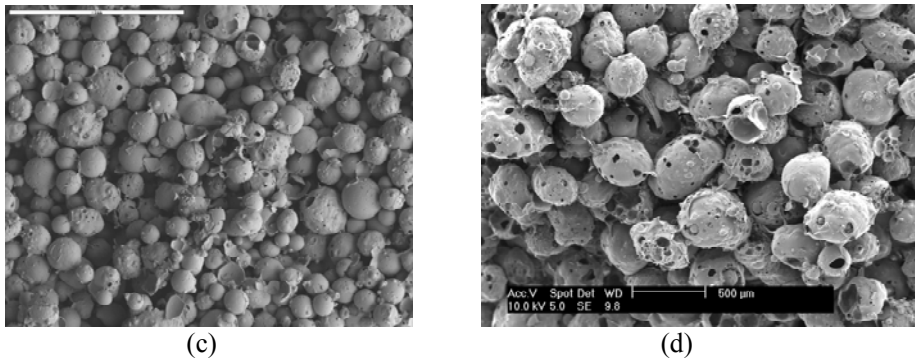


Figure 32. SEM images of fracture surfaces of compressive specimens with water/starch=70/1: (a) SL75, $v_b = 0.030$, pre-mould gel; (b) SL150, $v_b = 0.024$, pre-mould gel; (c) SL300, $v_b = 0.007$, post-mould gel; and (d) SL500, $v_b = 0.011$, pre-mould gel,. The scale bar in ‘(a)’ and ‘(b)’ represents 200 μ m, in ‘(c)’ 1mm, and in ‘(d)’ 500 μ m.

Note that binder content for all foams is still sufficiently low to be under the condition of $F_{ms} > F_b$ as seen in Figure 29(b). On the other hand, it is interesting to find that binder between microspheres formed two dimensional webs in some areas, which is obviously dried starch as a result of evaporation of water.

It might be possible to trace down contact points of microspheres prior to failure using the shape of dried binder. When a microsphere is contacted with other two microspheres as shown in Figure 33, wet binder can be trapped due to capillary action between microspheres and dries to form a 2D web.

No major difference in microscopic features between pre- and post-mould methods was found although pre-mould method allows foam to contain more starch than post-mould method as discussed in relation with data in Figure 29.

Compressive strength (Figure 34) and modulus (Figure 35) (with specific properties) of all the foams increase with increasing foam density as expected. They also increase as microsphere size decreases for a given density although SL500 displays some anomaly compared to others. Gelatinization timing (pre- or post-mould), however, does not seem to affect much compressive strength and modulus for a given volume fraction of starch.

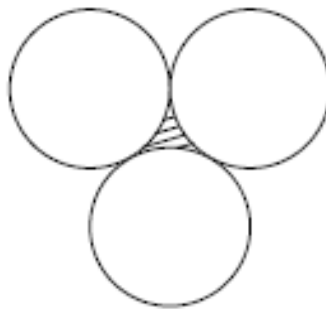


Figure 33. Formation of 2D web on a microsphere surface. Hatched area represents binder before drying.

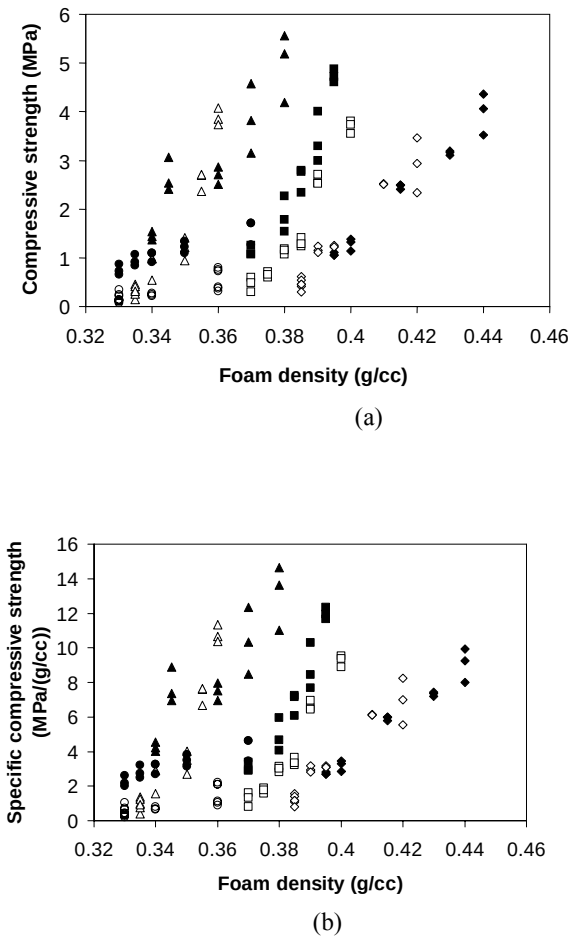


Figure 34. (a) Compressive strength and (b) specific compressive strength as function of foam density: $\blacktriangle$, SL75 pre-mould gelatinization; $\triangle$, SL75 post-mould gelatinization; $\blacksquare$, SL150 pre-mould gelatinization; $\square$, SL150 post-mould gelatinization; $\blacklozenge$, SL300 pre-mould gelatinization; $\lozenge$, SL300 post-mould gelatinization; $\bullet$, SL500 pre-mould gelatinization; and $\circ$, SL500 post-mould gelatinization.

Compressive strength is replotted as a function of volume fraction of dried binder (or starch) and is given in Figure 36.

In contrast to the previous plot in Figure 34, compressive strengths of SL75, SL150 and SL300 are seen to be approximately independent of microsphere size group as previously predicted by the rule of mixtures equations.

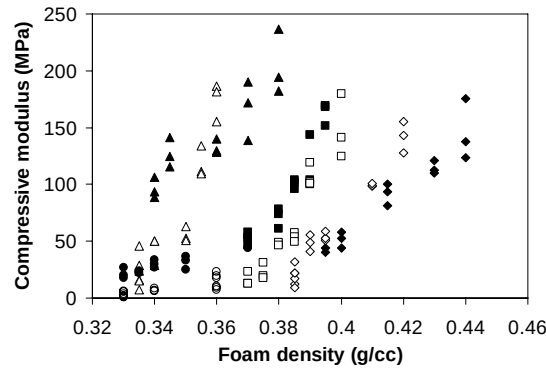
The three size groups have, in fact, similar constant volume fractions of microspheres as already shown in Figure 29. Therefore, the slopes and positions of line *A-B* (in Figure 23) for the three size groups are similar and would be approximately in parallel with that of voids–binder axis on the diagram in Figure 23.

Now, the compressive strength of syntactic foams in region $\alpha\text{-}\beta$ (in Figure 23) is directly affected by binder properties irrespective of compressive strength of microspheres under the condition of $[F_{ms} > F_b \text{ and } \sigma_{ms}^s > \sigma_{bond}]$ and hence Equation (16) or (17) can be employed.

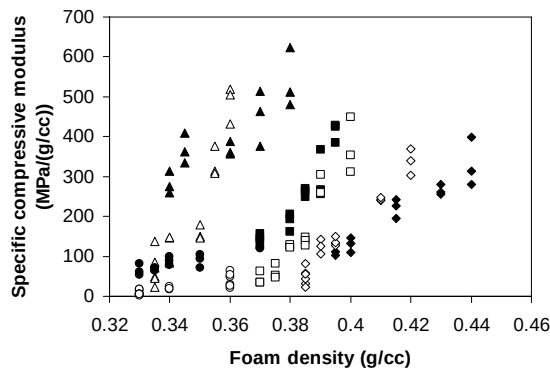
(Note that Equation (13) or (14) is not to be used because the condition of $[F_{ms} > F_b \text{ and } \sigma_{ms} < \sigma_{bond}]$ might have occurred at the end of the range as a result of increase in binder.)

Equation (17) is plotted in Figure 36, given void fraction is reasonably constant (approximately 0.5 except for SL500) and its correlation coefficient was found to be 0.956 with a value of 102MPa for $C\sigma_{bond}$ in Equation (17) for the three size groups (SL75, SL150 and SL300) collectively.

SL500 microspheres were excluded in the collective analysis because they are somewhat different from other size groups of microspheres as seen in Figure 32.



(a)



(b)

Figure 35. (a) Compressive modulus and (b) specific compressive modulus as function of foam density: $\blacktriangle$, SL75 pre-mould gelatinization; $\triangle$, SL75 post-mould gelatinization; $\blacksquare$, SL150 pre-mould gelatinization; $\square$, SL150 post-mould gelatinization; $\blacklozenge$, SL300 pre-mould gelatinization; $\lozenge$, SL300 post-mould gelatinization; $\bullet$, SL500 pre-mould gelatinization; and $\circ$, SL500 post-mould gelatinization.

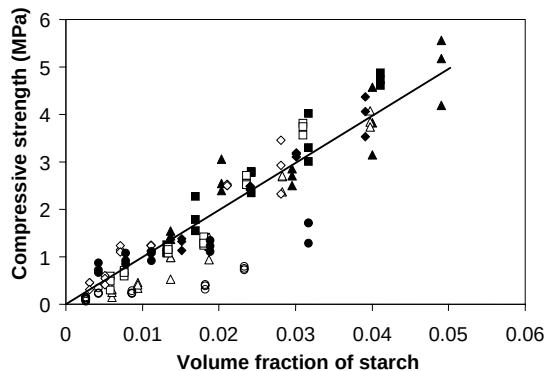


Figure 36. Compressive strength as function of volume fraction of starch in foam: $\blacktriangle$, SL75 pre-mould gelatinization; $\triangle$, SL75 post-mould gelatinization; $\blacksquare$, SL150 pre-mould gelatinization; $\square$, SL150 post-mould gelatinization; $\blacklozenge$, SL300 pre-mould gelatinization; $\lozenge$, SL300 post-mould gelatinization; $\bullet$, SL500 pre-mould gelatinization; and $\circ$, SL500 post-mould gelatinization. The least square line is for SL75, SL150 and SL300 collectively.

In addition to high void fraction (Table 4 and 5), they are porous, of poor roundness and posses rough surface texture, possibly resulting in different bond strength (σ_{bond}) to other size groups of microspheres for a given binder content.

Compressive modulus (E_{sy}) is also re-plotted as a function of binder content and given in Figure 37. Similarly to the compressive strength, it is mainly affected by binder content but not much by microsphere size.

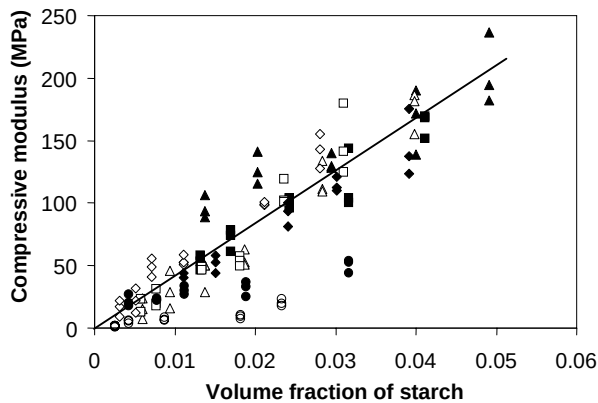


Figure 37. Compressive modulus as a function of volume fraction of starch in foam: $\blacktriangle$, SL75 pre-mould gelatinization; $\triangle$, SL75 post-mould gelatinization; $\blacksquare$, SL150 pre-mould gelatinization; $\square$, SL150 post-mould gelatinization; $\blacklozenge$, SL300 pre-mould gelatinization; $\lozenge$, SL300 post-mould gelatinization; $\bullet$, SL500 pre-mould gelatinization; and $\circ$, SL500 post-mould gelatinization. The least square line is for SL75, SL150 and SL300 collectively.

The least square line with a forced intercept at origin is plotted for the three sizes groups (SL75, SL150 and SL300) collectively and its correlation coefficient was found to be 0.937. SL500 was excluded again for the same reason as discussed for the compressive strength. Thus, the compressive modulus of three groups of microspheres (SL75, SL150 and SL300) appears to be approximately proportional to the binder content, supporting Equation (25).

7. SANDWICH COMPOSITES

7.1. Fabrication of Syntactic Foam Panel

Syntactic foam panels based on the pre-mould method were manufactured for sandwich composites. As described above, the top phase consisted of microspheres and binder, bottom phase consisted of starch rich binder as sediment and middle phase consisted of water. The bottom two phases were drained out through a hole at the bottom of the container and the left mixture was directly transferred using a scoop into an open mould with a cavity of $200 \times 100 \times 20$ mm placed on an aluminium base covered with a layer of news printed paper for easy demoulding later. The moulded mixture was placed in an oven at 80°C for 2 hours and the following procedure sequentially followed: (a) partially dried mixture was demoulded and slowly pressed with a flat aluminium plate after placing another layer of news paper on top of the mixture until a desired foam panel thickness was achieved; (b) and this lay-up was kept for further 5 hours in oven. Finally the aluminium plates and layers of news paper was removed, allowing the foam to fully dry for one more hour. The top and bottom aluminium plates contained small holes of 1 mm in diameter with a spacing of 15 mm for breathing.

Four different types of syntactic foam were manufactured. They were coded as SLxxWSxx. For example, SL75WS50 is for microsphere size group, SL75, and a mass ratio of water to starch, 50/1. Thus, the manufactured syntactic foams are SL75WS50, SL300WS30, SL75WS70, and SL300WS50.

A humidity chamber (Model 3033 Steri-Cult Incubator, Forma Scientific, Inc., Ohio) was used for moisture treatment on manufactured syntactic foam panels.

7.2. Skin Paper Preparation for Tensile Property Characterization

Brown plain paper (Visy Paper, 180 g/m^2 in mass and 0.30 mm in thickness) was used as skin for sandwich composites. Three different types of adhesive between skin and foam core were prepared by varying starch concentration in water (Table 7) i.e. three mass ratios of water to starch, 14/1, 30/1 and 70/1. Again, three different types of specimens for tensile properties of skin paper were prepared. The first type was for specimens without starch adhesive, second and third types were coated with starch adhesive in two different ways of drying starch adhesive. For both second and third types of skin paper, starch adhesive prepared with a ratio of 30/1 for water to starch (Table 7) was applied to skin paper using a roller with a single stroke of motion to control starch content. Subsequently, for the second type (slowly dried), skin paper was enveloped in wet cloth carefully not to be in contact with each other in a small chamber but to slow down drying starch adhesive for four hours at room

temperature and then finally fully dried in an oven. For the third type (fast dried), skin paper was just left in laboratory ambience for four hours at 20°C and then placed in an oven at 50°C until fully dried.

Table 7. Starch mass on skin paper after single stroke coating by a roller. The starch mass was measured after drying. The 95% confidence intervals are given in parenthesis

Mass ratio of water to starch	Starch (mg/cm ²)
14/1	1.56 (±0.010)
30/1	0.51 (±0.006)
70/1	0.18 (±0.002)

7.3. Sandwich Composite Manufacture

The paper skin was cut into rectangles with dimensions of 86 x 26 mm. Starch adhesive was applied to the paper skin using a roller with a single stroke of motion to control starch content on the paper skin. Sandwich composites were constructed by attaching skin paper with starch adhesive on to top and bottom surfaces of syntactic foam core. To maximize contact area between paper skin and syntactic foam core, four layers of sandwich composite between two aluminium plates were stacked up with soft inserts between sandwich composites so that the sequence of the lay-up is made of aluminium plate, Cling wrap (Home Brand, Woolworths Ltd, Australia)), two layers of paper towel (Handee Ultra, SCA Hygiene Australia Pty Ltd), Cling wrap, sandwich, so on. The lay-up was left at room temperature for 4 hours and then placed in an oven at 50°C up to 8 hours until no mass change was observed.

Sandwich composites manufactured will be referred to as SLxxWSxx - WSxx for microsphere size group used and mass ratio of water to starch for syntactic foam binder as previously denoted for syntactic foam panels, and, in addition, mass ratio of water to starch for starch adhesive between skin paper and syntactic foam core. For example, SL75WS50-WS30 denotes that microsphere size group is SL75 with a mass ratio 50/1 of water to starch for syntactic foam binder, and mass ratio of water to starch for adhesive between skin paper and core is 30/1.

7.4. Mechanical testing and Calculations

All mechanical tests were conducted on a universal testing machine (Shimadzu 5000) at a crosshead speed of 1.0 mm/min and at an ambient temperature range of 18-21°C.

Three point flexural tests with a span length (L) of 63.5 mm were conducted for syntactic foam panels and sandwich composites (Figure 38).

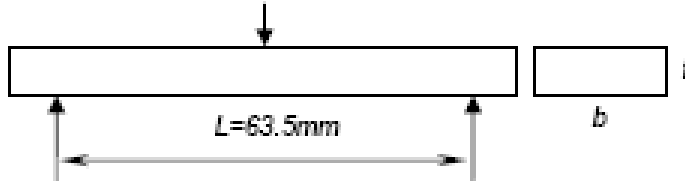


Figure 38. Three-point loading for flexural tests.

Flexural modulus (E) and stress (σ_f) for syntactic foam panels were calculated using the following equations given in ASTM D 790M – 93:

$$E = \frac{L^3 m}{4bt^3} \quad (26)$$

and

$$\sigma_f = \frac{3P_f L}{2bt^2} \quad (27)$$

where L is the support span, m is the slope of the tangent to the initial straight-line portion of the load-deflection curve, b is the width of panel, t is the thickness of panel, and P_f is the load. Flexural strengths (σ_{fc}) were calculated with the first peak load (P_{fc}). The maximum flexural strain (ε_f) for syntactic foam panels was also calculated using [35]

$$\varepsilon_f = \frac{6t\delta}{L^2} \quad (28)$$

where δ is the mid span deflection.

Tensile elastic modulus (E_t) for syntactic foam panels was calculated using [35]

$$E_t = E_c \left(\frac{\sqrt{\frac{E}{E_c}}}{2 - \sqrt{\frac{E}{E_c}}} \right)^2 \quad (29)$$

where E_c is the compressive elastic modulus.

Effective stiffness (S_{eff}) for sandwich composites was calculated using

$$S_{eff} = \frac{EI}{b} \quad (30)$$

where I is given by $I = \frac{bt^3}{12}$, and t is the total thickness for skin and core in the case of sandwich composite.

The location of neutral axis (y_0) [35] from the top surface (compression side) was calculated using

$$y_0 = \frac{t}{1 + \sqrt{E_C / E_T}} \quad (31)$$

where E_T and E_C are tensile modulus and compressive modulus respectively.

Average shear stress (τ_{av}) [36] produced by flexural loading was calculated using

$$\tau_{av} = \frac{VQ}{Ib} \quad (32)$$

where V is the shear force, Q is the first moment about the neutral axis of the portion of the rectangular cross section which is located either above or below the location for which shear stress is to be calculated, and I is the moment of inertia of the entire cross sectional area about the neutral axis.

Tensile tests on paper skin for sandwich composites were conducted at a relative humidity of 51%. Specimen geometry and dimensions are given in Figure 39. All other test specimens were oven dried before mechanical testing unless otherwise stated.

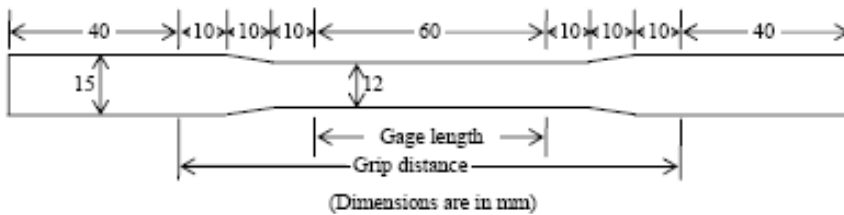


Figure 39. Tensile test specimen with dimensions for skin paper.

7.5. Constituent Materials Behaviour

Properties of syntactic foam panels for SL75WS50 and SL300WS30 are listed in Table 8. Two different microsphere size groups but a constant volume fraction of starch in syntactic foam was chosen. Flexural properties of both syntactic foams panels appears to be similar as expected from the common volume fraction of starch as discussed above for compressive behaviour. An example for flexural (maximum) stress versus maximum strain curve (grey line) obtained using Equations (27) and (28) is given in Figure 40. It appears to be linear and no energy absorption after the peak load is seen. Not much difference in behaviour between syntactic foam panel and skin paper is noticed even though a large difference in strength is found. Images of fracture surfaces for SL75WS50 and SL300WS30 are given in Figure 41.

Not much difference between compression and tension sides is found although it would have been possible to have more crushed microspheres on compression side than tensile side if inter-microsphere bonding was stronger.

Moisture absorption measurements in syntactic foam panels of SL75WS50, SL300WS30, SL75WS70, and SL300WS50 subjected to 70% relative humidity at 32°C are given in Figure 42. It is seen that moisture content increases rapidly in the first several hours and then is saturated afterwards. The saturated moisture content appears high for high starch volume fraction of syntactic foam panel for a given microsphere size as expected from the fact that microspheres hardly observe moisture but starch does. It also appears high for large microsphere size for a given volume fraction of starch, probably because of possible porosity between microspheres. Further, mechanical testing on syntactic foam panels after being subjected to moisture for about two months was conducted and results for SL75WS50, SL300WS30 are listed in Table 9.

Table 8. Properties of syntactic foam panels. The 95% confidence intervals are given in parenthesis

Syntactic foam	Flexural strength, σ_{fc} (MPa)	Flexural modulus, E (GPa)	Compressive modulus, E_c (MPa)	Tensile modulus [†] , E_t (GPa)	Maximum strain at fracture, $\varepsilon_f \times 10^3$	Density (g/cc)	Starch Volume fraction
SL75WS50	7.89 (± 1.50)	1.06 (± 0.07)	167 (± 64)	4.00 (± 0.93)	9.81 (± 1.66)	0.37	0.04
SL300WS30	7.57 (± 0.80)	1.13 (± 0.13)	146 (± 67)	1.88 (± 0.51)	7.44 (± 1.97)	0.44	0.04

[†] Calculated using Equation (29).

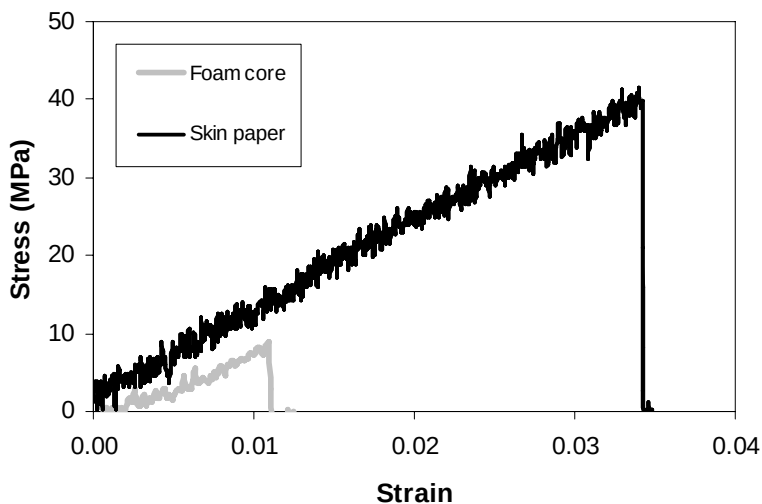


Figure 40. Examples for flexural (maximum) stress versus maximum strain curve (in grey) obtained using Equations (27) and (28) for syntactic foam panel SL75WS50; and for tensile stress strain curve (in black) obtained from skin paper without starch adhesive on.

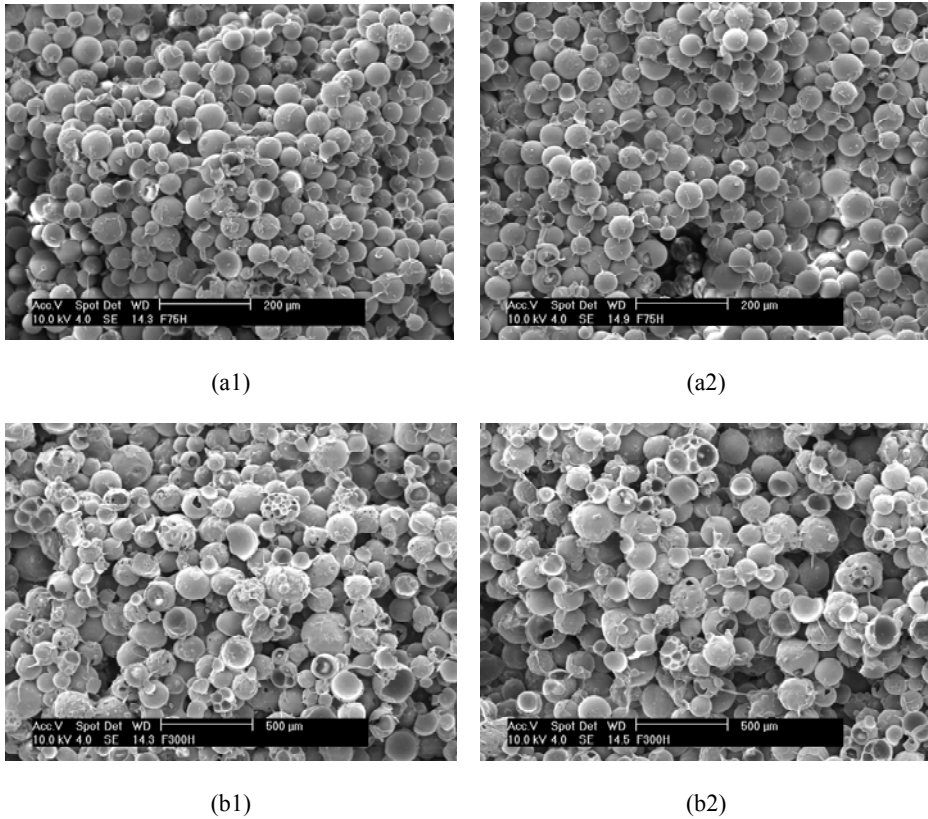


Figure 41. Scanning electron microscopic (SEM) images of fracture surfaces of syntactic foam panels from three-point flexural tests: (a1) compression side of SL75WS50; (a2) tension side of SL75WS50; (b1) compression side of SL300WS30; and (b2) tension side of SL300WS30.

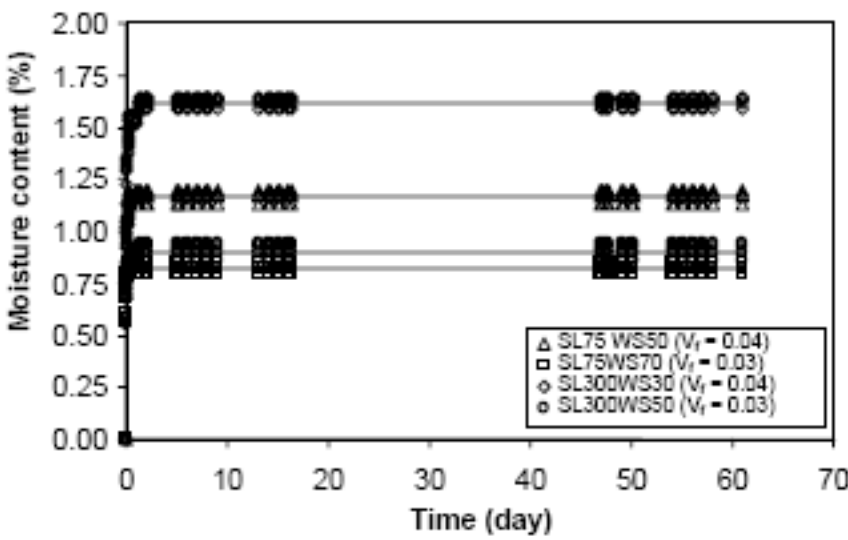


Figure 42. Moisture absorption in syntactic foam panels of SL75WS50, SL75WS70, SL300WS30, and SL300WS50 subjected to 70% relative humidity at 32°C. Starch volume fraction in each syntactic foam panel (V_f) is given.

Table 9. Properties of syntactic foam panels after moisture treatment for about two months. The 95% confidence intervals are given in parenthesis

Syntactic foam	Flexural strength, σ_{fc} (MPa)	Flexural modulus, E (GPa)	Maximum strain (ϵ_f) at fracture $\times 10^3$	Moisture mass content (%)
SL75WS50	7.57 (± 0.42)	1.09 (± 0.04)	10.02 (± 0.83)	1.18 (± 0.047)
SL300WS30	7.14 (± 0.56)	0.81 (± 0.04)	12.34 (± 0.42)	1.67 (± 0.150)

In comparison with results for oven-dried specimens given in Table 8, no significant moisture effect on flexural strength was found. Flexural strengths (σ_{fc}) for specimens SL75WS50 and SL300WS30 appear to be decreased by 4% and 6% respectively. Substantial effect of moisture was found to be 28% decrease in flexural modulus for SL300WS30 but not much effect was found for SL75WS50.

Tensile properties of skin paper for three different types of preparation were characterized and listed in Table 10.

Table 10. Tensile properties of skin paper for three different types of preparation. Starch adhesive for coating was prepared with a ratio of 30/1 for water to starch. The 95% confidence intervals are given in parenthesis

Tensile Strength (MPa)			Tensile Modulus (GPa)		
Without starch adhesive	Coated with starch adhesive (Fast dried)	Coated with starch adhesive (Slowly dried)	Without starch adhesive	Coated with starch adhesive (Fast dried)	Coated with starch adhesive (Slowly dried)
36.15 (± 2.56)	36.37 (± 1.34)	38.01 (± 1.11)	0.96 (± 0.03)	1.04 (± 0.08)	1.10 (± 0.05)

Results for the second (fast dried) and third (slowly dried) types were obtained from follow-up tests after realizing in the course of evaluation of sandwich composites that there might have been unknown effects of adhesive (between paper skin and core) on skin paper caused by adhesive drying process. Tensile strength and modulus of paper skin appear to increase by 0.6% and 8.3% respectively as a result of fast drying adhesive on, and further increase as a result of slow drying by 5.1% and 14.7% respectively. This indicates that the effect of starch adhesive is greater in stiffening than in strengthening. Figure 43 shows typical SEM images of skin paper surfaces prepared in three different ways. The number of fibre edge lines decreases and hence the level of details in the order of the first, second, and third types of preparation. The second type can further be compared with the third type for drying speed effect, indicating that gelatinized starch has permeated through the skin paper, giving more stiffening effect.

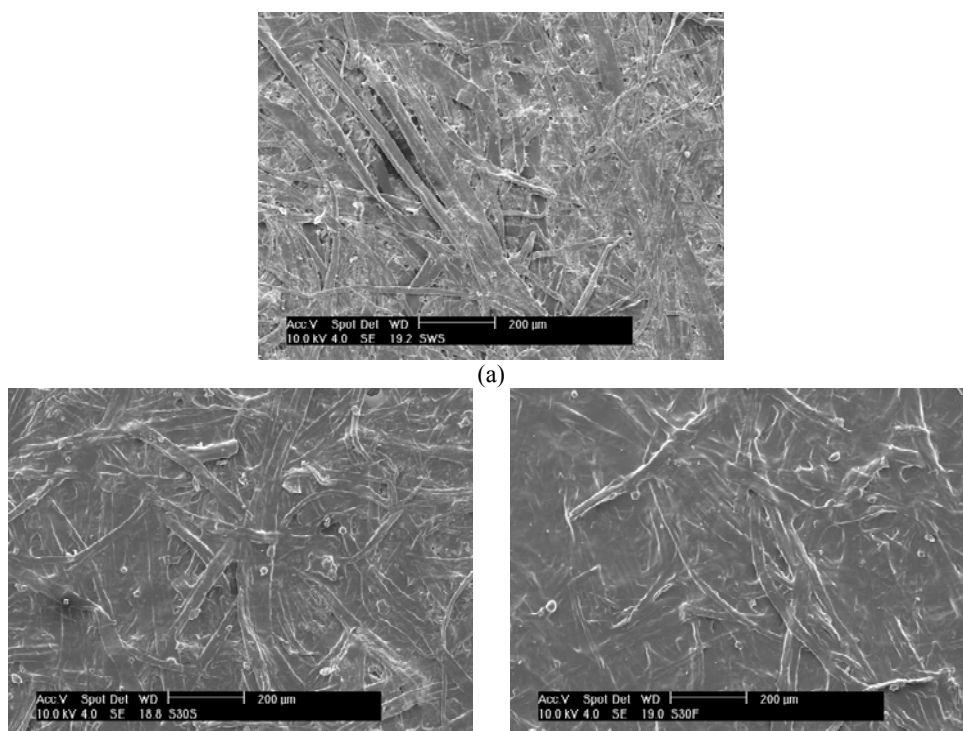


Figure 43. SEM images of typical skin paper surfaces: (a) without starch adhesive; (b) coated with starch adhesive, slowly dried; and (c) coated with starch adhesive, fast dried.

7.6. Sandwich Composites Behaviour

In general, mechanical performance of sandwich composites depends on adhesion strength between skin and core in addition to mechanical properties of constituent properties. When starch adhesive is used for skin and core for continuous production of sandwich, it is important to optimize starch content. As previously discussed for pre-mould method, there is a range of low viscosities in starch binder prior to a transition towards a higher rate of viscosity change (Figure 4). (The transition takes place when a volume fraction of gelatinized starch sedimentation after two phase separation closely approaches one (Figure 5).) The low range of viscosities may be preferred for coating starch adhesive on skin paper for sandwich composite manufacture. Starch adhesives with three different starch mass ratios (water/starch), 14/1, 30/1, and 70/1 respectively were prepared for attaching skin paper to surfaces of syntactic foam core for sandwich composites. The ratio of 14/1 is higher and the other two ratios (30/1 and 70/1) are lower than the aforementioned transitional point.

The mechanical performance under three-point flexural loading of manufacture sandwich composites is summarized in Table 11 in terms of load carrying capacity (=first peak load /width) and stiffness. Two different syntactic foam core types, SL75WS50 and SL300WS30, were chosen for the sandwich composites, given that the two types have a common starch volume fraction of 0.04 and hence similar mechanical properties (see Table 8) but different surface conditions due to different microsphere sizes as shown in Figure 44.

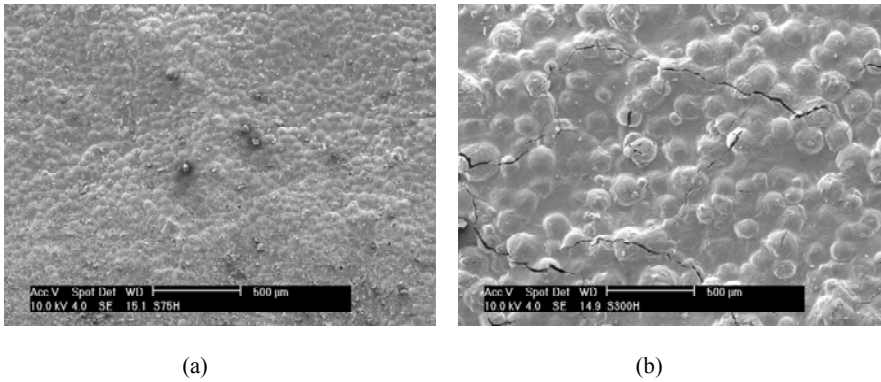


Figure 44. SEM images of the syntactic foam panel surfaces: (a) SL75WS50; and (b) SL300WS30.

Table 11. Three-point flexural test results for sandwich composites. The 95% confidence intervals are given in parenthesis

Sandwich composite	First peak load per unit width (N/mm)	Effective stiffness, EI/b (Nm)
SL75WS50-WS14	12.67 (± 0.683)	141 (± 1.982)
SL75WS50-WS30	10.73 (± 0.808)	128 (± 7.585)
SL75WS50-WS70	9.31 (± 0.430)	127 (± 4.115)
SL300WS30-WS14	11.48 (± 0.495)	104 (± 1.608)
SL300WS30-WS30	10.58 (± 0.740)	101 (± 2.287)
SL300WS30-WS70	8.02 (± 0.319)	101 (± 2.007)

Flexural load carrying capacity (Table 11) appears to increase with increasing starch content in adhesive for both SL75WS50 and SL300WS30, indicating that adhesive bonding between syntactic foam core and skin paper increases for large starch content in adhesive. However, effective stiffness (EI/b) is mostly marginal as expected from similar moduli between syntactic foam core and skin paper, and also as expected from negligibly small volume fraction of starch adhesive for skin in sandwich composites. Given that the elastic moduli of skin paper and syntactic foam core are similar (see Tables 9 and 10), estimation using Equation (27) for flexural strength for sandwich composites as homogeneous materials were conducted and shown in Figure 45 including syntactic foam core without skin paper on, allowing us to see the skin paper reinforcement effect as well on mechanical properties of syntactic foam core. Substantial enhancement on flexural strength up to 40% due to skin paper, depending on starch adhesive content in the skin paper, is seen.

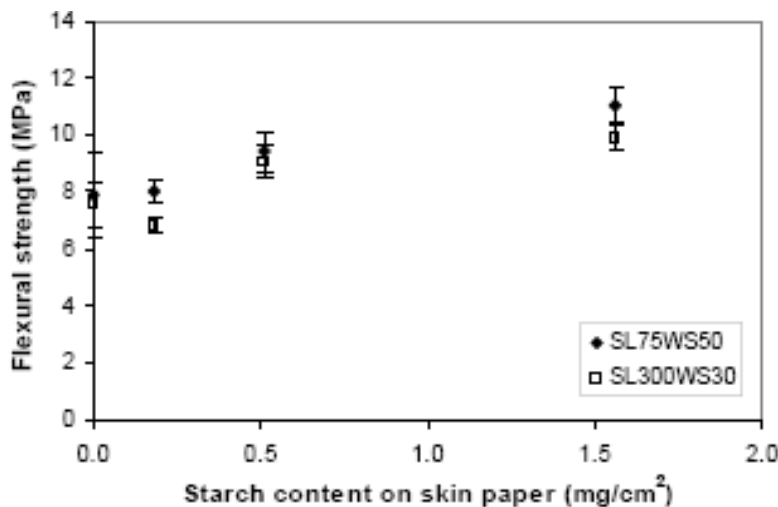


Figure 45. Estimated flexural strength based on Equation (27) for sandwich composites for different starch contents in adhesive contained in skin paper. The zero starch content is for syntactic foam core only without skin paper. The error bars indicate 95% confidence intervals.

As for failure sequence of a sandwich composite, three different failure sites such as core, skin, and interface between core and skin may be considered and hence six permutations of failure sequence are possible. The sequence depends upon constituent properties, loading conditions, sandwich dimensions such as thicknesses of core and skin. If a span length of sandwich specimen under three point flexural loading is long, delamination of skin paper is less likely because less shear stress exerts on interface. If thickness of sandwich panel is small, delamination of skin paper is also less likely for the same reason. In experiment, we were able to detect the first audible ‘pop’ sound from the syntactic foam core cracking prior to any failure. Thus, the failure sequence is narrowed down from six to two possibilities of sequence i.e. core → skin → interface, and core → interface → skin. An example of failure shown in Figure 46 (a), though, indicates core → interface only, leading to full delamination without skin failure. When starch content is high in interface and hence high interfacial adhesion strength as shown in Figure 46 (b), failure sequence would tend be core → skin → interface.

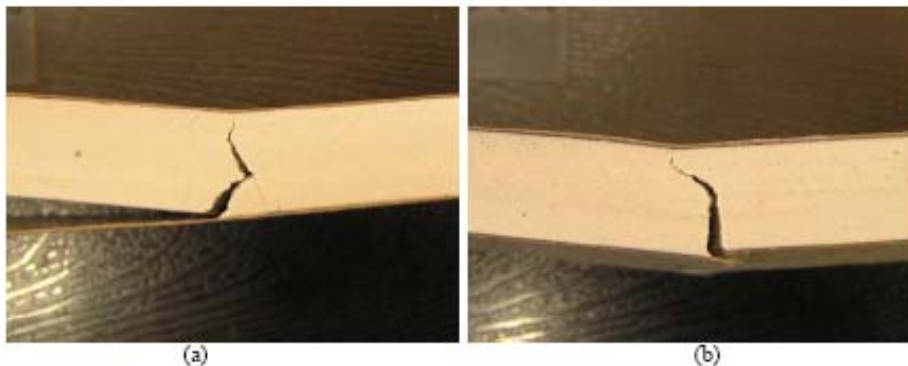


Figure 46. Examples for delamination after fracture under three point flexural loading: (a) SL75WS50-WS70, fully delaminated; and (b) SL75WS50-WS14, least delaminated.

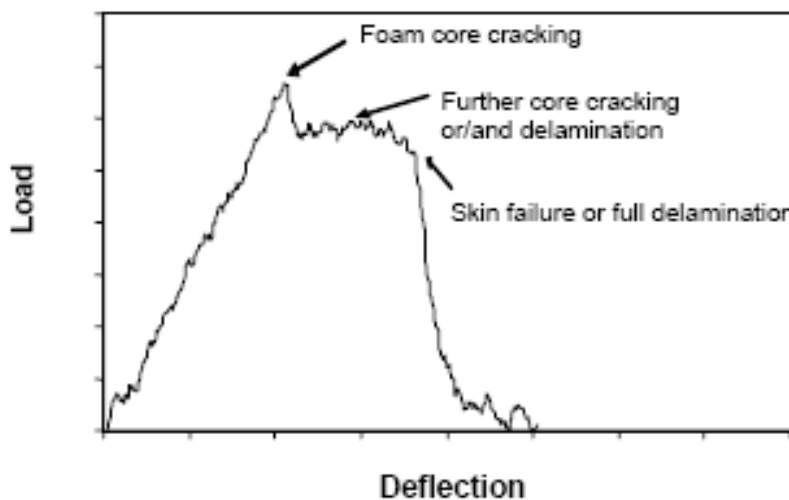


Figure 47. Schematic for different stages of failure/damage process.

As such, different stages of damage may be schematically described in Figure 47 based on the observation and discussion herewith. The syntactic foam core cracking first occurs at the first peak, further core cracking or/and delamination occurs in relatively flat region, and finally skin paper failure or full delamination of skin paper from syntactic foam core occurs. Experimentally obtained load-deflection curves superimposed together for sandwich composites (SL300WS30 and SL75WS50) under three-point flexural loading for different starch contents in skin paper are given in Figure 48.

In general, energy absorption (area under the curve) of the sandwich composites is much greater than those of syntactic foam core (see Figure 40). The energy absorption was observed to be due to damage in the form of mainly delamination of skin paper off syntactic foam core. Full delamination (Figure 46(a)) of skin paper on tensile side was taken place for some SL300WS30-WS70 and SL75WS50-WS70 but not for others with higher starch content in adhesive between syntactic foam core and skin paper. It was found that four in ten SL75WS50-WS70 specimens, and seven in ten SL300WS30-WS70 specimens were delaminated, indicating syntactic foam core SL75WS50 (small microsphere) had a relatively good adhesion with skin paper probably because of naturally smooth surface of small microspheres requiring small amount of adhesive to achieve a good adhesion. It is noted in Figure 48 that sandwich composites with high starch content on skin paper such as SL300WS30-WS14 and SL75WS50-WS14 have relatively low damage due to less delamination (Figure 46 (b)).

Since delamination on tensile side is due mainly to shear stress on the interface between syntactic foam core and skin paper, the shear stress was estimated using Equation (32), given that similar moduli of skin paper and syntactic foam core, and is given in Figure 49. As expected, shear stress increases with increasing starch content in interface between syntactic foam core and skin paper, and is high for SL75WS50 (small microsphere) syntactic foam core, supporting that syntactic foam core SL75WS50 (small microsphere) had a relatively good adhesion with skin paper.

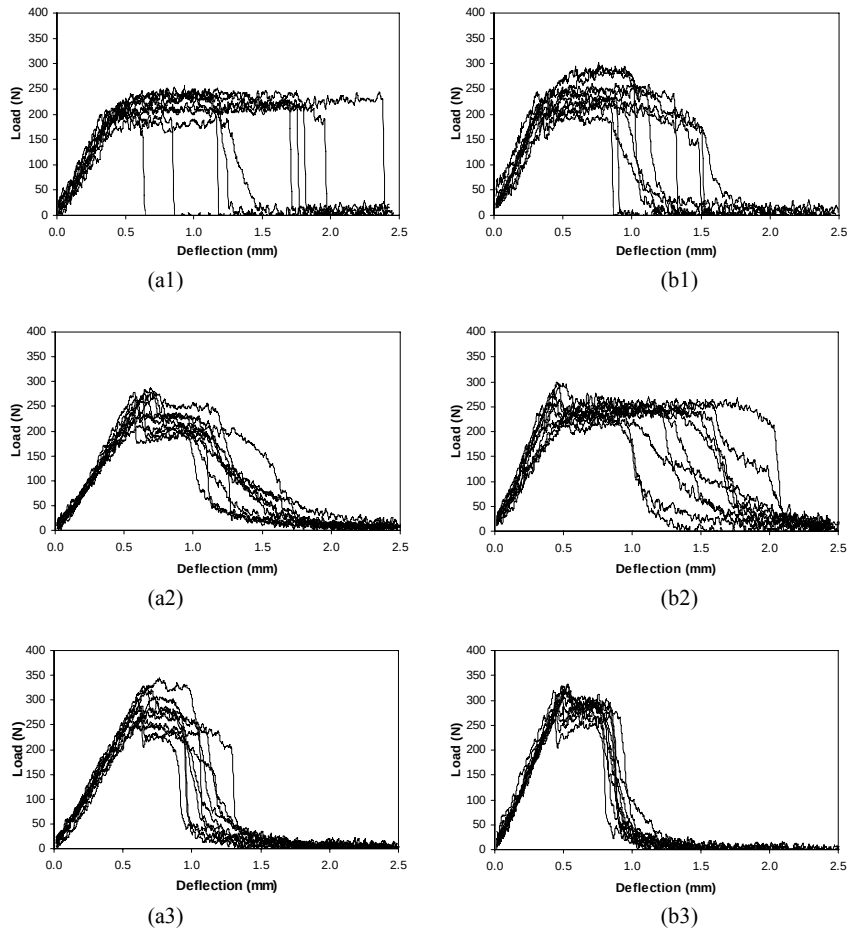


Figure 48. Load-deflection curves from three-point flexural testing on sandwich composites for different starch contents in interface between syntactic foam core and skin paper: (a1) SL300WS30-WS70; (a2) SL300WS30-WS30; (a3) SL300WS30-WS14; (b1) SL75WS50-WS70; (b2) SL75WS50-WS30; (b3) SL75WS50-WS14.

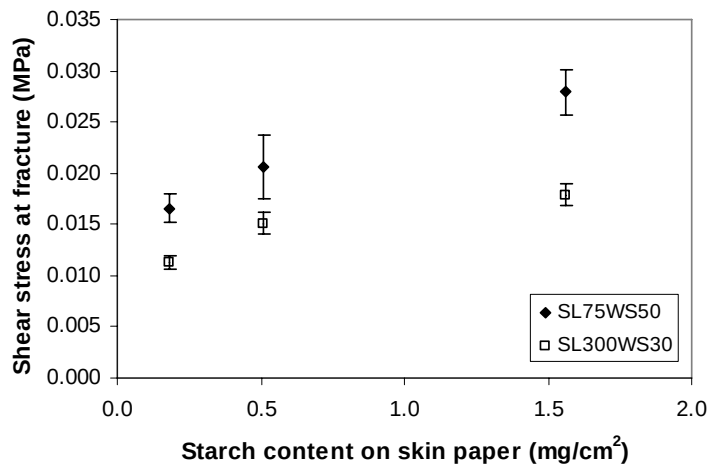


Figure 49. Shear stress on interface between syntactic foam and skin paper calculated using Equation (32) for different starch content on skin paper. The error bars indicate 95% confidence intervals.

CONCLUSION

Hollow microsphere behaviour in aqueous starch binder for various parameters for syntactic foam pre-mould method have been studied. Minimum inter-microsphere distance (MID) concept for volume expansion of bulk microspheres caused by gelatinized starch is introduced. MID has been numerically calculated for various volume expansion rates of bulk microspheres. An equation (Equation (2)) based on lattice unit cell models with MID for a relation between VER and microsphere size is derived and successfully used to predict experimental data. A simple method for estimation of syntactic foam composition prior to completion of manufacture is suggested. A two-step manufacturing process viz moulding and then forming is also suggested for syntactic foam dimensional control.

Interaction between hollow microspheres and starch binder particles for post-mould method has been studied. A transition in carrying starch particles by microspheres during phase separation has been found and explained using a calculated relative density value of 1 for an agglomerate consisting of multiple starch particles and one microsphere. It has been found for a hollow microsphere in attracting starch particles that (a) hollow microsphere size effect is relatively high, (b) initial bulk volume of hollow microspheres (IBVMS) effect is not relatively significant, and (c) water volume effect for a given diameter of cylindrical mixing container is not noticeable. A Simple Cubic cell model for the starch-microsphere inter-distance has been adopted to quantitatively explain various effects on starch content in agglomeration such as hollow microsphere size, IBVMS, and water volume. Volume fraction of starch in foam is found to be of linear relation with starch content in binder for a given experimental data range. Shrinkage of syntactic foam precursor is relatively high for small hollow microspheres and high starch content.

Syntactic foams composed of hollow ceramic microspheres, starch, and voids have been developed. Various parameters such as microsphere size, volume fractions of constituents, and gelatinization timing have been investigated for failure behaviour and mechanical properties of the syntactic foams. Compressive failure of all foams is found to be mainly by shear. Some conditions leading to the rule of mixture relationships have been developed for understanding of failure behaviour and compressive/shear strength. The developed rule of mixture relationships for compressive/shear strength are partially verified. It is found that syntactic foam compressive strength and modulus are not much affected by microsphere size and gelatinization timing.

Novel sandwich composites made of syntactic foam core, paper skin, and starch adhesive for interface between syntactic foam core and paper skin, are manufactured by varying starch content in adhesive for interface. Mechanical behaviour of manufactured sandwich composites in relation with properties of constituent materials has been studied. Two different microsphere size groups (SL75 and SL300) were employed for syntactic foam core manufacture. Moisture content was measured to be high for high starch content in syntactic foam. No significant moisture effect on flexural strength syntactic foam panels after being subjected to moisture about two months is found for both SL75 and SL300. However, substantial decrease (28%) in flexural modulus is found for syntactic foam panels made of large microspheres (SL300WS30) although not much moisture effect is found on those of small microspheres (SL75WS50). Properties of skin paper with starch adhesive on have been found to be affected by drying time of starch adhesive. Skin paper has contributed to increase

up to 40% in estimated flexural strength over syntactic foams depending on starch content in adhesive between syntactic foam core and paper skin. Small microsphere size group (SL75) for syntactic foam core has been found to be advantageous in strengthening of sandwich composites for a given starch content in adhesive. This finding is in agreement with calculated values of estimated shear stress at interface between paper skin and foam core. Failure process of sandwich composites has been discussed in relation with load-deflection curves and damage.

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Chapter 2

SALT WEATHERING OF NATURAL BUILDING STONES: A REVIEW OF THE INFLUENCE OF ROCK CHARACTERISTICS

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ABSTRACT

Soluble salts are one of the main decay agents of building materials, affecting both natural and man-made products applied in old and new constructions, endangering cultural significant structures and thwarting the performance of materials in new buildings. Salts could promote erosive decay (provoking loss of material, mainly by physical action but there are also references to chemical attack) and could also contribute to the formation of coatings, such as the (in)famous "black crusts". The present review will be focused on the response to salt pollution microscopic of macroscopic features of natural building stones, considering predictions of theoretical models, results of simulation experiments and field observations. Several types of rocks (igneous, sedimentary, metamorphic) will be considered, in order to gain information on the influence of textural, mineral-chemical and structural aspects, such as grain size, mineralogical composition (specially relevant to understand chemical susceptibility), presence of heterogeneities, natural anisotropy surfaces (such as bedding) and previous weathering state of the stones (weathering state when extracted from the quarry, before application, an aspect that is particularly relevant for igneous rocks, specially granites, since it affects properties, such as porosity and capillary rise kinetics, that control migration of salt solutions and influence the crystallization position of soluble salts). It is hoped that this review will contribute to identify susceptible geological features that affect the performance of building stones in relation to salt weathering and, in this way, contribute to the discussion on the basis for recommendations about selection of building stone, in relation to foreseeable salt contamination conditions.

“In my beginning is my end.” T. S. Eliot in *East Coker*, N.º 2 of *Four Quartets*. A digital copy can be found <http://www.tristan.icom43.net/quartets/coker.html>.

“The nitre!” I said; “see, it increases. It hangs like moss upon the vaults.”. Edgar Allen Poe in *The Cask of Amontillado*. A digital copy can be found in <http://www.gutenberg.org/dirs/etext97/1epoe10h.htm>.

1. INTRODUCTION

Frequently considered a durable material (“set in stone”, “written in stone” are classical expressions suggesting persistence), stone nevertheless suffers decay along time due to several agents.

This decay can be expressed as simple chromatic changes due to formation of coatings (Figure 1) or as erosion (removal) of elements, erosion that could achieve several centimetres (also Figure 1). On architectural and artistic utilizations of natural stone, even shallow erosive features can have a damaging impact Figure 2).

The characterization of stone decay begins necessarily on the field where observations such as those of Figure 1 and Figure 2 raise the problem of the susceptibility of this building material.

Classifications and nomenclature of decay (or weathering) forms can be found in several publications such as, for example, WINKLER (1994) and FITZNER and HEINRICHS (2002- a publication that was, in October of 2008, freely available on the internet in http://www.stone.rwth-aachen.de/decay_diagnosis.pdf). Some very brief comments could be relevant for the reader. Changes in visual appearance might be due to discolouration by alteration of rock constituents or by accretion of foreign matter such as the gypsum-rich (in)famous black crusts.





Figure 1. Examples of stone decay features: carbonate crusts on granite (a) and erosion of surface in stones made from volcanic rocks (b), granite (c) and limestone (d).



Figure 2. Erosion of surface causing damage to artistic stone works in limestone (a) and granite (b) stones.

Examples of erosive features include release of grains (sanding or granular disintegration/disaggregation) and planar detachments (such as those presented in Figure 3), that might be clearly associated to planar structures of the rocks or not (diverse designations have been used, according to form and relation to rock structures, such as scales, flakes and exfoliation).



Figure 3. Planar detachments in granite (a) and sedimentary stones (b, note the clear influence of the rock structure).

Salts are important geomorphologic agents in natural landscapes on Earth (and even on other planets) and affect natural and man-made materials, from stone to glass, in old and new structures, all around the world. Interest on the effects of salts on materials has come from a long time. The oldest reference I have seen, following a previous mention by CHAROLA (2000), is by Herodotus in his histories (you can consult the Project Gutenberg files, English translation by G. C. Macaulay, on <http://www.gutenberg.org/etext/2707>, volume 1), where it is mentioned that the pyramids are “eaten away” by the salts (Herodotus links this observations to Egypt running “out into the sea further than the adjoining Land”).

The Ten Books on Architecture by Vitruvius (in the English translation by Morris Hicky Morgan available trough Project Gutenberg in <http://www.gutenberg.org/etext/20239>) indicate some examples such as the spoiling of the surface of walls coated with stucco by salty efflorescences when sea-sand is used. Vitruvius also discusses the performance of some stones mentioning soft stones that “can be easily worked” but when used in the seacoast “the salt eats away and dissolves them”, while “travertine and all stone of that class can stand injury” related to the weather elements. In relation to a stone exploited “round the lake of Bolsena” that show a good persistence, this author mentions that “its structure is of *close texture*” (my italics) and, as evidence of durability, uses field observations in some monuments (yes, already) made from these rocks, in the neighbourhood of the town of Ferento, that “look as fresh as if they were only just finished”. Vitruvius recommends also a durability test, letting the stones two years on the open space.

The presence of salts on buildings pervaded our culture, being, for example, an element of one tale of Edgar Allen Poe (“The Cask of Amontillado”, a digital copy can be found in <http://www.gutenberg.org/etext/1062>).

A general list of salts that occur in man-made structures can be found in ARNOLD and ZEHNDER (1991). Several reviews of salt weathering referring specifically to effects on architectural stones, or including architectural stone, have been published (DOORNKAMP and IBRAHIM, 1990; GOUDIE and VILES, 1997; RODRIGUEZ-NAVARRO and

DOEHNE, 1999; ALVES and SEQUEIRA BRAGA, 2000; CHAROLA, 2000; DOEHNE, 2002; CHAROLA et al., 2007 – this last paper reviews specifically the effects of gypsum). These reviews addressed the several aspects relevant to the question, such as characteristics of rocks, salt solutions, environment and architectural context. This review will be “rock-oriented”, in the sense that it will be focused on the influence of rock features on susceptibility to salt decay. A, perhaps immediate, critic that this approach may provoke is that salt weathering is a complex process, strongly dependent on characteristics of salt solutions (salt load) and environmental conditions. But the evaluation of the characteristics of the building materials is a necessary step and, as have been addressed, for example, by DUFFY and O'BRIEN (1996), PAVÍA-SANTAMARIA et al. (1996), HONEYBORNE (1998b), SMITH (1999), BENAVENTE et al. (2001) and by HARTOG AND MCKENZIE (2004), information on the susceptibility of stone can be a useful contribution in the design of structures according to expectable conditions.

This review includes theoretical models, simulation tests and field observations (for general discussions on the basis of study of stone decay see, among others, JEANNETTE, 1997; GOUDIE and VILES, 1997; SMITH, 1999; TRUDGILL and VILES, 1998; VILES, 2001; SMITH et al., 2005; TURKINGTON and PARADISE, 2005 – these last references deal specifically with desert conditions and sandstones respectively, but most of the general principles discussed are relevant for simulation tests and for studies of other porous rocks). Some epistemological questions affect any of these approaches.

Theoretical principles allow the deduction of results from a set of initial conditions according to well-defined rules. It is the most rigorous approach from a logical point of view but its application requires the appropriate characterization of initial conditions and the knowledge of effective relations between parameters, being necessary to rely on physical theories that will never be definitely proved but may be corroborated (see POPPER, 1968); postulates must be accepted in an axiomatic matter.

Laboratory tests permit a great measure of control of conditions but, in the case of a naturally variable material as natural stone, limitations to reproducibility can affect the ability of the tests to separate the effects of overlapping agents and the evaluation of the evolution of properties. The most frequent ageing tests use geometrical cut specimens (with surface characteristics that are not necessarily those present on actual utilizations of natural stones) and, generally, treat samples in a bulk manner, providing, as highlighted by ORDÓÑEZ et al. (1997), little information regarding the behaviour of the stone in architectural work (It must be remembered that, as can be seen in Figure 2, decay on what we may call the “epidermis” of the object can cause important damage without requiring an important mass loss). Simulation studies in general also suffer of scale and time (specially regarding old monuments) effects. Field studies present several limitations regarding characterization of initial conditions and processes but field observations of actual performance of materials should be part of the evaluation program of rock durability (for reflections including economical and legal aspects see HARTOG AND MCKENZIE, 2004).

Field observations can help to check conclusions from laboratory and exposition tests (see, for example, comments on salt crystallization tests in SMITH, 1999 and also in HONEYBORNE, 1998b). Field characterisation of distribution of decay features is an important tool in studying stone decay, since it can point to possible agents. For example decay features such as those illustrated in Figure 4 are generally associated to capillary rise of

solutions and drying (a situation that can be described, e.g. HAMMECKER, 1995, as “wick-like conditions”).



Figure 4. Distribution of decay features suggestion capillary rising of salt solutions on granites (a, b).

Field studies should not be depreciated as “case studies” (namely in relation to laboratory studies) on the basis that they are not reproducible (the consideration of diverse field studies allows to compare different situations). One should remember that laboratory salt crystallization tests on natural stone work with a restricted set of samples of a restricted set of rocks and are destructive tests (given the variability of stone properties this means that laboratory studies cannot be reproduced and, consequently, could also be considered “case studies”).

Any of the empirical inductive approaches (simulation tests or field observations) suffers of what has been designed as equifinality (see TURKINGTON and PARADISE, 2005, and references therein), where similar end-products can result from different initial conditions and different processes. In the case of natural stone applications, besides the overlapping effects of naturally-driven processes it is necessary to considerer historical factors related to human procedures (see some examples in ARNOLD, 1996). The problem of equifinality is particularly relevant for erosive features, since several other mechanisms can be invoked to explain the disruption of porous materials such as thermal and moisture variations, freeze/thaw, etc. Attempts to control/evaluate the influence of different agents can be made on laboratory test by adapting experimental conditions and using blanks (believing that stone heterogeneity effects would not surpass the effects of the studied agents!) but it is a major drawback for field studies. Sometimes salts are not considered in the explanations of erosive features because they have not been detected, but in non-sheltered portions salts can be washed out and even in sheltered spaces, salts can disappear and appear due to climatic

variations (see ARNOLD and ZEHNDER, 1991). As the present author knows from personal experience, the detection of salts can depend on the time of year when the studies are done (driest times are the best for salt identification). This review will, primordially, discuss papers where salts are explicitly mentioned as being involved in the weathering mechanisms.

Certainly this review will not contain all publications that refer to rocks characteristics influencing salt weathering of natural stone, but it is hoped that it will constitute a contribution to the characterization of the present “problem-situation” (in the sense of POPPER, 1969) in this subject, reflecting some (one hopes most) of the main questions that are at stake (aspects related to rock characteristics; other questions are explicitly not addressed).

2. MINERALS AND OTHER CONSTITUENTS

In this section are reviewed references to interactions between salts and rock constituents (minerals and non-crystalline matter). This will include chemical and physical susceptibility of minerals as well as deleterious effects of rock constituents (concerning both effects favoured by salt solutions and contributions of these constituents to salt solutions).

2.1. Chemical Susceptibility

Salt effects on stone are mostly ascribed to physical effects and there are fewer references to chemical attack on rock materials as a significant decay process. However, MOTTERSHEAD (2000) discussed relations between durability of stones (sandstones and granites) and mineral composition (quartz and muscovite favoured durability; feldspars and chlorite were unfavourable) that were explained with reference to chemical stability.

Processes of sulphatation, where rock phases are replaced by salts are not considered in this review (since in this case salts are mainly the product and not the agents of decay) but reviews of this subject can be found in (CAMUFFO et al., 1983; CAMUFFO, 1995; GOUDIE and VILES, 1997; CHAROLA, 2000; CHAROLA and WARE 2002; CHAROLA et al., 2007). As example, these processes may promote the epigenetic replacement of calcite by gypsum (VERGES-BELMIN, 1994) while SCHIAVON (1996) refer the pseudomorphic replacement of silicate minerals (especially feldspars) by gypsum in granites.

Dissolution of carbonates related to waters with low pH (acid rain) is nowadays mentioned in highschool books. ASHURST (1998) relates surface siliceous compounds to acidic attack of sandstones. There are also a few references to dissolution related to high pH that could affect silicates. This is mentioned as a possibility by WINKLER (1994) for quartz and amorphous silica, while BERNABÉ et al. (1995) associates the presence of alkaline salts with silicates dissolution (especially feldspars) and granular disintegration. Alkaline and saline conditions are used to support hypothesis of quartz dissolution on sandstones (PYE and MOTTERSHEAD, 1995). GARCÍA-TALEGÓN et al. (1996) refer to the susceptibility of “red and white” granite variety to alkaline solutions due to the presence of high content of opal-CT. LOPEZ-ARCE et al. (2008) review a paper by Caner and collaborators, from 1985,

that found laboratory evidences of magnesium release from dolomitic stones by dissolution of dolomite in contact with an alkaline medium.

Another aspect is the effect of the ionic strength (that would be significantly higher on concentrated salt solutions than in pure water) on minerals (increasing solubility), which could favour dissolution processes on limestones (GILLOTT, 1978; GALAN et al., 1996; DELALIEUX et al., 2001; CARDELL et al., 2003a,b; CARDELL et al., 2008) and dissolution of quartz on sandstones (TURKINGTON et al., 2003; see also review by TURKINGTON and PARADISE, 2005) and limestones (CARDELL et al., 2003a). It must be noted that GILLOTT (1978) refers that salt solutions could present acid pH values. The same author, based on laboratory tests, indicated that calcite was more readily attacked than dolomite. Solutions resulting from salt spray laboratory tests of marbles (SKOULIKIDIS et al., 1996) showed increasing calcium, magnesium and iron contents with testing time (but there was also release of particles from the test specimens). Field occurrences of marble dissolution have been linked to salt solutions (ZEZZA and MACRÌ, 1995; CHABAS and JEANNETTE, 2001). DIBB et al. (1983) and CARDELL et al. (2008) observed, in laboratory tests, the formation of new salt phases that were associated with the dissolution of carbonates. ZEZZA and MACRÌ (1995) have reported the formation of amorphous substances resulting from salt weathering of carbonate rocks.

Other chemical decay process has been proposed. In VALLS-DEL-BARRIO et al. (2000) dedolomitisation was attributed to circulation of Ca-rich solutions from mortars trough dolostone (dedolomitisation seem to further favour granular disintegration). A similar process of dedolomitisation has been considered by DREESEN et al. (2007), related to calcium sulphate solutions associated with oxidation of sulphides in the stones. These authors also included the effects of the strong ion pair sulphate-magnesium in dolomite dissolution.

2.2. Physical Susceptibility

There are indications that some minerals are more prone to salt weathering due to crystallization in features such as cleavage planes (e.g., mica minerals or calcite), observations that have been referred by several authors (images of gypsum crystals along mica flakes are particularly favoured). The different decay behaviour of different minerals could clearly promote differential weathering. The observations of NEILL and SMITH (1996) on coastal sites seem so indicate that decay could begin by the disruption along micas cleavages, a process that would provide further promote channel access for salt solutions. An interesting observation is presented in the study of ALONSO et al. (2008) where granites with high plagioclase and mica contents showed higher surface roughness increase during salt crystallization tests.

2.3. Deleterious Effects of Rock Constituents

Salt solutions seem to also promote the deleterious effects of rock components, namely clays, since salts favour water fixation (depending on hygroscopic point) and, therefore, wetting and drying of rocks and the effects of clays (RODRIGUEZ-NAVARRO et al., 1997a). According to PYE and MOTTERSHEAD (1995), salt solutions appear to increase the

volumetric expansion of clays. ORDÓÑEZ et al. (1997) explain the deleterious effects of clay layers by referring to the differential absorption of salt solutions. RUEDRICH et al. (2007) present a decay conceptual model for sandstones that combine clay swelling and salt filling.

We could also include here processes where constituents of the stone react with the environment and give ionic contributions to solutions that could affect these stones or other building materials; processes such as mobilization of salts present in the pores, dissolution of minerals present in the rock (namely carbonates), oxidation of sulphides, *etc.* ARNOLD and ZEHNDER (1991) refer studies, by Zehnder in 1982 and by Bläuer in 1987, that found high amounts of soluble salts on the natural occurrences of sandstones; and that a sandstone plate with 10 cm could contain up to 300 g of sulphate. HEISS et al. (1991) present sulphate contents up to 0.19 % in mass in sandstone quarry samples. WÜST and SCHLÜCHTER (2000) present another example of soluble salt contents on rock pores. Illustrative examples of contributions of stones to salt solutions, and its effects, are given in:

- (COOPER et al., 1991; ZANNINI et al., 1991; WEAVER, 1991; DUFFY and O'BRIEN, 1996; SMITH, 1999; FIGUEIREDO et al., 2007a)- dissolution of calcite (or dolomite- RODRÍGUEZ-NAVARRO et al., 1997b) from elements made from carbonate rocks contributes to contamination of other stones placed below those elements (a situation that is sometimes formulated as a problem of incompatible materials when different kinds of rock are involved, with limestones usually playing the "bad guy" role);
- HANEEF et al. (1992)- a similar effect (dissolution of calcite on top carbonate stones, contamination of other stones below them) observed in simulation tests;
- A paper published in 1991 by Blanco-Varela e collaborators (according to LOPEZ-ARCE et al., 2008)- ionic interchange between magnesium (present in chlorite) and calcium (in solutions with sulphates) leading to magnesium sulphate crystallization;
- BENEÀ (1996)- iron-rich solutions from oxidation of pyrite in greenschists contaminated neighbouring limestones;
- ROBERT et al. (1996)- images of gypsum crystals spatially associated with pyrite crystals;
- HONEYBORNE (1998a)- reaction of iron compounds with air sulphur-based acids forming soluble forms that can migrate and precipitate at the surface;
- BHARGAV et al. (1999) formation of salts by a sequence of reactions initiated by reaction between iron oxides in the stone and atmospheric SO₂;
- SMITH et al. (2002)- contribution of actinolite weathering to gypsum formation;
- STOREMYR (2004)- formation of calcium and magnesium sulphates related to soapstone weathering;
- HUANG (2007)- contribution to grottoes decay from soluble salts coming from sandstone layers;
- DREESEN et al. (2007)- contribution of sulphides oxidation to staining of limestones and to dedolomitization or dissolution (or both) of dolomite through calcium sulphate solutions;
- LOPEZ-ARCE et al. (2008)- magnesium and potassium salts linked with lixiviation from slate aggregates.

Chromatic changes due to reaction of rock constituents with salt solutions could also be included here, including colour changes in limestones, attributed to oxidation of organic matter (LEA, 1970; see also several references in HARTOG AND MCKENZIE, 2004), and in granites, related to oxidation of iron minerals (TRUJILLANO et al., 1996; ALONSO et al., 2008).

3. TEXTURE AND STRUCTURE

Grainsize has been related to decay features. According to BROMBLET et al. (1996) coarse grained kersantite presented lower durability in monuments than fine grained kersantite, a result explained by pore related properties (see below). MATIAS and ALVES (2002) report field observations that suggested higher susceptibility of coarse-grained granites to erosive processes. Salt laboratory experiments by CARDELL et al. (2003b) point to higher susceptibility to salt weathering of medium to coarse-grained granites. According to ALONSO et al. (2008) salt crystallization tests induced higher changes on fissural network of coarse-grained granites. ALBERTI et al. (2000) observed greater decay on coarser marbles. HEINRICHS (2008) report that the more compact fine-grained sandstones present higher durability than the more porous coarse-grained sandstones (that also presented lower matrix content and mechanical strength).

There seems to be a clear trend of higher decay for coarser-grained igneous rocks even regardless of porosity: RIVAS-BREA et al. (2008) observed, in laboratory tests, that thick-grained granodiorite showed similar susceptibility as a fine grained two-mica granite that had a higher (around thrice) porosity.

Grainsize also seem to influence decay forms, according to field observations by CASAL-PORTO et al. (1991- scales occur almost exclusive on fine to medium grained granites and alveolization produces more pronounced features on coarse-grained granites) and by SILVA et al. (1996a- alveolization developed on medium-coarse grained granite ashlar or in medium-fine grained granites in carved portions). The thickness of planar detachments has been related to grainsize on granites (GARCÍA-TALEGÓN et al., 1996) and sandstones (HEINRICHS and FITZNER, 2000)

There are references to worst behaviour of finer grained limestones in field observations (TÖRÖK, 2002, 2007) and laboratory tests (TÖRÖK and PÁPAY, 2007), as well as worst performance of finer grained sandstones in laboratory tests (WARKE et al., 2006, among decay features these authors report the bowing of fine-grained, more clayed, sandstones tablets). HAMMECKER (1995) developed laboratory measurements of properties related to solutions transport in sedimentary rocks and concluded that grainsize was not relevant to these properties.

Grainsize distribution has also been invoked: RUEDRICH and SIEGESMUND (2007) indicate that sandstones with a good sorting of detrital components typically present a narrow pore radii distribution, a characteristic that favoured resistance to salt decay.

The proportion of different constituents might influence durability. KOZLOWSKI et al. (1990) considered that the presence of large fossils on the studied limestones promote an open pore structure and the transportation and removal of salts, while quartz content was listed as a characteristic unfavourable for durability (due to weak contact between calcite and quartz).

According to NIJS and DEGEYTER (1991) the contact between coarse grains (calcite fossils and detritic quartz) and fine cement in a sandy limestone constituted initial places for gypsum crystallization. SCHIAVON (1992) proposed different decay processes for oolitic limestones according to cement characteristics, with limestones having sparitic cement being affected by crystallization of gypsum in the cement micro-discontinuities (e.g. cleavage) while micrite cemented limestones were affected by dissolution of gypsum that replaced the original micrite (leading to separation of grains). The author concluded that sparitic cemented limestones appeared to have better resistance. In a similar vein, BLOWS et al. (2003) suggested that micritic-rich limestones (namely micritic cement) may be more susceptible to salt weathering than limestones having high sparite and ooliths proportions (the authors relate this relation to higher microporosity associated with the micritic component). But CALIA et al. (2000a) proposed that microsparitic texture could make calcarenites more susceptible to stresses developed in salt crystallization tests. In a similar vein, KAMH (2007) considered that sparitic cement have a negative impact on salt weathering resistance of limestones. CALIA et al. (2000b) indicated that the presence of crystalline cement could promote stone durability. RODRIGUEZ-NAVARRO and DOEHNE (1999) observed, in laboratory tests, cracks in sparitic cement, and salt crystallization at contacts between ooliths and cement and between sparitic crystals. GOUDIE (1999) calls attention to the effect of shell content in the evaluation of durability of limestones by laboratory salt weathering tests. In a study of “tuffeau” (chalky limestones), DESSANDIER et al. (2000) concluded that facies with calcite and opal-CT rich cements were more durable than facies with high contents of clastic minerals (poorer cementation). Variations in cementation could also promote differential weathering in limestones (GATT, 2006).

There are several references to textural features that could promote salt decay by favouring microporosity (a characteristic that would increase salt weathering) usually related to the presence of clay minerals (MCGREEVY and SMITH, 1984; GAURI and BANDYOPADHYAY, 1999; THICKETT et al., 2000, CASSAR, 2002 and also a 1985 paper of Ordaz and Esbert quoted by THICKETT et al., 2000). CASSAR (2002), in a study of limestones, also included other minerals from the non-carbonate fraction as contributing to the occlusion of the pore space. KAMH (2007) considered the presence of silica sand grains and illite as having a negative impact on limestone resistance to salt weathering.

Laboratory tests with sandstones (MCGREEVY and SMITH, 1984; WARKE and SMITH, 2000, 2007) have collected evidences of the preferential breaking of clay-rich laminations (in comparison with clay-poor ones). ROBINSON and WILLIAMS (1996), making a synthesis of some previous papers on laboratory experiments, indicate differences in clay content, organic matter and porosity as factors that affect the durability of sandstones blocks. FRANZEN and MIRWALD (2000) observed that large scales were found on the more argillaceous facies of the studied sandstones. PARADISE (2000), based in field observations, concluded that sandstones with silica and iron oxides in the matrix were more durable. HEINRICHS (2008) found increasing susceptibility from the older sandstones to the younger sandstones (the author related this age and susceptibility differences with several physical properties). ULUSOY (2007), following a laboratory crystallization test with igneous rocks, concluded that those with higher silica content presented lower mass loss.

The differential behaviour of constituents could result in heterogeneous weathering, with some elements or portions of the stone being more susceptible than others (see some examples in natural stones in Figure 5, while in Figure 6 is presented an example of

heterogeneous erosion of an artificial material- this resembles some features that occur in some clastic sedimentary rocks).

Curiously (when compared with was discussed above), it has been observed in field studies of granite stones that phenocrysts resist better to salt decay and stand in positive relief (CHABAS and JEANNETTE, 2001; MATIAS and ALVES, 2002).



Figure 5. Differential relief in granite stones (a) and differences in patterns of efflorescences in volcanic stones (b) related to rock heterogeneity.



Figure 6. Heterogeneous erosive behaviour of artificial material due to heterogeneous constituents.

Also regarding granite stones, SILVA et al. (1996a) refer that the presence of asperities (that could be related to heterogeneous textural features such as megacrystals) was one of the factors necessary for the development of alveolization (honeycomb features). Studies of volcanic tuffs report erosion of clasts due to groundmass disruption (DECASA et al., 1994; TÖRÖK et al., 2007) with DECASA et al. (1994) asserting that fissuration generally starts on the zeolitic or glassy matrix.

ZEZZA and MACRÌ (1995) characterised salt weathering of limestones as having a selective character, influenced by structural (see below) and textural features (mineral grains, micrite, calcitic cement and fossils). BENEÀ (1996) reported the selective attack of fossils on oolitic limestones and also differential relief of more resistant components on siliceous nodular limestones. TERREROS and ALCALDE (1996) noted that surface changes of an oolitic limestone implied loss of ooliths and disaggregation of matrix. ANGELI et al. (2007) refer the differential behaviour of fossils. BENAVENTE et al. (2007b) discuss the effects of textural differences in laboratory tests of dolostones, with strong unaltered dolomite clasts being eroded due to matrix disruption. CULTRONE et al. (2008) observed, in field studies, selective weathering concerning algal nodules on limestones. CARDELL et al. (2008) suggested that disruption areas (with an orange-brownish tonality) in limestones subjected to salt crystallization tests could be related to presence of clay minerals.

ZEZZA and MACRÌ (1995) discuss differential salt weathering of limestones related to features such as stylolites (the authors point to the influence of clays in stylolites), fractures and lamination. MCGREEVY (1996) noted, in laboratory tests, preferential decay around stylolite seams in chalks (the author suggested that this was explained by the presence of smectites on the stylolites). ZEZZA (1996) linked selective weathering on limestones to variations in porosity associated with bioturbation structures. Similar relations are proposed by GATT (2006), associating bioturbation structures with textural (grainsize) and pore size variations. DREESSEN et al. (2007) indicated stylolites as favourable structures to decay process related to circulation of salt solutions.

Preferential orientation characteristics can influence decay features (see Figure 3 and Figure 7). Sandstones blocks with bedding parallel to exposed surface can suffer fast deterioration due to separation of layers (WEAVER, 1991). The image in Figure 8e of RUEDRICH and SIEGESMUND (2007) shows separation along bedding planes with bedding planes in the horizontal orientation (see also Figure 7 of this chapter). Clay contents may promote the development of slaty cleavage on limestones, contributing to conditions favourable to gypsum crystallization on cleavage cracks (NIJS and DEGEYTER, 1991). BENEÀ (1996) also reported the splitting of calcarenite stones, related to clay content, in stones both with vertical and horizontal orientated bedding. In the sandstones studied by UCHIDA et al. (1999) separation of planar detachments due to salt efflorescences was more severe in stones with bedding in the vertical position (the authors emphasized the role of mica minerals). Laboratory studies of BENAVENTE et al. (2007b) pointed to the importance of the orientation of weakness planes on decay of anisotropic dolostones. The results of RUEDRICH et al. (2007) showed anisotropy in the expansion of sandstones (comparing directions parallel and normal to bedding) that, at least for the sandstone with stronger anisotropy, was attributed to the preferred orientation of quartz grains (producing a preferential orientation of pore geometry). The laboratory studies of ROTHERT et al. (2007) indicated more accentuated erosion parallel to sedimentary structures in limestones. Field observations of planar detachments related to planar orientation structures have been reported

for marls (WÜST and SCHLÜCHTER, 2000), soapstones (STOREMYR, 2004), argillites (KAMH, 2005) and siltstones (HEINRICHS, 2008). Detachment of planar portions is reported to have significant impact on anisotropic marbles by ALBERTI et al. (2000). TÖRÖK et al. (2007) associated crumbling with layered tuffs.

Igneous rocks could also have some anisotropic fabric with relevance for salt weathering. ORDAZ et al. (1996) performed microscopic studies of granite specimens prepared according to orientation in relation to anisotropic planes and submitted to salt crystallization tests, concluding that the presence of a structural anisotropy promotes preferred directions for crack growing and mechanical weakness that would explain the formation of planar detachments (in preference to other decay features such as granular disintegration).



Figure 7. Decay patterns apparently related to bedding.





Figure 8. Black crusts on granite stones (a) and efflorescences and planar detachments on a granite wall.

SILVA et al. (1996b) observed (in thin sections of a granite stone removed from a building) that transgranular fissures seemed to be largely influenced by the orientation of mica crystals, but the separation planes of detachments were always parallel to the stone surface. According to these authors the anisotropy of the studied granite did not seem to be a direct cause of detachments; however they highlighted the possible effects of the anisotropy of physical properties (specially tensile strength) and admit that placing stones with the weaker (lesser bending strength) plane parallel to the exposed stone surface may favour planar detachments. WRIGHT (2002) observed, in field studies of sandstones, flaking perpendicular to bedding. RIVAS-BREA et al. (2008) found that scaling occurred related to cracking parallel to the drying face, both parallel and normal to anisotropy planes in the studied igneous rocks but mentioned previous study (Rivas, published in 1997; Silva and collaborators, published in 2003) that indicated that planar detachments would be more likely when anisotropy (weakness) planes were parallel to the drying face.

MOTTERSHEAD (1997) observed, in greenschists blocks, different patterns of cavities distributions according to orientation of surface in relation to the foliation. CHABAS and JEANNETTE (2001) also related development of cavities to orientation in foliated granite (small holes following the foliation). These authors further reported that when granites stones with foliation in a vertical orientation suffered from granular disintegration, this decay features developed along the length of the stone.

Discontinuities also play a role in the development of decay features. It has been observed in laboratory salt crystallization tests, that salt crystallization begins in cracks and other irregularities with random distribution (LÓPEZ-ACEVEDO et al., 1997). BENAVENTE et al. (2007b) also noted the effects of discontinuities of diverse dimensions, concluding that narrow fissures promote decay (a result attributed by the authors to higher crystallization pressures) while macro-fissures initially did not contribute to decay (but they contribute to migration of solutions and constitute weakness of the stone).

4. PORE SPACE

Since, mostly, salts decay action involves migration of solutions, the study of the pore space has been an important research line in this subject and characteristics of pore space have even been used in recommendations for selection of stones. For example DUFFY and O'BRIEN (1996), discussing recommendations for selection of stones for different portions of façades, indicate macroporous limestones as a more suitable choice for places where it is expected an important salt contamination. PAVÍA-SANTAMARIA et al. (1996) recommended that, due to its high capillary suction, a certain sandstone should not be used on making plinths of buildings. HARTOG and MCKENZIE (2004) reported recommendations for the use of limestones with very low ("exceptionally low") water absorption for paving to be used in a coastal area. A more elaborate discussion of the "ideal" characteristics of the pore structure that would promote stone durability in relation to salt weathering is found in HAMMECKER (1995).

In the next paragraphs are discussed bulk properties that are dependent on pore space (porosity, water absorption, drying) and, afterwards, the influence of characteristics of pores (microcharacterization) will be reviewed.

4.1. Bulk Properties

Porosity seems to be an important stone property for salt weathering but a universal relation between porosity and decay intensity is not evident. Of course, if a material does not have pores (but all stones have voids) salt solutions could no migrate through it and decay would be limited to surface/interface processes (see the study on salt weathering of marbles by CHABAS and JEANNETTE, 2001). For examples, according to HONEYBORNE (1998b) slates and marbles will be resistant to salt weathering due to its very low porosity values, and a similar indication is given in relation to granites (but in the case of marbles and granites, thermal variations on-site can affect porosity values of applied stones; see also HONEYBORNE 1998a). LATHAM et al. (2006) states that armourstone with low water absorption values (bellow 0.5 % to 1 %) have a good resistance to salt weathering. The text of the European standard EN 12370 (Natural stone test methods - Determination of resistance to salt crystallization, see, for example <http://www.thenbs.com/PublicationIndex/DocumentSummary.aspx?PubID=76andDocID=256487>) indicates that the test described in the standard is for natural stones with open porosity above 5 % (which could be read as suggesting that less porous rocks are not so prone to salt weathering). This seems to be supported by ALONSO et al. (2008) that, in salt laboratory tests of granites, report that mass losses were insignificant and related this to porosity values of the studied rocks being bellow 5 %.

However, MIGON (2006) highlighted the discordance between results obtained in laboratory tests with granites (showing low decay intensity) and observations of intense and generalized decay on granitic rocks with low porosity values (as can be seen from the diverse references in this chapter). There also references to salt related cracking and erosive decay of marbles (WINKLER, 1991; ZEZZA and MACRÌ, 1995; FASSINA, 1996; ZEZZA, 1996; ALBERTI et al., 2000; CHABAS and JEANNETTE, 2001). STOREMYR (2004) presents

field observations of erosive decay in soapstones with maximum water-accessible porosity of 1 %. It must also be considered that, as images presented in Figure 2 illustrate, intense damage of architectural objects does not require important mass losses. In the context of this discussion, it must be called attention to a paper by RIVAS et al. (2000) with results on laboratory salt crystallization tests of granites, reporting mass losses around 35 % for a granite with a open porosity around 4 % (for other granites with open porosity around 2 % mass losses did not exceed 10 %). SOUSA et al. (2005) recorded losses above 3 % in laboratory salt crystallization tests with granite rocks having porosity values below 5 %. GAURI and BANDYOPADHYAY (1999) presents an equation (with a worked example) that relates increasing crystallization pressure to increasing porosity. DELGADO-RODRIGUES (1991) indicates that very porous stones are more susceptible to salt weathering (even if all petrographic types can be affected). Laboratory tests have found some positive association between salt weathering susceptibility and porosity on limestones (SKOULIKIDIS et al., 1996; BIRGINIE, 2000; NICHOLSON, 2001) and marbles (SKOULIKIDIS et al., 1996). RIVAS et al. (2000) found higher decay (disaggregation was more intense) in more porous granites in laboratory tests and a similar relation for granites and limestones was found by CARDELL et al. (2003b), also in laboratory tests. Results of SOUSA et al. (2005) in salt crystallization tests performed on several granites show more porous granites generally presenting higher mass losses.

CORRAO et al. (1996) compared the weathering features of different limestones in similar climatic conditions and concluded that the more porous stones (that also presented lower mechanical strength) presented lower durability. CARDELL et al. (2003a) defended that higher porosity, besides promoting deeper salt impregnation, would imply higher salt uptake. Besides grain size, WARKE et al. (2006) refer lower porosity (and permeability) to explain higher resistance of coarse-grained sandstones in laboratory tests. WELLS et al. (2006), discussing results of laboratory tests of schists, suggested that lesser porosity explained higher resistance. RUEDRICH and SIEGESMUND (2007) observed better resistance to salt weathering tests of sandstones having lower porosity and linked higher porosity with higher absorption of salt solutions and more salts crystallizing in the pore space (however the authors also stressed that more porous rocks tend to have lower physical strength). FIGUEIREDO et al. (2007b) related higher mass losses in laboratory tests of limestones to higher free porosity available under atmospheric conditions. FORT et al. (2008) found that dolostones with higher porosity (and water absorption) present lower durability in salt crystallization laboratory tests.

While strong decay has been observed in relatively low porosity granites, several field studies (ALVES et al., 1996; ALVES and SEQUEIRA BRAGA, 2000; BEGONHA and SEQUEIRA BRAGA 2000; BEGONHA and TELES, 2000; MATIAS and ALVES, 2002) relate higher granite stone decay to development of a pore structure that promotes fast capillary migration of salt solutions and that very low porosity granites are less decayed. STOREMYR (2004) observed that more porous soapstones with higher desorption were more susceptible in salt crystallization tests.

There are references of more porous rocks showing higher durability than other less porous stones, a result that has been explained by other characteristics of the pore space (MARTIN-GIL et al., 1991; FITZNER et al., 1996; HONEYBORNE, 1998a; CALIA et al., 2000a; TÖRÖK et al., 2007; RUEDRICH et al., 2007; CULTRONE et al., 2008; ANGELI et al., 2008) and also by differences in mechanical strength (PAPIDA et al., 2000). ALONSO et

al. (2008) found that low porosity granites presented higher changes in the crack network after salt crystallization tests. SMITH et al. (2002), comparing the behaviour of sandstones, suggest that lesser porosity may favour deeper penetration of salt solutions with an atmospheric origin, since it would require lesser amounts of salt solution to fill pore space.

Porosity characteristics had also been related to development of coatings such as black crusts. (SAIZ-JIMENEZ and GARCIA-DEL-CURA, 1991), refer preferential development of black crusts apparently linked to higher porosity. A similar relation seems to be suggested by MATIAS and ALVES (2002) in granites (black crusts develop preferentially on more weathered, more porous stones). MONTANA et al. (2008) refer that stones with lower open porosity are less prone to capillary migration and noted that these stones present thinner black crusts. HARTOG AND MCKENZIE (2004) defend that high porosity might favour salt solutions migration and staining in limestones. TÖRÖK (2008), comparing black crusts on oolitic limestone and travertine relates surface stability to porosity with less porous stones (travertine) presenting greater surface stability. However, KOZLOWSKI et al. (1990) relates the development of black crusts to lower porosity (with slower migration of solutions) limestones (in more porous limestones gypsum was preferentially washed from the surface). STOREMYR (2004) observed black crusts in soapstones with low water-accessible porosity.

Pore network affects transport properties that control salt migration, an aspect used to explain salt decay effects that can be the base for recommendations towards the selection of stone. Several authors have tried to establish empirical relations between susceptibility to salt decay and bulk properties related to pore space, namely those affecting solutions migration such as saturation coefficients, capillary uptake and desorption (FOCKENBERG, 1991; MOH'D et al., 1996; TÖRÖK et al., 2007) as well as other physical and mineralogical properties (DESSANDIER et al., 2000; see also BENAVENTE et al., 2004a, 2007a). A review of several durability estimators that used pore-related properties as well as parameters related to pore-size distribution (microporosity) can be found in YATES and BUTLIN (1996). HONEYBORNE (1998b) present a brief review of some parameters related to pore space with comments on its significance as durability estimators. LEWIN (1982) proposed that when migration of solutions is very slow salt deposition occurs deep inside the stone and does not became evident at the surface. KOZLOWSKI et al. (1990) relates gypsum concentration in limestones to migration of solutions, with faster migration of solutions in more porous coarser limestones promoting the surface formation and rainwashing of gypsum, while in finer, less porous, limestones, hindered migration of solutions would promote concentration of gypsum inside the stone. The development of a pore network that promotes capillary migration of solutions had been considered a process that favours salt weathering in granitic rocks (ALVES et al., 1996; BEGONHA and TELES, 2000). BROMBLET et al. (1996) reported that coarse grained kersantite presented lower durability than fine grained kersantite due to higher porosity and solution migration properties (capillary uptake, drying), factors that promote higher absorption of salt solutions and greater amounts of gypsum crystallization. PAVÍA-SANTAMARIA et al. (1996) observed decay related to capillary rise of solutions affecting sandstone building plinths and referred its high capillary suction. GAURI and BANDYOPADHYAY (1999) proposed that rocks with lower saturation coefficient are less susceptible to salt weathering. GOUDIE (1999) found a general association between lower limestone durability in laboratory tests and higher water absorption capacity and higher salt uptake (referring also that lower durability tended to be related to lower modulus of elasticity). CARDELL et al. (2003a) proposed that in limestones with slow

water flow and low capillary migration coefficients salt solution would penetrate to a lesser distance (these stones would be less susceptible to salt decay). Fast capillary migration properties were also used by ANGELI et al. (2008) to explain the low durability of a limestone. HEINRICHS (2008) relates increasing susceptibility to increasing values of porosity and water uptake properties in sandstones.

A somewhat opposing view results from the reading of FITZNER et al. (1996) that explained the different salt weathering behaviour of limestones varieties based on water uptake and desorption (and related these properties to pore size distribution), with the more porous variety behaving better (“good” quality stone) due to higher values in these properties (the higher values of water migration properties were also used by these authors to explain the formation of calcite crusts and alveolization of the “good” quality stone). LATHAM et al. (2006) refer that rocks that are porous but present a free drainage structure are less susceptible to salt weathering. VAN et al. (2007) study of limestones based on laboratory experiments and field observations associated higher decay with lower capillary transfer (favouring salt crystallization inside the stone).

Based on the characterization of solution migration properties, CHABAS and JEANNETTE (2001) concluded that decay of marbles was mainly dependent on the effects of airborne salts, due to its low capillary migration values, while granite, with higher capillary migration results, was affected by both capillary rising solutions and airborne salts.

BENAVENTE et al. (2007a) study of laboratory tests on sedimentary rocks found associations between mass loss and pore space properties such as porosity (positive association) and water transport properties (negative association).

BIRGINIE (2000) pointed out that more porous stones had also higher permeability to explain decay features of limestones. Results obtained by BIRGINIE et al. (2000) show that limestones with different initial values of permeability may present different evolution under salt weathering simulation tests. WARKE and SMITH (2007), based on laboratory results of granites, limestones and sandstones highlight the influence of initial range of permeability values on durability (rocks with greater range were more susceptible).

SMITH et al. (2002) consider that slower drying in clayey sandstone would promote migration of salts in solutions to the surface (causing efflorescences and disintegration), while in sandstones that experienced fast surface drying the accumulation of salts at a certain depth and the formation of scales (planar detachments) is favoured. RUIZ-AGUDO et al. (2007) defends that slow drying promotes crystallization inside the stone (limestone) contributing to decay.

WRIGHT (2002) pondered heterogeneities in pore size characteristics of sandstones to explain the formation of blisters.

It might be appropriated to mention, at this point, the work of MCGREEVY (1996). This author proposed that excepting some values bellow or above certain lower and upper thresholds, water content and porosity may be clearly insufficient to explain the behaviour of stones in salt decay and that relations between decay and parameters such as Hirschwald saturation coefficient may be obtained because this parameter is correlated with other more relevant parameters (such as pore size). It is also interesting to refer that TOPAL and SÖZMEN (2003), comparing several durability estimators applied to volcanic rocks, concluded that saturation coefficient was not a good one (as will be seen further on the authors supported the use of estimators related to variation of rock strength with moisture content).

The balance between solution migration and drying is frequently considered a decisive factor in salt weathering, since it influences the position where salts develop. Salt crystallization at the stone surface promotes efflorescences and the formation of gypsum-rich black crusts (Figure 8), decay forms that can be responsible for intense visual impact but frequently involve a limited erosive damage (in some situations it may even be considered to form a protective crust -GAURI and BANDYOPADHYAY, 1999). Conversely, crystallization inside the porous media (cryptoflorescences) causes physical disruption (Figure 8 illustrates both efflorescences and planar detachments in the same wall).

LEWIN (1982) presented mathematical models for the calculation of position of salt crystallization in situations of capillary feeding and drying (backed up by experiments on situation of capillary migration), proposing an explanation for the development of planar detachments. WENDLER et al. (1990) developed simulations of surface wetting and drying cycles to calculate the depth of maximum moisture behind the surface (an explain scales thickness). HAMMECKER (1995) developed models for simulating water balance for simple drying condition and for wick-like condition that include the water migration parameters (related to capillary imbibition and drying) and the presence of salt. For simple drying conditions extreme diffusivity values would conditioned the critical water content, prevailing over the influence of external conditions (very low diffusivity would promote salt crystallization inside the porous media). For the wick-like condition the relevant rock characteristic would be the capillary migration parameters. This author also refers the importance of the critical water saturation (or critical water content or critical higric content) related to drying conditions: the most favourable case for stone durability, in terms of material loss, would very low values of critical water content on drying, a situation that would promotes surface drying of solutions and formation of physically less harmful efflorescences.

Following the previous discussion, it is interesting to consider the results presented by MCGREEVY (1996) for five types of limestones. While the author discusses the effect of drying considering drying rates, the comparison of drying curves and weight loss results shows that, with the exception of one type, higher weight loss correspond to higher critical moisture content on drying.

But if high values of moisture critical content would promote salt weathering (since a greater amount of solution would dry “inside” the stone) the inverse relation is not monotonously decreasing and lower critical moisture values my not imply best durability. In the case of the kersantites studied by BROMBLET et al. (1996) the less durable coarse grained kersantite showed lower critical higric content (however values where, in absolute terms very high, above 75 %). In the case of granites, it has been observed that less weathered and less porous granites fare better on buildings than yellowish previously weathered and more porous granites, being the critical moisture content lower in the second case (this could be explained by differences on mechanical strength, porosity and capillary migration, as well as by high enough critical contents on the weathered types). RUEDRICH and SIEGESMUND (2007) point to critical moisture measured on drying tests as a relevant factor on the salt weathering behaviour of the studied sandstones with planar detachments being favoured for critical moisture values above a certain threshold and sanding (granular disintegration) favoured bellow that threshold.

A different perspective is presented by DESSANDIER et al. (2000), proposing that higher critical moisture would favour durability in the case of salt weathering.

4.2. Pore Characteristics

The characteristics of the pore network are the substrate characteristic most frequently used in the modelling of salt weathering of porous media, involving its influence in salt crystallization pressures or transport properties (or both).

Most publications that attempt to estimate stone resistance to salt weathering, based on characteristics of the pore space, consider the possible influence of pore size distribution on the crystallization pressures of salts. WELLMAN and WILSON (1965) related the effects of salt weathering on rocks to the relation between the size of small pores and mechanical strength of rocks, proposing that, for equal mechanical strength, rocks with micro-porous portions between large pores will be more liable to salt weathering. Use of equations that relate crystallization pressure to pore size characteristics (and discussions on its applications) can be found in a high number of references (some examples can be found in ROSSI-MANARESI and TUCCI, 1991; LAIGLESIA et al., 1997; THEOULAKIS and MOROPOULOU, 1997; GAURI and BANDYOPADHYAY, 1999; SCHERER, 1999; STEIGER, 2005b). This type of relation has been the basis for propositions of indexes of durability. ORDÓÑEZ et al. (1997) discussed results of indexes based on pore size distribution of porosity and trapped porosity. THEOULAKIS and MOROPOULOU (1997) proposed an energy-based analysis to evaluate possible alternatives associated with salt crystallization in pores. GAURI and BANDYOPADHYAY (1999) derived durability index based on pore size distribution by statistical and artificial neural networks, as well as thermodynamic considerations and characterization of fractal dimension.

HONEYBORNE (1998a) associates susceptibility to salt weathering to fineness of pores for limestones (curiously the author relates that the relation is not so clear cut for sandstones), referring that durable limestones present a pore space with relatively large pores. According to MOROPOULOU et al. (1998), the contact between micro and macropores may promote selective fissuring. RODRIGUEZ-NAVARRO and DOEHNE (1999), RODRIGUEZ-NAVARRO et al. (2000), BENAVENTE et al. (2004b), based on laboratory tests, propose that micropores would promote saturation and crystallization of soluble salts like sodium sulphate inside the stones. RODRIGUEZ-NAVARRO et al., 2000 and BENAVENTE et al., 2004b discuss the effects of micropores on water activity. CULTRONE et al. (2008), in a study of limestone involving field observations and laboratory tests, refer that higher microporosity, by hindering water movements, promotes salt crystallization inside the porous media and stone scaling, while in limestone with low microporosity faster water migration would promote efflorescences (and lesser erosive decay). ESPINOSA-MARZAL and SCHERER (2008) explain the detrimental effect of micropores by the effect of a larger contact area and, consequently, larger stress for the same crystallization pressure.

The presence of micropores is, therefore, frequently considered a potentially damaging characteristic. However, MCGREEVY (1996) had concluded that limestones with coarser pores suffer higher damage and discuss possible explanations in relation to the influence of the properties affecting migration of solutions, namely in drying. NICHOLSON (2001) indicate that susceptibility to salt crystallization tests of limestones increased with decreasing microporosity (this author suggest that smaller pores might not be so easily accessible to salt solutions). An explanation in a similar trend of tough is found in CARDELL et al. (2003a): limestones with higher microporosity were more resistant to salt weathering due to lower salt solution penetration. THEOULAKIS and MOROPOULOU (1999) propose a model where

growing of columnar crystals in coarse pores lead to disruption and granular disintegration. CARDELL et al. (2003a) proposed that salts could cause fissuring and damage in stone even for low crystallization pressure. ANGELI et al. (2008) in a laboratory study of limestones and sandstones states that pores of all sizes (from nanometers to several micrometers) were affected by salt crystallization and that the more microporous rock had high durability. These authors proposed that other characteristics of the pore network could affect durability, such as tortuosity, connectivity, existence of cylindrical pores and the presence of previous cracks (crack density helped to explain unexpected low durability results). YATES and BUTLIN (1996) review studies where the effect of microporosity is made dependent of saturation coefficient values. BENAVENTE et al. (2001) considered that the effects of crystallization pressure were less intense when the salt solution did not fill all the pore space.

Pore space characteristics also affect transport properties. JEANNETTE (1997) presents a general discussion of pore structure influence on migration of salt solutions by capillarity and stone drying with reference to diverse stone decay forms. HAMMECKER (1995) used pore space characterisation to model transport of salt solutions, drying and precipitation of salts. SCHERER (2004) presents an extended review of the physical models (and its relevant equations) for salt transport and crystallization pressure both in capillary rise situation and cyclical wetting-drying.

5. STRENGTH

Pressures related to salts (crystallization, hydration) must be higher than mechanical strength of rocks to cause disruption and it seem reasonable that tensile strength should be the parameter used for evaluation. But tensile strength is a most difficult parameters to measure in rocks, being frequently evaluated by indirect tests (e.g. the Brazilian test) or considering, as indirect indicators, other properties, such as flexural strength (BENAVENTE et al., 2004a). Compressive strength is also used to evaluate rock strength (see examples in THEOULAKIS and MOROPOULOU, 1997; BENAVENTE et al., 2004a, 2007a).

Other mechanical properties might be relevant to explain salt weathering results. DIBB et al. (1983), starting with theoretical considerations and also using results from laboratory tests, proposed fracture toughness as estimator of cohesive strength of rock particles against physical disruption processes, including salt crystallization. THEOULAKIS and MOROPOULOU (1997) included the consideration of the modulus of compressibility in their theoretical energy-based analysis of salt decay of porous media. GOUDIE (1999) found a positive association between modulus of elasticity and resistance to salt weathering in laboratory tests of limestones.

The real importance of mechanical strength as decisive factor in defining resistance to salt weathering is somehow in dispute. STEIGER (2005a) concluded that even at moderate supersaturations salt crystallization would produce pressures that exceed typical tensile strength values of rocks. BENAVENTE et al. (2001) used flexural strength values (considered indicators of degree of coherence of the rocks) to explain differences in durability, evaluated by laboratory salt crystallization tests, of sedimentary rocks with similar pore size distribution (and consequently with similar results of salt crystallization pressure).

RUEDRICH et al. (2007), in a laboratory study of sandstones, concluded that tensile strength did not seem to be the key factor in the explanation of salt weathering susceptibility.

There is an additional difficulty in that rock strength and other mechanical properties are influenced by several rock characteristics, some of them relevant to salt weathering (namely porosity). For example, besides the relation with modulus of elasticity previously mentioned, GOUDIE (1999) found an association of limestone durability with water absorption, with higher durability rocks presenting lower water absorption capacity. An extensive laboratory study of sedimentary rocks by BENAVENTE et al. (2004a) found moderate correlation between durability and estimators depending only in pore properties or mechanical properties and proposed estimators that used both (the authors favoured the estimator that used tensile strength, as estimated by flexural tests). The statistical analyses of BENAVENTE et al. (2007a) with sedimentary rocks seem to point to the predominant role of rock strength in the prediction of salt weathering durability (over pore space properties).

It must be remembered that, as happens with other rock properties, mechanical strength can present important variations. Rock strength is commonly anisotropic. For example, MOTTERSHEAD (1997) reports values of tensile strength for greenschists that are four times lower parallel to foliation than normal to foliation. The anisotropy of rock strength has been considered in the explanation of the development of planar detachments in granite stones (ORDAZ et al., 1996; SILVA et al., 1996b; RIVAS-BREA et al., 2008).

The different parameters of mechanical strength are also affected by the rock water content, especially in the presence of clays (WINKLER, 1994). The importance of wet/dry ratio of mechanical strength is stressed in a study of tuff monuments by TOPAL and SÖZMEN (2003). Furthermore, there are some studies that suggest that the composition of pore solutions could also affect rock strength (see examples on sandstones by FEUCHT and LOGAN, 1990; on granites by FENG et al., 2001).

6. ALTERATION HISTORY

Previous alteration (that can be related to hydrothermal and meteoric agents) of stones while still in rock masses (before extraction) contributes to variability of properties of applied stone blocks, namely affecting pore space characteristics (filling voids, creating new voids) and strength as well as originating new deleterious phases (clays). Weathering is particularly important in the study of igneous rocks (most of the examples refer to granites).

One can include here stress relief, since it is a process involved in the beginning of natural weathering, and has been indicated as a possible contribution to subsequent decay processes of building stones (WINKLER, 1994; WARKE, 1996). Stress relief has been, for example, pointed as a factor involved in the formation of scales in granites (such as those seen in Figure 3 and in Figure 4). However, the existence of some space distribution patterns of these decay features (see Figure 4) cast some doubts on the importance of stress relief for formation of granite scaling. Also, as would be discussed further on, previously weathered yellowish granite, granite that has already been in contact with atmospheric agents (and that has experienced some stress relief before extraction) show stronger decay on buildings than less weathered greyish granite.

Stones with previous weathering, resulting from alteration of rock masses, tend to be more susceptible to salt decay, due to the development of pores and fissures (DELGADO-RODRIGUES, 1991). This could be particularly important in the case of otherwise generally low porosity rocks such as granites. HONEYBORNE (1998b) refers to granites that have suffered previous kaolinization, with poor performance and that usually present higher porosity than it is normally expected. These previously weathered granite stones (rock mass weathering) can present a pore structure that is favourable to salt solutions migration by capillarity (ALVES et al., 1996; BEGONHA and SEQUEIRA BRAGA, 2000). Besides the time component considered by MIGÓN (2006), the variations in porosity related to variations in the intensity of previous rock mass weathering might help in explaining the contrast between high durability results of granites in laboratory tests and intense decay observed in actual granite building stones, since these variations in porosity can have an important impact in capillary water uptake, namely in the initial stages of weathering. MOTTERSHEAD (2000) considered differences in previous (before application) weathering state to explain different durability of granite stones in coastal environments. In extreme cases paleoweathering can give origin to “granitic” varieties with high porosity and that suffer intense decay (GARCÍA-TALEGÓN et al. 1996; TRUJILLANO et al, 1996).

Besides the effects on pore space and related properties, there is also the formation of clay minerals, especially relevant in igneous rocks (DELGADO-RODRIGUES, 1991). WARKE (1996) points out that chemical weathering can create portions more susceptible to physical processes (such as salt weathering). This aspect is referred by HUANG (2007) as well as the increase of fine pores by clay formation.

Differences in previous weathering characteristics can result in macroscopic evidence that may be useful in understanding stone decay. For example, the presence of biotite in granites can promote rock discolouration (with a variable yellowish/brownish tonality, see examples in Figure 9) during natural weathering that can be related to weathering intensity in the first stages of weathering (when the rocks is usable as material for building stone) and it has been observed, in field studies, that granites with more intense discolouration tend to suffer higher decay (ALVES et al., 1996; MATIAS and ALVES, 2002).



Figure 9. Different tonalities (discolouration) in applied granite stones related to previous weathering of rock masses (a, b). It is frequently observed that granite stones with different discolouration tonalities (representing different previous weathering intensity) present different decay intensity (b).

Weathering after stone emplacement in man-made structures should also be considered, being a dynamic process with evolution along time (MCKINLEY and WARKE, 2007). Thermal and moisture cycles could promote the development of fissures (AIRES-BARROS et al., 1975), increasing pore space and reducing stone strength, allowing damage by salt crystallization (HONEYBORNE, 1998a). The development of hard and impervious surface coatings may contribute to the concentration of salts (behind the coatings) and further promote decay processes (see examples in SMITH et al., 1994; WINKLER, 1994; ROBINSON and WILLIAMS 1996; FITZNER et al., 1996; CASSAR, 2002; TÖRÖK, 2002; THOMACHOT and JEANNETTE, 2004; RESCIC et al., 2007).

7. HETEROGENEITY

After discussing the effects of textural, small-size heterogeneity, this section will consider features that are (due to its dimension in relation to size of test specimens) usually disregarded by laboratory test, being mainly studied by field observations, and that can be disregarded by petrographic characterizations solely based on the study of thin sections. These features correspond to what DIBB et al. (1983) design as “macro-flaws” (these authors highlight the limitations of laboratory test for the evaluation of the effect of macro-flaws on the performance of rock products). Laboratory tests commonly deal with what is usually referred in Engineering Geology studies as “intact rock” (test specimens are generally homogeneous).

Frequently these coarser heterogeneities are avoided on the preparation of the specimen tests and its presence usually considered a problem in laboratory tests; for example, the porosity-related durability index proposed by ORDÓÑEZ et al. (1997) did not seem to work for samples that broke along rich layers (see also discussion of results on laboratory specimens of LÓPEZ-ACEVEDO et al., 1997 concerning the presence of random irregularities). WARKE and SMITH (2007) ascribe irregularities in mass loss evolutions to breaking of clay layers. Some examples of field observations in natural stone are presented in Figure 10, Figure 11 and Figure 12.



Figure 10 (Continued).



Figure 10. Differential relief related to heterogeneous constituents on volcanic (a) and granitic (b) rocks.

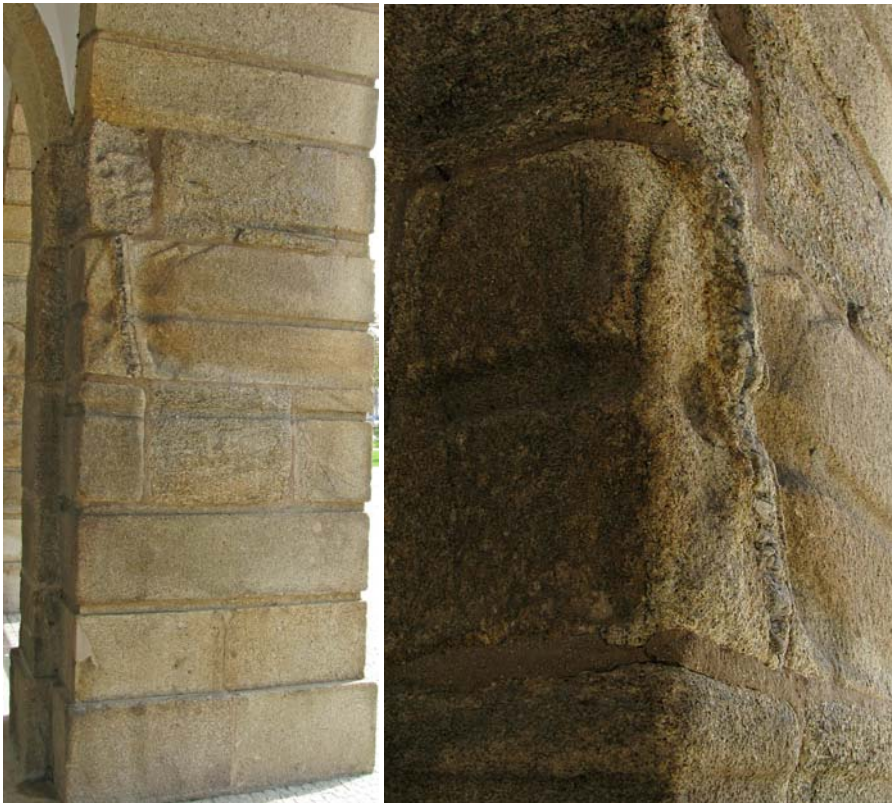


Figure 11. General view (a) and detail (b) of differential erosion related to presence of veinlet in granite stone.



Figure 12. Differential erosion features in limestones related to heterogeneity (a, b).

According to HELMI (1994), a paper by Caner and Türkmenoglu from 1985 refers the effects of soluble salts on basalts microveins. Differential erosion on sandstones along layers or bands is frequently observed (WINKLER 1994; ROBINSON and WILLIAMS, 1996; MATOVIC et al., 2000; WRIGHT, 2002). SILVA et al. (1996a) mentioned features such as nodules, xenoliths and layers of different composition as characteristics that influence the development of alveolization on granites. MATIAS and ALVES (2002) also observed differential relief on granite stones with basic nodules being associated with positive relief while micaceous nodules favoured negative relief. SMITH (1999) called attention to the effects on masonry durability of soft seams in generally strong rock. Based on field observations, GATT (2006) proposed that dissolution seams acted as barrier to capillary rising solutions (see image 2P in Figure 3 of GATT, 2006). A similar process would explain images of Figure 12 (and also of Figure 11) where decay is more intense around the

heterogeneous features (the more impervious features, not allowing the circulation of solutions would promote salt concentration around it).

Discontinuities can also affect strongly the evolution of decay features. TRUJILLANO et al. (1996) noted that the presence of a crack in a granite specimen promoted non-homogeneous crystallization and stone detachment in a rock that, otherwise, presented low erosive decay. Discontinuities can favoured migration of water and salt solutions (as is referred by WÜST and SCHLÜCHTER, 2000, and has been observed in water imbibition laboratory tests by the present author) and propagation of salt contamination. Joints and thin talc and carbonate veins are indicated as factors that promote decay of soapstones (STOREMYR, 2004).

The variations in characteristics that affect resistance to salt decay in a single real-size block could also be included here. An example of the study of variations of properties is presented in MCKINLEY and WARKE (2007) where permeability measurements are discussed in terms of spatial characterisation and its relevance for stone decay. A feature that might be particularly relevant for igneous rocks is the variation of previous weathering intensity in stone elements marked by discolouration (as illustrated in Figure 9) and the concomitant variation in rock properties.

CONCLUSION

The first comments would concern some methodological points, since they condition what can be extracted from this review. In the set of publications considered here there is a clear bias towards empirical, inductive studies that deals with a given set of observations (field studies) or with a restricted set of samples of a restricted set of rock types (laboratory tests). Deductive studies that proceed from theories to predict results are almost exclusively limited to calculations of crystallization pressure by reference to pore size distribution (in some cases also with energy considerations), with the exception of a few works concerning water transport or rock strength properties.

It seems that crystallization pressure tends to play a highly important, perhaps excessive, role in the explanation of stone decay related to salt crystallization. Calculations based on salt crystallization pressure consider salt weathering as an isotropic and globally (at the stone scale at least) homogeneous process, which does not cover several of the situations that can be observed on actual stone elements. The question of falsifiability (in the sense proposed by POPPER, 1968) would be relevant to this point and salt crystallization pressure theory should be used to formulate clearly testable predictions (that can be assessed both in laboratory tests and in field observations). But the implications of the Duhem-Quine thesis (see, for example, MORAD, 2004) must also be considered, namely in what concerns our “belief” in pore size characterisation and whether the techniques used for this characterisation produce similar good and representative results for all types of rocks. Deductive studies involving water transport properties (including drying) applied to actual structures that are also testable are needed. There is a strong, perhaps excessive, trend towards reliance on pore size characterisation and one wonders if, to study salt transport and crystallization, an approach based on bulk macroscopic properties that predict macroscopic stone behaviour would not be more appropriated to the size of the actual stone elements. After all, Darcy’s law had been

successfully used by hydrogeologists all over the world without recourse to detailed pore size characterisation.

A comment about the application of salt crystallization tests: considering these tests as an evaluation tool of stone performance, there seems to be evidence that support its application to all rocks, regardless of porosity values.

Regarding the representation of rock types, as the references collected in this review show, limestones and sandstones are clearly the more studied types regarding salt weathering effects, with granites, dolostones and, in a way, also marbles, in a second place (while there are immense publications about black crusts in marbles, few works were found concerning other effects of salt weathering and the susceptibility of marble to salt solutions, namely in relation to marbles properties). In spite of one dedicated meeting in the last decade of the previous century, there are scarce studies of volcanic rocks, namely if one considers the mineralogical, textural and structural complexity of these rocks. Excepting marbles, metamorphic rocks have been, with few exceptions, ignored by salt weathering studies (this could reflect the low importance of these rocks in historical heritage buildings).

Decay effects of salt solutions have been related to several physical properties and petrographic characteristics, and while a unifying theory of these characteristics and stone durability has not been produced, the diverse features are an indispensable part of any attempt for a scientific characterisation/definition of natural stone behaviour. Some contradictions seem to arise from comparing diverse studies. These contradictions would be more fruitful if regarded as points that require/merit further research (see general discussion on the importance of the problem-situation in science by POPPER, 1969) instead of being simply disregarded as indication of a case-study character (the alleged case-study character should also not be used as a general excuse for the apparent contradictions; these contradictions are indicators of points that require further research).

A special word concerning water-accessible porosity: while it is clear that by itself alone cannot be a universal estimator, it might be possible that petrographic criteria could allow the definition of sets where easy, relatively fast and generally non-destructive tests related to this property can be used in the prediction of stone behaviour.

Regarding the real importance of rock strength, it would be useful to compare of results of rocks with similar porosities and similar pore size distribution and different values of tensile strength. A starting point could be to focus research in low porosity rocks presenting diverse physical strength values.

While most research publications reviewed here considers mainly physical consequences of salt weathering, there are several indications that point to chemical effects. It must be considered that in some situations there could be important accumulations of salt-rich solutions in prolonged contact with stone constituents.

Some comments are also appropriated in relation to possible contributions to the discussion of stone selection. While it was not possible in this chapter to define a universal relation between salt weathering resistance and porosity or pore space characteristics, as was already mentioned, there seems that there is a certain trend of, at least, increasing risk with increasing porosity. The relation might not follow explicit functions in a monotonous manner (in the sense of increasing porosity implies increasing decay risk) but the concept of threshold (as referred by MCGREEVY, 1996) could be decisive. However, will there be a universally low porosity threshold value (different of the obviously unattainable zero)? Besides the physical decay effects, chemical susceptibility needs also some consideration. Considering

some papers that have focused specifically on chemical effects comparing different rocks (DIBB et al. 1983; CARDELL et al., 2003a) it seems that limestones are more susceptible to chemical attack by salt solutions (which is not surprising given the higher solubility of calcite), but, as this chapter has referred, there are several constituents that may constitute weakness phases in relation to salt attack and that might contribute to salt weathering of the containing stone or other stone in the neighbourhood (for example, avoiding limestone above other stones seem to be a common recommendation).

The problem of the inherent variability of natural stone, both regarding variations in properties that follow identifiable patterns as well as more irregular heterogeneity, is an important aspect that must be considered in salt weathering of natural stone and that might be particularly relevant in the selection of stones. At several scales of observation there are examples where the presence of elements with different properties favoured differential behaviour and it may be interesting to speculate whether this suggest that rock heterogeneity could be a particularly negative feature in salt infected environments regarding both an quantitative evaluation (higher decay as expressed, e.g., by greater erosive depth or extension) and also aesthetic considerations (since differential weathering could act as a visual highlighter of decay).

Variations of stone properties must be studied and identified since they could imply very different decay behaviour. In this respect a special note about granite weathering might be added. Granite is frequently presented as extremely durable stones and in its unweathered, low porosity, original state this could generally be the case, but weathering could cause very important effects in granite properties that do not necessarily follow a linear trend. While sometimes being favoured by a certain aesthetic appeal (yellowish tonality), granite stones that present higher previous weathering intensity tend to show lower durability in salt weathering conditions (no reference to a contradiction of this alleged trend in granites was found in the review performed for this chapter).

A final comment returning to methodology: laboratory tests should advance towards conditions similar to those found in buildings (as is already done in seismic testing) both in scale and complexity (see, for example, CULTRONE et al., 2007; CULTRONE and SEBASTIÁN, 2008; LAYCOCK et al., 2008) including the problem of the interfaces between different materials. It will be also an important step for conservation of stone structures.

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Chapter 3

STUDY ON ADSORPTION AND THERMOELECTRIC COOLING SYSTEMS USING BOLTZMANN TRANSPORT EQUATION APPROACH

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ABSTRACT

In this chapter, the Boltzmann Transport Equations (BTE) is used to formulate the transport laws for equilibrium and irreversible thermodynamics and these BTE equations are suitable for analyzing system performance that are associated with systems ranging from macro to micro dimensions. In this regard, particular attention is paid to analyze the energetic processes in adsorption phenomena as well as in semiconductors from the view point of irreversible thermodynamics. The continuity equations for (i) gaseous flow at adsorption surface, and (ii) electrons, holes and phonons movements in the semiconductor structures are studied. The energy and entropy balances equations of (i) the adsorption system for macro cooling, and (ii) the thermoelectric device for micro cooling are derived that lead to expressions for entropy generation and system's bottlenecks. The BTE equation is applied to model the adsorption cooling processes for single-stage, multi-stage and multi-bed systems, and the simulated results are compared with experimental data. This chapter also presents a thermodynamic framework for the estimation of the minimum driving heat source temperature of an advanced adsorption

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cooling device from the rigor of Boltzmann distribution function. From this thermodynamic analysis, an interesting and useful finding has been established that it is possible to develop an adsorption cooling device as a green and sustainable technology that operates with a driving heat source temperature of near ambient. Moreover, the Onsager relations are applied to model the thermoelectric transport equations and, after coupling with Gibbs law and BTE, the temperature-entropy flux derivations are further developed and presented the energetic performances of thermoelectric cooling systems.

ABBREVIATIONS

A	area	m^2
A_{te}	cross sectional area of a thermoelectric element	m^2
COP	the Coefficient of Performance	--
c	the mass fraction	kg kg^{-1}
c_p	specific heat capacity	$\text{J kg}^{-1} \text{K}^{-1}$
$c_{p,sg}$	specific heat of silica gel	$\text{J kg}^{-1} \text{K}^{-1}$
$c_{p,te}$	specific heat capacity of thermoelectric material	$\text{J kg}^{-1} \text{K}^{-1}$
c_v	specific heat capacity at constant volume	$\text{J kg}^{-1} \text{K}^{-1}$
D_{so}	a kinetic constant for the silica gel water system	
d^3	3-D operator	
E	electric field	volt
E_a	activation energy of surface diffusion	J kg^{-1}
e	the total energy per unit mass	J kg^{-1}
F	the Faraday constant	Coulomb mol^{-1}
F	the external force	N
f	the statistical distribution function	
h	enthalpy per unit mass	$\text{J kg}^{-1} \text{K}^{-1}$
h	convective heat transfer coefficient	$\text{W m}^{-2} \text{K}^{-1}$
I	the current	amp
J	heat flux	W m^{-2}
J_s	entropy flux	$\text{W m}^{-2} \text{K}^{-1}$
JE	electric field	W m^{-3}
$J(=I/A)$	the current density	amp m^{-2}
J_k	diffusion flow of component k	
J_p	the momentum flux	N m^{-3}
$J_{s,pn}$	the entropy flux both the p and n leg	$\text{W m}^{-2} \text{K}^{-1}$
k	the thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
K_o	pre-exponential coefficient	kPa^{-1}
k_{te}	thermal conductivity of thermoelectric element	$\text{W m}^{-1} \text{K}^{-1}$
L	length	m
L_{te}	characteristics length of thermoelectric element	m
M	current pulse magnitude	--
m^*	the mass of a single molecular particle	kg
m	mass	kg
m_a^*	mass of adsorbate under equilibrium condition	kg

n	carrier density	m^{-3}
n_m	number of thermoelectric modules	
$\mathbf{p}$	the momentum vector	
P	pressure	Pa
P_l	saturated pressure	Pa
$P_{in,ncolli}$	power input with non-collision effect	mW
$P_{in,colli}$	power input with collision effect	mW
Q	the total heat or energy	W or J
Q_o	the heat transport of electrons/ holes	J mol^{-1}
$Q_{H,ncolli}$	heating power at hot side with non-collision effect	mW
$Q_{H,colli}$	heating power at hot side with collision effect	mW
$Q_{L,ncolli}$	cooling power at cold side with non-collision effect	mW
$Q_{L,colli}$	cooling power at hot side with collision effect	mW
Q_{colli}	power dissipation due to collisions	mW
R_p	average radius of silica gel particle	m
R_g	universal gas constant	$\text{J kg}^{-1} \text{K}^{-1}$
$\mathbf{r}$	the particle position vector	
$\mathbf{r}'$	the new position vector at an infinitesimally time dt	
s	total entropy	$\text{J kg}^{-1} \text{K}^{-1}$
S_{te}	the total Seebeck coefficient	V K^{-1}
s	entropy per unit mass	$\text{J kg}^{-1} \text{K}^{-1}$
T	temperature	K
t	time	s
t_l	the Tóth constant	--
t_{cycle}	cycle time	s
U	a peculiar velocity	m s^{-1}
U	total internal energy of the system	J.kg^{-1}
u	internal energy per unit mass	$\text{J kg}^{-1} \text{K}^{-1}$
V	volume of the system	m^3
V	Input voltage to the TE modules	volt
$\mathbf{v}''$	the particle velocity vector	m s^{-1}
$\mathbf{v}'$	the particle velocity vector at an infinitesimally time dt	m s^{-1}
$\mathbf{v}$	velocity	m s^{-1}
$v (= 1/\rho)$	specific volume	$\text{m}^3 \text{kg}^{-1}$
w	energy flow (the combination of thermal and drift energy)	J
X	any sufficiently smooth vector field	
Y	energy dissipation during collision ($= \rho e$)	J m^{-3}
Z	thermoelectric figure of merit	K^{-1}
z	the total electric charge	coulomb
ΔT	temperature difference between the hot and cold junctions	K

ΔH_{ads}	enthalpy of adsorption	kJ kg^{-1}
Φ	the source of momentum	
Π	tensor part of a pressure tensor	
π	Peltier coefficient	V
α	the Seebeck coefficient	VK^{-1}
χ	the substantive derive of any variable	
ρ	the effective density	kg m^{-3}
τ	average collision time	fs
Γ	the Thomson coefficient	VK^{-1}
λ	the thermal conductivity	$\text{W m}^{-1} \text{K}^{-1}$
λ	the phonon wavelength	nm
ψ	potential energy per unit mass	J kg^{-1}
μ	the thermodynamic or chemical potential	
μ_l	liquid viscosity (equation 5.35)	kg/ms
σ	the entropy source strength	$\text{W m}^{-3} \text{K}^{-1}$
σ_s	Surface tension (equation 5.35)	N m^{-1}
σ'	the electrical conductivity	$\text{ohm}^{-1} \text{m}^{-1}$
$\nabla \phi$	the electric potential gradient	V m^{-1}

Subscripts

a	adsorbate
ads	adsorption
b	barrier
b,e	electrons in the barrier of superlattice
b,h	holes in the barrier of superlattice
b,g	phonons in the barrier of superlattice
$colli$	the collision term
$colli\ e-h$	collision between electrons and holes
$colli\ e-g$	collision between electrons and phonons
$colli\ h-e$	collision between holes and electrons
$colli\ h-g$	collision between holes and phonons
$colli\ g-e$	collision between phonons and electrons
$colli\ g-h$	collision between phonons and holes
$cond$	condenser
$cycle$	cycle time
des	desorption
e	electron
eff	effective value
$evap$	evaporator
f	liquid phase
$f-m$	fluid-metal
$fin-s$	fin-silica gel
g	phonons or gas

<i>gas</i>	gaseous phase
<i>H or hj</i>	hot junction
<i>HX</i>	heat exchanger
<i>h</i>	hole
<i>in</i>	inlet
<i>irr</i>	irreversible
<i>L or cj</i>	cold junction
<i>l</i>	liquid phase
<i>m</i>	mean (average)
<i>max</i>	maximum
<i>min</i>	minimum
<i>m-s</i>	metal-silica gel
<i>np</i>	non-pulsed period
<i>o</i>	outlet
<i>p</i>	the pulse period
<i>pr</i>	Prediction
<i>q</i>	Joulean heat flux
$\dot{\mathbf{r}}$	rate of change of position vector
<i>ref</i>	refrigerant
<i>rev</i>	reversible
<i>s</i>	saturation
<i>sys</i>	system
<i>TE</i>	thermoelectric modules
<i>te</i>	thermoelectric device
<i>th</i>	theoretical
<i>tu</i>	tube
$\dot{\mathbf{v}}''$	rate of change of velocity vector
<i>w,e</i>	electrons in the well of superlattice
<i>w,h</i>	holes in the well of superlattice
<i>w,g</i>	phonons in the well of superlattice
<i>w</i>	well or water refrigerant
<i>w,i</i>	water inlet
<i>w,o</i>	water outlet

Superscripts

<i>sg</i>	silica gel
<i>evap</i>	evaporator
<i>cond</i>	condenser
<i>bed</i>	sorption bed
<i>chill</i>	chilled water
<i>f</i>	liquid phase
<i>g</i>	gaseous phase
<i>in</i>	inlet

<i>tube</i>	heat exchanger tube
<i>a</i>	adsorbate
<i>cool</i>	cooling fluid
<i>heating</i>	heating fluid

1. INTRODUCTION

In the past few decades, significant progress has been made in development of adsorbents and semiconductor materials for cooling applications, for example, (i) the adsorption cooler employing silica gel, zeolites, activated carbon; and (ii) the thermoelectric coolers using the Bismuth-Telluride (Bi_2Te_3), Antimony-Telluride (Sb_2Te_3), Silicon-Germanium (SiGe) [1]. The adsorption chillers are also miniaturized with micro-technology based miniature adsorbers and desorbers for heat pump and cooling applications [2-4]. With greater needs for miniaturization of micro or mini-chillers, these semi-conductors are fabricated within a few microns thick using the chemical-vapor deposition (CVD) techniques for making the thin-film materials in layers of the positive-negative or p-n junctions. The law of equilibrium thermodynamics as well as the conservation laws, which are well established for analyzing energy and mass transfers of macro control volumes or systems such as adsorption or bulk thermoelectric device, may not be sufficient to handle the systems of micro dimensions such as thin film superlattice thermoelectric element [5, 6], in particular, their inability to handle the dissipation phenomena associated with high density electrons, holes and phonons collisions or flows and these dissipations are known to have set real limits to the performance of micro systems.

In this chapter, the Boltzmann Transport Equation (BTE) [7, 8] is used to formulate the transport laws for equilibrium and irreversible thermodynamics. The BTE equations are deemed to be suitable for analyzing micro-scaled systems because they account for the collisions terms associated with the high density fluxes of electrons and phonons in the thin films. In Figure 1, the relative merits of applying the classical Gauss theorem (control volume approach), BTE and the molecular dynamics model is elaborated with respect to the length and time scales. For example, at wavelengths ranging from a phonon (1~2 nm) to its mean free path (300 nm), the molecular dynamic model is usually employed [9]. In regions higher the mean free path of phonons, the BTE models could be utilized to capture the collision contributions of particles and the BTE model can be extended into the realm of the Gauss theorem or control volume approach.

In this regard, particular attention is paid to the energy, momentum and mass conservation properties of the collision operator in sub-micron semiconductor devices. It is noted that the dissipative effects from the collision terms are translated into unique expressions of entropy generation where one could analysis systems performance using simply the classical temperature-entropy (T-s) diagrams that capture the rate of energy input, the dissipation and the useful effects.

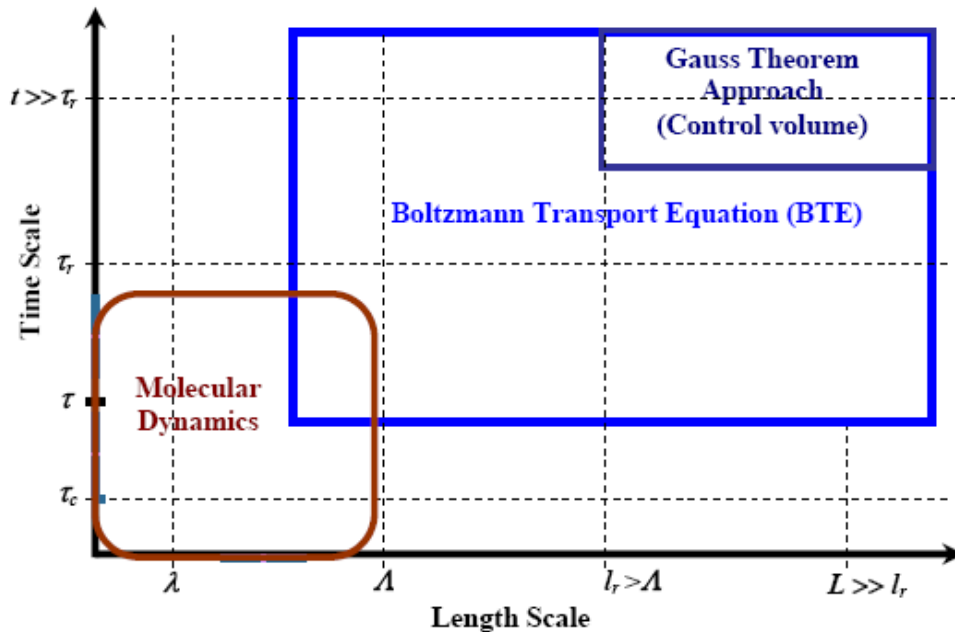


Figure 1. Schematic diagram of a thermal transport model showing the applicability of Boltzmann Transport Equation (BTE) in the thin films, where τ_c is the wave interaction time (100 fs), τ defines the average time between collisions, τ_r is the relaxation time, λ indicates the phonon wavelength (1~2 nm), Λ is the mean free path (~300 nm) and l_r is the distance corresponding to relaxation time. (Lee, 2005). Hence when $L \sim \lambda$, wave phenomena exhibit, when $L \sim \Lambda$ and $t \gg \tau, \tau_r$, ballistic transport and there is no local thermal equilibrium, when $L \gg l_r$ and $t \sim \tau, \tau_r$, statistical transport equations are used, when $L \gg l_r$ and $t \gg \tau, \tau_r$, local thermal equilibrium can be applied over space and time, leading to macroscopic transport laws.

Another advantage of using the BTE approach is that when the systems to be analyzed enters into a macro-scale domain, the collision terms could simply be omitted (as the effects are known to be additive) and the conservation laws revert back to that of the classical thermodynamics, a method similar to the direction taken by the works of de Groot and Mazur [10].

Prior to writing down the BTE formulation below, some aspects of classical thermodynamic development in the recent years are first reviewed. One such topic that has been greatly discussed in the literature is the finite time thermodynamics (FTT) [11], which has been applied to problems of isothermal transfers to chiller cycles called the reversible cycle. In the FTT analysis, the processes of heat transfer (from and to the heat reservoir) are time dependent but all other processes (not involving heat transfers) are assumed reversible. Take for example, an endo-reversible chiller that has been commonly modelled [12]. Invariably, they assumed reversibility for the flow processes of its working fluid but irreversible processes are arbitrary applied and restricted to the heat interactions with the environment or heat reservoirs. Owing to the arbitrary assumption of reversibility for the flow processes of working fluid within the chiller cycle, the FTT faces an “uncertain treatment” [13] and hence, it renders itself totally impractical in the real world.

On the other hand, there has been an excellent development in the general argument of equilibrium and irreversible that applies to macro systems. It is built upon an approach following the method of de Groot and Mazur [10]. They proposed the theory of fluctuations

that describes non-equilibrium (irreversible) phenomena, based on the basic reciprocity relations [14], and relied on the microscopic as well as drawing phenomenon about macroscopic behavior. Most non-equilibrium thermodynamics assumes linear processes occurring close to an equilibrium thermodynamic state and assumes that the phenomenological coefficients are constant [15].

For the microscopic and sub-microscopic domains, the transport equations are developed from the rudiments of the Boltzmann Transport Equation (BTE) but conforming to the First and Second Laws of Thermodynamics. In the sections to follow, the main objective is to discuss and formulate the basic conservation laws (mass, momentum and energy balances) for the thin films and based on the specific dissipative losses encountered in these layers, the entropy generation with respect to the electrons, holes and phonons fluxes will be formulated.

The organization of this chapter is as follows: Section 2 describes the general form of conservation equations. The equations to be discussed are the mass, momentum and energy conservation and the properties of the collision operator. In section 3, the mathematical rigor of the BTE with respect to irreversible production of entropy is presented. Following the Gibbs expression on entropy, the entropy balance equation is established in relation with the conservation equations, which comprise a source term or entropy source strength term. Section 3 tabulates a list of the common entropy generation mechanisms and demonstrates the manner the terms are deployed in the BTE formulation. For application examples of this demonstration presented in the previous sections, section 4 demonstrates the mathematical modeling and the performance analysis of adsorption cooling systems. Based on the conservation laws and the entropy balance equations, section 5 develops the temperature-entropy formulations of a solid state thermoelectric cooling device, a pulsed thermoelectric cooler and a micro-scale thermoelectric cooler. The thermodynamic performances of these solid state coolers are discussed graphically with T-s diagrams. In this section, the mathematical modelling of the thin film superlattice thermoelectric element is developed from the basic Boltzmann Transport Equation where the collision terms are included. This chapter finally ends with a conclusion.

2. GENERAL FORM OF BALANCE EQUATIONS

In this section, the transport processes involving the mass, momentum, and energy are described from the basic conservation laws, developed together with the transport of heat or energy by molecular fluxes such as electrons, holes and phonons within the micro layers in a system.

2.1. Derivation of the Thermodynamic Framework

Figure 2 shows a schematic of an ensemble or a group of molecular particles, such as an electrons, holes or phonons, represented initially at a time t where their positions and velocities are expressed in the range $(d^3\mathbf{r})$, $(d^3\mathbf{v})$ near $\mathbf{r}$ and $\mathbf{v}$, respectively. The operator, d^3 indicates the three dimensional spaces of the variables $\mathbf{r}$ and $\mathbf{v}$.

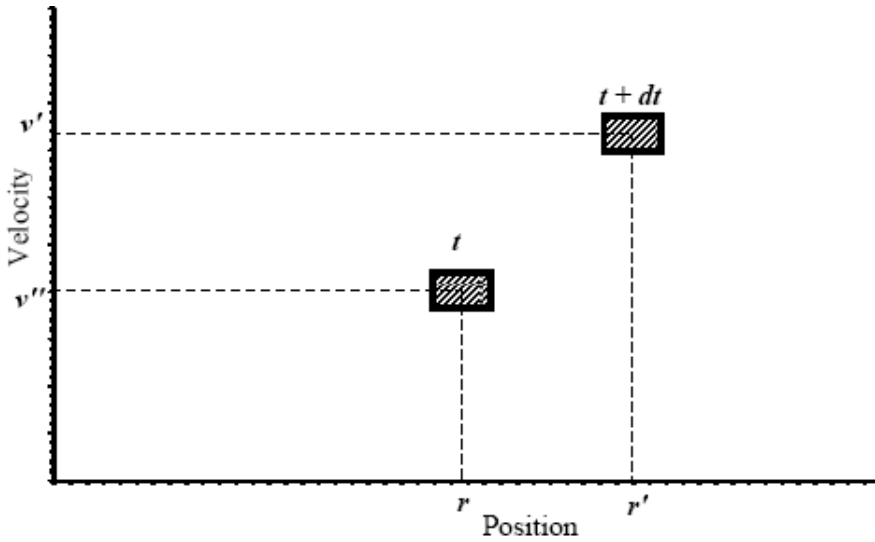


Figure 2. The motion of a particle specified by the particle position r and its velocity v'' .

At an infinitesimally small time dt later, the molecular particles move, under the presence and influence of an external force $\mathbf{F}(\mathbf{r}, \mathbf{v}'')$, to a new position $\mathbf{r}' = \mathbf{r} + \dot{\mathbf{r}}dt$ and attaining a velocity $\mathbf{v}' = \mathbf{v}'' + \dot{\mathbf{v}}'' dt$. Owing to collisions of molecular particles, the number of molecules in the range $d^3\mathbf{r} d^3\mathbf{v}''$ could be also changed where particles or molecules originally outside the range $(d^3\mathbf{r})(d^3\mathbf{v}'')$ can be scattered into the domain under consideration. Conversely, molecules originally inside the domain range could be scattered out. Following the framework of Reif, F. [16], the generic form of the conservation laws is additive and is given by,

$$\overbrace{f(\mathbf{r}', \mathbf{v}', t') d^3(\mathbf{r}') d^3(\mathbf{v}')}^{\text{Molecules\_at\_}(t'), (r') \& v'} = \overbrace{f(\mathbf{r}, \mathbf{v}'', t) d^3(\mathbf{r}) d^3(\mathbf{v}'')}^{\text{Molecules\_at\_}(t), (r) \& v''} + \overbrace{f_{\text{colli}}(\mathbf{r}, \mathbf{v}'') d^3(\mathbf{r}') d^3(\mathbf{v}'')}^{\text{Molecules\_at\_}(r') \& v''} \quad (1)$$

where $t' = t + dt$, the range $(\mathbf{r}' = \mathbf{r} + \dot{\mathbf{r}}dt)$ and $(\mathbf{v}' = \mathbf{v}'' + \dot{\mathbf{v}}'' dt)$. $f(\mathbf{r}, \mathbf{v}, t)$ is the statistical distribution function of an ensemble particle, which varies with time t , particle position vector $\mathbf{r}$, and velocity vector $\mathbf{v}$.

For convenience, we drop the implied 3-D operator, d^3 , the equation reduces to a more readable form, i.e.,

$$f(\mathbf{r} + \dot{\mathbf{r}}dt, \mathbf{v}'' + \dot{\mathbf{v}}'' dt, t + dt) = f(\mathbf{r}, \mathbf{v}'', t) + f_{\text{colli}}(\mathbf{r}, \mathbf{v}'', t) dt$$

or the collision term is

$$f_{\text{colli}}(\mathbf{r}, \mathbf{v}'', t) dt = f(\mathbf{r} + \dot{\mathbf{r}}dt, \mathbf{v}'' + \dot{\mathbf{v}}'' dt, t + dt) - f(\mathbf{r}, \mathbf{v}'', t)$$

By invoking the partial derivatives, the basic Boltzmann transport equation is now expressed for a situation that handles the molecular flux over a thin layer of materials, i.e.,

$$\frac{\partial f_{\text{colli}}}{\partial t} = \left(\frac{\partial f}{\partial \mathbf{r}} \frac{\partial \mathbf{r}}{\partial t} + \frac{\partial f}{\partial \mathbf{v}''} \frac{\partial \mathbf{v}''}{\partial t} \right) + \frac{\partial f}{\partial t}$$

rearranging

$$\frac{\partial f}{\partial t} = - \left(\frac{\partial f}{\partial t} \right)_{\text{drift}} + \frac{\partial f_{\text{colli}}}{\partial t}$$

and the subscript “drift” refers to the flow of flux through space ($\mathbf{r}$) and convective velocity ($\mathbf{v}$) and the second term is the effect of collisions with time. It is noted that the term “drift” is a non-equilibrium transport mechanism that associates with the external force $\mathbf{F}(\mathbf{r}, \mathbf{v}'')$, i.e.,

$$\left(\frac{\partial f}{\partial t} \right)_{\text{Drift}} = \frac{\partial f}{\partial \mathbf{r}} \frac{d\mathbf{r}}{dt} + \frac{\partial f}{\partial \mathbf{v}''} \frac{d\mathbf{v}''}{dt}, \quad (2)$$

where $\mathbf{r}$ is the position vector, $\mathbf{v}''$ is the velocity vector, i.e., $\mathbf{v}'' = \frac{d\mathbf{r}}{dt}$, and the rate of change of $\mathbf{v}''$ is $\frac{d\mathbf{v}''}{dt} = \frac{\mathbf{F}}{m^*}$, where m^* is the mass of a single molecular particle.

The physical meanings of velocity and electric field are described in the drift term of equation (2) is now fully elaborated as,

$$\left(\frac{\partial f}{\partial t} \right)_{\text{Drift}} = \mathbf{v}'' \frac{\partial f}{\partial \mathbf{r}} - \frac{\mathbf{F}}{m^*} \frac{\partial f}{\partial \mathbf{v}''} = \mathbf{v}'' \frac{\partial f}{\partial \mathbf{r}} - \mathbf{F} \frac{\partial f}{\partial \mathbf{p}},$$

where the momentum $\mathbf{p} = m^* \mathbf{v}''$, is that associated with a molecular particle. Substituting back into equation (2), the general form of the transport equation with respect to $\mathbf{r}$, $\mathbf{p}$ and t becomes

$$\frac{\partial f}{\partial t} = -\mathbf{v}'' \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} + \frac{\partial f_{\text{colli}}}{\partial t}. \quad (3)$$

Having formulated the basic form of the Boltzmann transport equation or BTE in short, and two other functions will be used along the BTE and they are: Firstly, the carrier density of the molecular flux is now incorporated by defining the carrier density as the integral of the product between the molecular particles and the change in their momentum [7], i.e.,

$$n = \int f d\mathbf{p}. \quad (4)$$

Secondly, the substantive derive of any variable, χ , that varies both in time and in space can be expressed in vector notation as $\frac{d}{dt} = \frac{\partial}{\partial t} + \nabla \chi \cdot \mathbf{v} = \frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla) \chi$, or simply can be

written as $\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla$. The following conservation equations can now be formulated with the BTE format and they are elaborated here below.

2.2. Mass Balance Equation

For a given space and time domain, the basic Boltzman transport equation (3) is now invoked to give

$$\frac{\partial f}{\partial t} = -\mathbf{v}'' \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \frac{\partial f}{\partial \mathbf{p}} + \frac{\partial f_{\text{colli}}}{\partial t}$$

where the partials of f to the momentum and space in 3-dimensions can be represented by applying the “Del” operator, i.e., $\nabla_p f = \frac{\partial f}{\partial \mathbf{p}}$, $\nabla f = \frac{\partial f}{\partial \mathbf{r}}$. Thus, integrating on both sides of equation (3) with respect to the momentum space, and noting the definition of the carrier density n (equation 4), yields:

$$\frac{\partial n}{\partial t} = -\nabla(\mathbf{v}'' n) + \mathbf{F} \int \nabla_p f d\mathbf{p} + \frac{\partial n_{\text{colli}}}{\partial t} \quad (5)$$

Should $d\mathbf{p}$ be small in the space, the second term of right hand side of equation (5) can be omitted and equation (5) reduces to a familiar expression of the form;

$$\frac{\partial n}{\partial t} = -\nabla(\mathbf{v}'' n) + \frac{\partial n_{\text{colli}}}{\partial t}, \quad (6)$$

where the collision effects from molecular particles are still retained. Defining the effective density as $\rho = m^* n$, where m^* is the mass of single molecular particle. For simplicity, assuming the particles move with an average velocity, then $\mathbf{v} = \mathbf{v}''$, and rearranging gives the mass conservation as

$$\frac{\partial \rho}{\partial t} = -\nabla(\mathbf{v} \rho) + \frac{\partial \rho}{\partial t} \Big|_{\text{colli}}. \quad (7)$$

The advantage of equation (7) is that it is perfectly valid for describing electrons or phonons flow within submicron semiconductor devices and the collision term takes them into account. In the case of a macro-scale domain, the mass balance omits the collision term, i.e.,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}). \quad (8)$$

The form of equation (8) can also be derived using the Gauss theorem within a control volume method [16]. For example, the rectangular coordinates nomenclature for the component velocities for $\mathbf{v} = u\hat{\mathbf{i}} + v\hat{\mathbf{j}} + w\hat{\mathbf{k}}$ would yield the continuity equation as

$$\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z} = 0. \quad (9)$$

Only when steady state is considered, i.e., $\frac{\partial \rho}{\partial t} = 0$; and a case of constant-fluid density, the following simplified continuity equation reduces to

$$\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0 \quad (10)$$

In vector notation, the mass conservation for a macro domain and constant density situation is simply expressed as

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\nabla \cdot (\rho \mathbf{v}) \\ \frac{d\rho}{dt} &= -\rho \nabla \cdot \mathbf{v} \end{aligned} \quad (11)$$

2.3. Momentum Balance Equation

Starting from the basic transport equation, $\frac{\partial f}{\partial t} = -\mathbf{v}'' \cdot \frac{\partial f}{\partial \mathbf{r}} + \mathbf{F} \cdot \frac{\partial f}{\partial \mathbf{p}} + \frac{\partial f_{\text{colli}}}{\partial t}$, and multiply the momentum, $\mathbf{p}$, on both sides before integrating over the momentum space yields;

$$\frac{\partial}{\partial t} \int \mathbf{p} f d\mathbf{p} = -\int \mathbf{p} (\mathbf{v}'' \cdot \nabla f) d\mathbf{p} + \int \mathbf{p} (\mathbf{F} \cdot \nabla_p f) d\mathbf{p} + \int \mathbf{p} \frac{\partial f_{\text{colli}}}{\partial t} d\mathbf{p} \quad (12)$$

Invoking the definition of the carrier density, n , and the left hand term of equation (12) can be expanded as, $\frac{\partial}{\partial t} \int \mathbf{p} f d\mathbf{p} = \frac{\partial(n\mathbf{p})}{\partial t} = \frac{\partial(nm^* \mathbf{v})}{\partial t} = \frac{\partial(\rho \mathbf{v})}{\partial t}$ whilst the first term on the right hand side of equation (12) is reduced to $\int \mathbf{p} (\mathbf{v}'' \cdot \nabla f) d\mathbf{p} = \nabla \cdot \int (\mathbf{v}'' \mathbf{p} f) d\mathbf{p} = \nabla \cdot \mathbf{J}_p$, where $\mathbf{J}_p$ is a tensor. This flux density of momentum can further be transformed to

$$\nabla \cdot \mathbf{J}_p = \nabla \cdot (\mathbf{v}'' \mathbf{p} \int f d\mathbf{p}) = \nabla \cdot (\rho \mathbf{v}'' \mathbf{v}'') = \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}),$$

where according to Reif, F. [16], the velocity vector $\mathbf{v}'' (= \mathbf{v} + \mathbf{U})$ consists of a mean velocity $\mathbf{v}$ and a peculiar velocity $\mathbf{U}$, and the pressure tensor is given by, $\mathbf{P} = \rho \mathbf{U}_\alpha \mathbf{U}_\gamma = \rho \mathbf{U} \mathbf{U}$.

The second term on the right hand side of equation (12) is given by,

$\int \mathbf{p} (\mathbf{F} \cdot \nabla_p f) d\mathbf{p} = \mathbf{F} \int \nabla_p \cdot (\mathbf{p} f) d\mathbf{p} + \mathbf{F} \int f \nabla_p \cdot \mathbf{p} d\mathbf{p} = \mathbf{\Phi}$, known as the source of momentum, and the last term on the right hand side refers to as the collision integral, $\int \mathbf{p} \left(\frac{\partial f}{\partial t} \right)_{colli} d\mathbf{p} = \frac{\partial(\rho \mathbf{v})}{\partial t} \Big|_{colli}$. Combining these expressions from above, equation (7) is now summarized in terms of the physical variables ($\rho, \mathbf{v}, \mathbf{p}$) as

$$\frac{\partial(\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\mathbf{P} + \rho \mathbf{v} \mathbf{v}) + \mathbf{\Phi} + \frac{\partial(\rho \mathbf{v})}{\partial t} \Big|_{colli}. \quad (13)$$

The vector product $\mathbf{v} \mathbf{v}$, is also known as the Dyadic product which is given by a set of matrix functions with respect to the component velocities. Detailed manipulation of the Dyadic product can be found in many mathematics texts. In general, two kinds of external forces may act on a fluid: (i) the body forces which are proportional to the volume such as the gravitational, centrifugal, magnetic, and/or electric fields, and (ii) the surface forces which are proportional to area, for example, the static pressure drop due to viscous stresses. From a microscopic viewpoint, the pressure tensor, $\mathbf{P}$, is related to short-range interaction between the particles of system, whereas the body forces, $\mathbf{\Phi}$, pertains to the external forces in the system. Equation (13) describes a balance for the momentum density ($\rho \mathbf{v}$), the momentum flow, $(\mathbf{P} + \rho \mathbf{v} \mathbf{v})$ with a convective portion ($\rho \mathbf{v} \mathbf{v}$), and $\mathbf{\Phi}$, is a source of momentum. Some examples of the type of source terms employed in two different application scenarios are outlined in Table 1.

For a macro scale flow situation, the collision term is omitted and equation (13) reduces to the conventional form as

$$\begin{aligned} \frac{\partial(\rho \mathbf{v})}{\partial t} &= -\nabla \cdot (\mathbf{P} + \rho \mathbf{v} \mathbf{v}) + \mathbf{\Phi} \\ \rho \frac{d\mathbf{v}}{dt} &= -\nabla \cdot \mathbf{P} + \mathbf{\Phi} \end{aligned} \quad (14)$$

It is noted that the total pressure tensor can be further divided into a scalar hydrostatic part p , and a tensor part, Π .

Table 1. Examples of the source term, Φ , for two common applications

Field	Φ
Fluid mechanics [18]	$-\nabla \cdot \boldsymbol{\tau} + \rho \mathbf{g}$, the first term indicates the viscous force per unit volume where $\boldsymbol{\tau}$ is the stress tensor. The second term shows the gravitational force.
Electric flow [10]	$\rho \mathbf{z} \mathbf{E}$, where z is the total electric charge per unit mass in the control volume and E is the electric field acting on the conductor.

2.4. Energy Balance Equation

Associated with the flow of a carrier density, n , there is a corresponding energy flow, $\mathbf{w}$, such as the thermal energy and the drift energy term. By multiplying both sides of the basic BTE, i.e., equation (3), by $\mathbf{w}$ and integrating over the momentum space (product of mass and velocity) yields

$$\frac{\partial}{\partial t} \int \mathbf{w} f d\mathbf{p} = - \int \mathbf{w} (\mathbf{v}'' \cdot \nabla f) d\mathbf{p} + \int \mathbf{w} (\mathbf{F} \cdot \nabla_p f) d\mathbf{p} + \int \mathbf{w} \frac{\partial f_{\text{colli}}}{\partial t} d\mathbf{p} \quad (15)$$

Expanding the left hand side of equation (15), $\frac{\partial}{\partial t} \int \mathbf{w} f d\mathbf{p} = \mathbf{w} n = nm^* \mathbf{e} = \rho \mathbf{e}$, where e is the total energy per unit mass and $e = \frac{1}{2} \mathbf{v}^2 + \psi + u$. On the right hand side of equation (2.15), the spatial gradient (i.e., the first term) can be placed outside the integral to give, $\int \mathbf{w} (\mathbf{v}'' \cdot \nabla f) d\mathbf{p} = \nabla \cdot \int \mathbf{v}'' \mathbf{w} f d\mathbf{p} = \nabla \cdot \mathbf{J}_w$, where $\mathbf{J}_w$ represents the energy flux, defined here as $\mathbf{J}_w = \int \mathbf{v}'' \mathbf{w} f d\mathbf{p} = \rho \mathbf{e} \mathbf{v} + \mathbf{P} \cdot \mathbf{v} + \sum_{k=1}^n \psi_k \mathbf{J}_k + \mathbf{J}_q$, and $\rho \mathbf{e} \mathbf{v}$ is a convective term, $(\mathbf{P} \cdot \mathbf{v})$ is the mechanical work in the system, $\sum_{k=1}^n \psi_k \mathbf{J}_k$ equals to a potential energy flux due to diffusion, $\mathbf{J}_q$ is the heat flow. The second term on the right hand side of equation (15) can be expanded as:

$$\int \mathbf{w} (\mathbf{F} \cdot \nabla_p f) d\mathbf{p} = \mathbf{F} \cdot \int \mathbf{w} \nabla_p f d\mathbf{p} = \frac{\rho \mathbf{v} \mathbf{F}}{m^*} = \Phi \cdot \mathbf{v}$$

The collision term can also be expressed in terms of the energy dissipated Y , i.e.,

$$\int \mathbf{w} \frac{\partial f_{\text{colli}}}{\partial t} d\mathbf{p} = \frac{\partial(n\mathbf{w})}{\partial t} \Big|_{\text{colli}} = \frac{\partial \mathbf{Y}}{\partial t} \Big|_{\text{colli}}.$$

Combining the above expressions, the energy balance equation is now summarized that includes the collision terms as;

$$\frac{\partial(\rho \mathbf{e})}{\partial t} = -\nabla \cdot \mathbf{J}_w + \Phi \cdot \mathbf{v} + \frac{\partial \mathbf{Y}}{\partial t} \Big|_{\text{colli}} \quad (16)$$

To further understand the usage of the energy balance equation (i.e., equation 16), a minor digression is needed to demonstrate the presence of kinetic and potential energy terms. Multiplying the equation of motion [equation (13)] by $\mathbf{v}$, a balance equation for the kinetic energy can be obtained, i.e.,

$$\frac{\partial(\rho \mathbf{v})}{\partial t} \cdot \mathbf{v} = -[\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P})] \cdot \mathbf{v} + \Phi \cdot \mathbf{v} \Rightarrow \frac{\partial \left(\frac{1}{2} \rho \mathbf{v}^2 \right)}{\partial t} = -\nabla \cdot \left(\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \mathbf{P} \cdot \mathbf{v} \right) + \mathbf{P} : \nabla \mathbf{v} + \Phi \cdot \mathbf{v} \quad (17)$$

which is commonly known as the mechanical energy term. Note that the vector reduction could be performed on equation (14), as given by de Groot, [10]

$$[\nabla \cdot (\rho \mathbf{v} \mathbf{v})] \cdot \mathbf{v} = \left(\sum_{i=1}^3 \frac{\partial}{\partial x_i} \rho v_i v_j \right) v_j \quad i, j = 1, \dots, n = \sum_{i=1}^n \frac{\partial}{\partial x_i} \frac{1}{2} \rho v_i v_j^2 = \nabla \cdot \left(\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} \right)$$

and

$$\begin{aligned} -\nabla \cdot (P \cdot \mathbf{v}) + P : \nabla \mathbf{v} &= -\sum_{i=1}^n \frac{\partial}{\partial x_i} \left(\sum_{j=1}^n P_{ij} v_j \right) + \sum_{i=1}^n \sum_{j=1}^n P_{ij} \frac{\partial}{\partial x_i} v_j \quad i, j = 1, 2, 3, \dots, n \\ &= -\sum_{i=1}^n \sum_{j=1}^n \left(v_j \frac{\partial}{\partial x_i} P_{ij} + P_{ij} \frac{\partial}{\partial x_i} v_j \right) + \sum_{i=1}^n \sum_{j=1}^n P_{ij} \frac{\partial}{\partial x_i} v_j = -\sum_{j=1}^n v_j \sum_{i=1}^n \left(\frac{\partial}{\partial x_i} P_{ij} \right) = -(\nabla \cdot P) \cdot \mathbf{v} \end{aligned}$$

Similar simplifications can also be made on the rate of change of potential energy density, as shown below;

$$\begin{aligned} \frac{\partial(\rho \psi)}{\partial t} &= -\nabla \cdot \left(\rho \psi \mathbf{v} + \sum_{k=1}^n \psi_k J_k \right) - \sum_{k=1}^n J_k F_k + \sum_{k=1}^n \sum_{j=1}^r \psi_k \mathbf{v}_{kj} \cdot J_j \\ \frac{\partial(\rho \psi)}{\partial t} &= -\nabla \cdot (\rho \psi \mathbf{v} + \psi J) - \mathbf{J} \mathbf{F} \end{aligned} \quad (18)$$

The above results indicate that should $\sum_{k=1}^n \psi_k \mathbf{v}_{kj} = 0 \quad (j=1, \dots, r)$, this implies that the potential energy is conserved into the chemical reaction situation. $\sum_{k=1}^n J_k F_k = \mathbf{JF}$ which is referred to the source term where the particles interact with a force field such as the gravitational field or the electric charge experienced within an electric field. Adding equations (17) and (18), the combined effects become

$$\begin{aligned} \frac{\partial \left(\frac{1}{2} \rho \mathbf{v}^2 \right)}{\partial t} + \frac{\partial (\rho \psi)}{\partial t} &= -\nabla \cdot \left(\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \mathbf{P} \cdot \mathbf{v} \right) + P : \nabla \mathbf{v} + \Phi \cdot \mathbf{v} - \nabla \cdot (\rho \psi \mathbf{v} + \psi J) - \mathbf{JF} \\ \frac{\partial \rho \left(\frac{1}{2} \mathbf{v}^2 + \psi \right)}{\partial t} &= -\nabla \cdot \left(\frac{1}{2} \rho \mathbf{v}^2 \mathbf{v} + \mathbf{P} \cdot \mathbf{v} + \rho \psi \mathbf{v} + \psi J \right) + \mathbf{P} : \nabla \mathbf{v} - \mathbf{JF} + \Phi \cdot \mathbf{v} \end{aligned}$$

From the energy balance equation (16) and substituting for these derived functions, one obtains working form of the energy equation which gives in terms of the internal energy, u , heat flux, J_q , and the associated source and collision terms;

$$\begin{aligned} \frac{\partial (\rho e)}{\partial t} &= -\nabla \cdot \mathbf{J}_w + \Phi \cdot \mathbf{v} + \left. \frac{\partial (\rho e)}{\partial t} \right|_{\text{colli}} \\ \therefore \frac{\partial (\rho u)}{\partial t} &= -\nabla \cdot (\rho u \mathbf{v} + \mathbf{J}_q) - \mathbf{P} : \nabla \mathbf{v} + \mathbf{JF} + \left. \frac{\partial \mathbf{Y}}{\partial t} \right|_{\text{colli}} \end{aligned} \quad (19)$$

It is noted that $\rho u \mathbf{v} + \mathbf{J}_q$ is the energy flow due to convection and thermal energy transfers which contributes to the internal energy change, while the vectors $\mathbf{P} : \nabla \mathbf{v} + \mathbf{JF}$ is deemed as the source term associated with the internal energy.

Further simplification of the energy balance equation (19) leads to its concise form of having only 4 terms and it is applicable to micro or thin layer flow of electrons or phonons;

$$\begin{aligned} \frac{\partial (\rho u)}{\partial t} &= -\nabla \cdot (\rho u \mathbf{v} + \mathbf{J}_q) - \mathbf{P} : \nabla \mathbf{v} + \mathbf{JF} + \left. \frac{\partial \mathbf{Y}}{\partial t} \right|_{\text{colli}} \\ \rho \frac{du}{dt} &= -\nabla \cdot \mathbf{J}_q + \Psi + \left. \frac{\partial \mathbf{Y}}{\partial t} \right|_{\text{colli}} \end{aligned} \quad (20)$$

It is noted that the last term of the right hand side indicates the rate of change of energy as a result of collisions of the molecular particles such as electrons or phonons. Collision occurs by four processes in the micro-sublayer, i.e., (i) the increase in carrier kinetic energy due to interactions between electrons and holes or phonons, (ii) the heat dissipation arising from electrons or phonons interaction with the lattice vibrations, (iii) the heat dissipation by

the electrons to the holes and vice versa, and (iv) the heat generation arising from the recombination and generation of the molecular particles.

Equation (20) could be extended to macro analysis (adsorption cooling systems) by simply dropping the collision term which has its form known conventionally as the energy balance equation;

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q + \Psi \quad (21)$$

Another name for equation (20) is the equation of internal energy, as it is known in some texts [10, 17].

At this juncture, it is perhaps appropriate to elaborate these terms in terms of some common application examples. For example, the source term Ψ , in equilibrium and irreversible thermodynamics has two parts: (i) One aspect is the reversible rate of the internal energy attributed by effects of compression and (ii) the other is the irreversible rate of internal energy contributed by any dissipative effect. For most engineering applications involving real gasses, the internal energy is expressed in terms of the fluid temperature and the heat capacity. In such cases, the internal energy u may be considered as a function of v and T , and assuming constant specific heats, i.e.,

$$du = \left(\frac{\partial u}{\partial v} \right)_T dv + \left(\frac{\partial u}{\partial T} \right)_v dT = \left[-p + T \left(\frac{\partial p}{\partial T} \right)_v \right] dv + c_v dT$$

and the substantial derivative term becomes

$$\rho \frac{du}{dt} = \left[-p + T \left(\frac{\partial p}{\partial T} \right)_v \right] \rho \frac{dv}{dt} + \rho c_v \frac{dT}{dt} = \left[-p + T \left(\frac{\partial p}{\partial T} \right)_v \right] \nabla \cdot \mathbf{v} + \rho c_v \frac{dT}{dt}$$

Invoking the energy balance equation (21), it becomes

$$\rho c_v \frac{dT}{dt} = -\nabla \cdot \mathbf{J}_q - T \left(\frac{\partial p}{\partial T} \right)_{\hat{v}} (\nabla \cdot \mathbf{v}) + \mathbf{JF} \quad (22)$$

Should the gas be assumed ideal, then $\left(\frac{\partial p}{\partial T} \right)_{\hat{v}} = \frac{p}{T}$ and the second term of right hand side equation (22) becomes zero, i.e.,

$$\rho c_v \frac{dT}{dt} = -\nabla \cdot \mathbf{J}_q + \mathbf{JF} \quad (23)$$

In another example, the internal energy u is considered to be a function of p and T , as in a real gas. Hence,

$$h = u + p v \Rightarrow \frac{dh}{dt} = \frac{du}{dt} + p \frac{dv}{dt} + v \frac{dp}{dt}.$$

Invoking the constant pressure assumption, it can be shown that $\rho \frac{dh}{dt} = \rho c_p \frac{dT}{dt}$.

$$\frac{dh}{dt} = \frac{du}{dt} + p \frac{dv}{dt} \Rightarrow \rho \frac{dh}{dt} = \rho c_p \frac{dT}{dt} \quad (24)$$

From equation (24) and substituting for the energy balance equation for $\rho \frac{du}{dt}$, it can be demonstrated that the substantial derivative for the enthalpy, $\rho c_p \frac{dT}{dt}$, comprise only two terms, i.e.,

$$\begin{aligned} \rho c_p \frac{dT}{dt} &= \rho \frac{du}{dt} + \rho p \frac{dv}{dt} \\ \rho c_p \frac{dT}{dt} &= -\nabla \cdot \mathbf{J}_q - p \nabla \cdot \mathbf{v} + \mathbf{JF} + \rho p \frac{dv}{dt} \end{aligned} \quad (25)$$

From the continuity equation (11) we show that

$$\rho p \frac{dv}{dt} = p \nabla \cdot \mathbf{v}$$

Equation (25) is written as,

$$\rho c_p \frac{dT}{dt} = -\nabla \cdot \mathbf{J}_q + \mathbf{JF} \quad (26)$$

The right hand side of equation (26) comprises (i) the heat flux term, $\mathbf{J}_q$ and (ii) the energy source term $\mathbf{JF}$. Table 2 tabulates three scenarios where the source energy could be elaborated. For example, in the study of adsorption, where many chapters of the thesis are devoted, the source energy is derived by considering adsorbate mass and the isosteric heat of adsorption, i.e., $\dot{q} \Delta H_{ads}$. Other examples in fluid mechanics and electrically powered semi-conductors are also explained.

It should be emphasized that equations (21-26) are valid for macro-scale devices simulation. However, for the analysis of sub-micron devices, the collision terms, which are provided in equation (20), must be included.

Table 2. Explanation of energy source in different fields

Field	Source of energy JF
Fluid mechanics	$\tau : \nabla v$; This term indicates the irreversible internal energy increase due to viscous dissipation.
Electrical	$\rho_{\text{elect}} J^2$; this is the Joulean heat.
Chemical/Adsorption	$\dot{q} \Delta H_{\text{ads}}$, where $\dot{q}$ is the adsorption or desorption rate and ΔH_{ads} is the isosteric enthalpy of adsorption.

2.5. Summary of Section 2

In section 2, the conservation laws, i.e., mass, momentum and energy are derived from the transportation of molecules using the Boltzmann Transport Equation (BTE). The thermodynamic framework for describing the conservation laws is applicable to both the macro-scale and micro-scale systems. This approach differs from the control volume approach of de Groot and Mazur [10] Bird, R. B. [18], etc., where the Gauss theorem was employed. The latter approach could not embrace the collision terms, as what has been shown here using the BTE approach. For thin films or micro-scale systems, the collisions of electrons with electrons, electrons with holes, holes with holes are deemed to have significant dissipative effects, a source of irreversibility as quantified in the next section.

3. CONSERVATION OF ENTROPY

The change of entropy of a system relates not only to the entropy (s) crossing the boundary between the system and its surroundings, but also to the entropy produced or generated by processes taking place within the system. Processes inside the system may be either reversible or irreversible [19]. The reversible process may occur during the transfer of entropy from one portion to another of the interior without entropy generation. On the other hand the irreversible process invariably leads to entropy generation inside the system.

The entropy per unit mass is a function of the internal energy u , the specific volume v and the mass fractions c_k i.e. $s = s(u, v, c_k)$. In equilibrium the total differential of s is given by the Gibbs relation [10]

$Tds = du + pdv - \sum_{k=1}^n \mu_k dc_k$, where p is the equilibrium pressure and μ_k is the thermodynamic or chemical potential of component k .

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{dv}{dt} - \sum_{k=1}^n \mu_k \frac{dc_k}{dt} \quad (27)$$

From mass balance we get

$$\frac{\rho P}{T} \frac{d\nu}{dt} = \frac{P}{T} \nabla \cdot \mathbf{v} + \frac{P}{\rho T} \frac{\partial \rho}{\partial t} \Big|_{\text{colli}}$$

The mass balance equation, equation (7), is written as,

$$\frac{d\rho_k}{dt} = -\rho_k \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{J}_k + \frac{\partial \rho_k}{\partial t} \Big|_{\text{colli}}$$

where $\mathbf{J}_k (= \rho_k (\mathbf{v}_k - \mathbf{v}))$ is the diffusion flow of component k defined with respect to the ‘barycentric motion’. Defining the component mass fractions c_k as

$$c_k = \frac{\rho_k}{\rho} \quad \text{so that} \quad \sum_{k=1}^n c_k = 1,$$

and equation (7) can be simplified as

$$\begin{aligned} \frac{d\rho_k}{dt} &= -\rho_k \nabla \cdot \mathbf{v} - \nabla \cdot \mathbf{J}_k + \frac{\partial \rho_k}{\partial t} \Big|_{\text{colli}} \\ \rho \frac{dc_k}{dt} &= -\nabla \cdot \mathbf{J}_k \end{aligned}$$

From equation (27) we have,

$$\begin{aligned} T \frac{ds}{dt} &= \frac{du}{dt} + p \frac{d\nu}{dt} - \sum_{k=1}^n \mu_k \frac{dc_k}{dt} \\ \rho \frac{ds}{dt} &= \frac{\rho}{T} \frac{du}{dt} + \frac{\rho p}{T} \frac{d\nu}{dt} - \sum_{k=1}^n \frac{\rho \mu_k}{T} \frac{dc_k}{dt} \\ &= -\nabla \cdot \left(\frac{\mathbf{J}_q - \sum_{k=1}^n \mu_k \mathbf{J}_k}{T} \right) - \frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^n \mathbf{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} \right) + \frac{1}{T} \mathbf{J} \mathbf{F} + \frac{1}{T} \frac{\partial \mathbf{Y}}{\partial t} \Big|_{\text{colli}} + \frac{P}{\rho T} \frac{\partial \rho}{\partial t} \Big|_{\text{colli}} \end{aligned} \quad (28)$$

where $\mathbf{J}_k (= \rho_k (\mathbf{v}_k - \mathbf{v}))$ is the diffusion flow of component k defined with respect to the ‘barycentric motion’.

From equation (28), one observes that the entropy flow is given by two terms:

$$\mathbf{J}_s = \frac{1}{T} \left(\mathbf{J}_q - \sum_{k=1}^n \mu_k \mathbf{J}_k \right), \quad (29)$$

and the entropy source strength by

$$\sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^n \mathbf{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} \right) + \frac{1}{T} \mathbf{JF} + \frac{1}{T} \frac{\partial \mathbf{Y}}{\partial t} \Big|_{\text{colli}} + \frac{P}{\rho T} \frac{\partial \rho}{\partial t} \Big|_{\text{colli}} \quad (30)$$

$$\Rightarrow \sigma = \sigma_{\text{irreversible}} + \sigma_{\text{collision}}$$

The expression of entropy generation (equation 30) provides the key to irreversible thermodynamics. The first two terms indicate entropy generation as a result of irreversible transport processes whilst the third term represents entropy increase due to source applied to the system. The last two terms on the right hand side entropy increase due to (1) heat transfers from the other systems via collision processes, (2) free energy changes associated with recombination and generation of electron-hole pairs.

From equation (28) the general form of entropy balance equation is written as,

$$\frac{dS}{dt} = \nabla \cdot \mathbf{J}_s + \sigma \quad (31)$$

It is noted here that equation (31) has a similar form to the expression for total entropy, i.e.,

$$\frac{dS}{dt} = \left(\frac{dS}{dt} \right)_{\text{rev}} + \left(\frac{dS}{dt} \right)_{\text{irr}}, \quad (32)$$

Comparing the first term of the right hand side of both equations, the reversible entropy flux is $\left[\left(\frac{dS}{dt} \right)_{\text{rev}} = \nabla \cdot \mathbf{J}_s \right]$. This is the net sum of quantities carried into the system by transfers of matter, plus the net sum of quantities of entropy carried in by the transfer of heat.

The second term yields $\left[\left(\frac{dS}{dt} \right)_{\text{irr}} = \sigma \right]$, which is the entropy generation rate produced by irreversible processes taking place inside the system. Table 3 shows some common examples of the irreversible processes (hence the internal entropy generation) of common engineering processes.

The details of the BTE for analyzing the mass, momentum, energy and entropy conservation equations in macro and micro scales have been discussed in this section. This section concludes with the summary of all conservation equations as shown in Table 4 using Gauss and BTE approaches so that these two methods could be compared.

Table 3. Example of processes leading to the irreversible production of entropy

Entropy generation $\sigma = \left(\frac{dS}{dt} \right)_{irr}$		Equations
Dissipation	Mechanical energy (due to friction or viscosity)	$\frac{1}{T} \left(\frac{dF}{dt} \right)$ (Richard et. al., 1948), where $\frac{dF}{dt}$ is the rate at which work is done against force or viscous force.
	Electrical energy (by the passage of electric current through a resistance)	$\frac{I^2 R}{T}$, where I is the flow of current through a resistance R in conductor or semiconductor at temperature T.
Irreversible heat flow in a conducting medium		$\mathbf{q} \cdot \nabla \left(\frac{1}{T} \right)$. Here $\mathbf{q} (= K \nabla T)$ is the vector which expresses the rate of heat flow. The final expression is $\left(\frac{dS}{dt} \right)_{irr} = \frac{k \nabla T \nabla T}{T^2}$.
Free expansion of gas without absorbing heat [19]		The approximate expression for the irreversible increase in entropy accompanying the transfer of any particle element of the gas, consisting of dN moles, from pressure P_1 to P_2 is $dS_{irr} = R dN \log \left(\frac{P_1}{P_2} \right)$
Chemical reaction [19]		$\left(\frac{dS}{dt} \right)_{irr} = R \left(\log K_p - \log \frac{f_c^c f_D^d \dots}{f_A^a f_B^b \dots} \right) \frac{dx}{dt}$, where K_p is equilibrium constant at temperature T , R is the gas constant, $f_A f_B \dots f_C f_D \dots$ etc., are the actual instantaneous values of the fugacities, $a, b, \dots, c, d, \dots$ are the number of moles and $\frac{dx}{dt}$ is a factor.
Collisions (electron and hole transport in submicron semiconductor or thin film devices)		$\left(\frac{dS}{dt} \right)_{colli} = \frac{1}{T} \frac{\partial Y}{\partial t} \Big _{colli} + \frac{P}{\rho T} \frac{\partial \rho}{\partial t} \Big _{colli}$, where the first term of right hand side indicates the collision due to change of energy between electrons-electrons, electrons-holes, holes-holes interactions, and the second term defines the collision because of change of carrier density.

Table 4. Summary of the conservation equations

	Gauss theorem approach (Appendix)	Boltzmann Transport Equation approach
	$\int_V \nabla \cdot \mathbf{X} dV = \int_{\Omega} \mathbf{X} \cdot \vec{n} d\Omega = \int_{\Omega} \mathbf{X} \cdot d\Omega$	$\frac{\partial f}{\partial t} = - \left(\frac{\partial f}{\partial t} \right)_{drift} + \frac{\partial f_{colli}}{\partial t}$
Mass	$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v})$	$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) + \frac{\partial \rho}{\partial t} \Big _{colli}$
Momentum	$\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}) + \Phi$	$\frac{\partial (\rho \mathbf{v})}{\partial t} = -\nabla \cdot (\mathbf{P} + \rho \mathbf{v} \mathbf{v}) + \Phi + \frac{\partial (\rho \mathbf{v})}{\partial t} \Big _{colli}$
Energy	$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q + \Psi$	$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{J}_q + \Psi + \frac{\partial Y}{\partial t} \Big _{colli}$
Entropy	$\rho \frac{ds}{dt} = -\nabla \cdot \left(\frac{\mathbf{J}_q - \sum_{k=1}^n \mu_k \mathbf{J}_k}{T} \right)$ $- \frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^n \mathbf{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} \right)$ $+ \frac{1}{T} \mathbf{J} \mathbf{F}$	$\rho \frac{ds}{dt} = -\nabla \cdot \left(\frac{\mathbf{J}_q - \sum_{k=1}^n \mu_k \mathbf{J}_k}{T} \right) - \frac{1}{T^2} \mathbf{J}_q \cdot \nabla T$ $- \frac{1}{T} \sum_{k=1}^n \mathbf{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} \right)$ $+ \frac{1}{T} \mathbf{J} \mathbf{F} + \frac{1}{T} \frac{\partial Y}{\partial t} \Big _{colli} + \frac{P}{\rho T} \frac{\partial \rho}{\partial t} \Big _{colli}$

This section is followed by the detailed thermodynamic modeling of adsorption cooling system (section 4), bulk thermoelectric module as examples of macro scale device, and thin film superlattice thermoelectric for micro scale system (section 5) to understand their thermal transport phenomena.

4. ADSORPTION COOLING

The physical adsorption process occurs mainly within the pores of adsorbent and at the external adsorbent surface, and is determined by its adsorption isotherms, thermodynamic property surfaces of energy and entropy, heats of adsorption and adsorption kinetics. In a physisorption, the adsorbed phase is held near to the pores of the adsorbent by the existence of van der Waals forces as shown in Figure 3.

The development of adsorption cooling system is based on the thermodynamic property surfaces of adsorbent-refrigerant system and the thermal compression of natural working refrigerants like water or alcohols and lies in its ability to operate with motive energy derived from fairly low temperature sources such as waste heat in process industries or sun light which indicates the adsorption process as an avenue for avoiding the use of ozone depleting substances [20]. The principal advantage of adsorption chillers (ADC) is that it is amenable to regenerative use of adsorption heat. Adsorption system incorporates no mechanical moving

parts and generates no noise or vibration. A certain number of adsorbent-adsorbate pairs have been tested theoretically and experimentally for evaluating the performances of ADCs. These are silica gel-water, zeolite-water, silica gel-methanol, activated carbon-methanol, activated charcoal-NH₃, zeolite-CO₂, etc. Recently, a new family of composite sorbents called Selective Water Sorbents (SWSs) has been presented for sorption cooling and heat pumping [21].

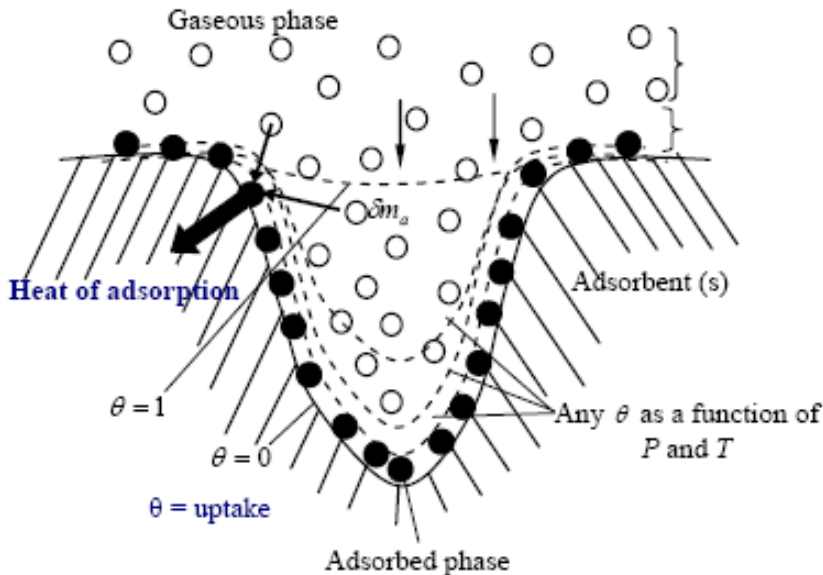


Figure 3: The schematic diagram of a single component adsorbent + adsorbate system for any uptake, x as a function of pressure, P and temperature, T . The effects of gaseous phase are also shown here.

It is based on a porous host matrix (silica, alumina, etc.) and an inorganic salt (CaCl₂, LiBr, MgCl₂, MgSO₄, Ca(NO₃)₂, etc.) impregnated inside pores [22, 23]. Building from the previous works, this article presents both the steady-state and dynamic behaviors of SWS-1L in a two-bed solid sorption cooling system using a transient distributed model. These results are compared with those of commercial adsorption cooler based on Fuji RD type silica gel such that a device for new generation of cooling can be enlightened. Both the heat and mass transfer resistances of the adsorption heat exchanger as well as the temporal energetic behavior in the evaporator and condenser are also taken into account in the present model. In this section, we also elucidated the effects of the isosteric cooling and heating times as well as the total cycle time on the system performances, and demonstrate that the current cooler design tends at optimum conditions.

4.1. Description of Adsorption Cooling Model

The adsorption cooling system which utilizes the adsorbent-adsorbate characteristics and produces the useful cooling effects at the evaporator by the amalgamation of “adsorption-triggered-evaporation” and “desorption-resulted-condensation” was described elsewhere [24-26]. Figure 4 shows the schematic layout of the adsorption chiller.

It comprises the evaporator, the condenser and the reactors or adsorbent beds. For continuous cooling operation, firstly a low-pressure refrigerant (hence water) is evaporated at the evaporator due to external cooling load (or chilled water) and is adsorbed into the solid adsorbent located in the adsorber.

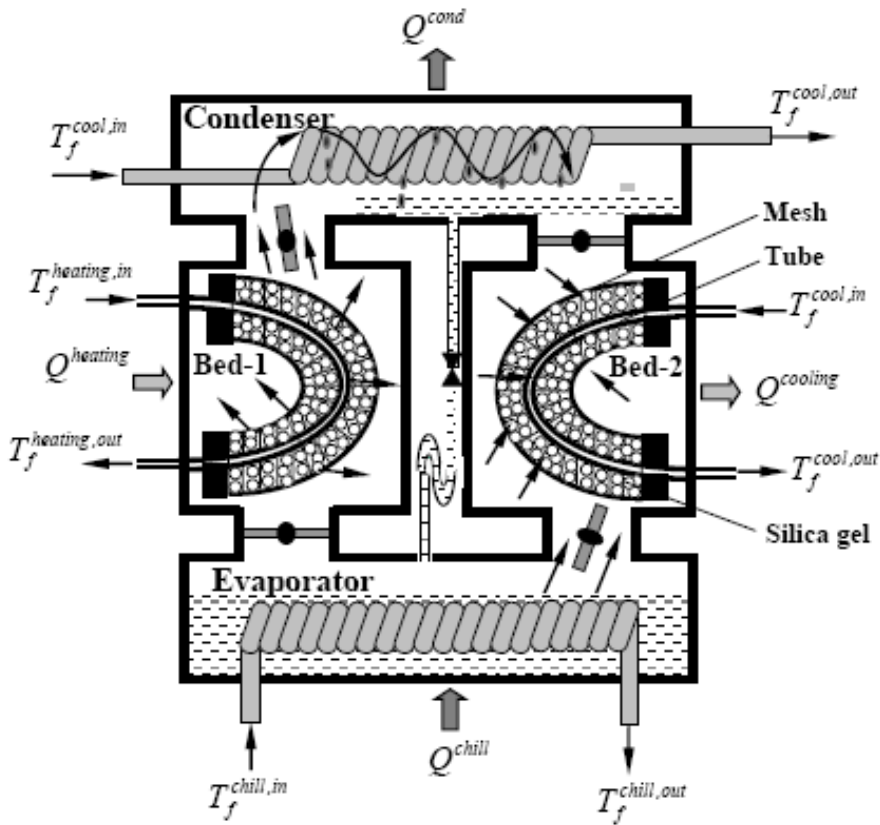


Figure 4: Schematic of a two-bed adsorption chiller.

The process of adsorption results in the liberation of heat of adsorption at the adsorber providing a useful heat energy output and a cooling effect in the condenser/evaporator heat exchanger. Secondly, the adsorbed bed is heated by the external heat source and the refrigerant is desorbed from the adsorbent and goes to the condenser for condensation by pumping heat through the environment. The condensate (refrigerant) is refluxed back to the evaporator via a pressure reducing valve for maintaining the pressure difference between the condenser and the evaporator. Pool boiling is affected in the evaporator by the vapor uptake at the adsorber, and thus completing the refrigeration close loop or cycle. These phenomena are expressed mathematically using the mass and energy balances between major components of the adsorption chiller system.

Evaporator

The energy balance becomes

$$(\rho c_p)_{eff}^{evap} \frac{\partial T^{evap}}{\partial t} \left(\frac{d_{evap,o}^2 - d_{evap,i}^2}{4} \right) = \lambda^{evap} \frac{\partial^2 T^{evap}}{\partial z^2} \left(\frac{d_{evap,o}^2 - d_{evap,i}^2}{4} \right) - d_{evap,i} h_{evap} (T^{rvap} - T^{chill}) \quad (33)$$

where $(Mc_p)_{eff}^{evap}$ is the sum of all mass capacities of the evaporator. The first term on the right hand side defines the latent heat of evaporation that goes to adsorption bed, the second term is the enthalpy of liquid condensate and the last term denotes the cooling capacity of evaporator, which rises from the cooling of chilled water. Temperature boundary conditions

$$\text{are } \left. \frac{\partial T^{evap}}{\partial z} \right|_{z=0} = 0 \text{ and } \left. \frac{\partial T^{evap}}{\partial z} \right|_{z=L^{cond}} = 0, \text{ respectively.}$$

The energy balance equation on the chilled water control volume is written as

$$\rho_f^{chill} c_{p,f}^{chill} \frac{\partial T^{chill}}{\partial t} = -u_f^{chill} \rho_f^{chill} c_{p,f}^{chill} \frac{\partial T^{chill}}{\partial z} + \lambda_f^{chill} \frac{\partial^2 T^{chill}}{\partial z^2} - \frac{(UA)_{chill}}{V_f^{chill}} (T^{chill} - T^{evap}) \quad (34)$$

Hence the terms, $\frac{dx_{ads}^{bed}}{dt}$ and $\frac{dx_{des}^{bed}}{dt}$ indicate the adsorption rate and the desorption rate.

The boundary conditions of the chilled water tube are $T^{chill}(z=0, t) = T^{chill,in}$ and $\frac{\partial T^{chill}}{\partial z}(z=L^{tube}, t) = 0$.

Adsorption Isotherms and Kinetics

The adsorption/desorption rate is calculated from the knowledge of adsorption equilibrium and kinetics and is given by the conventional linear driving force (LDF) equation [27]

$$\frac{dx}{dt} = \frac{15D_{so}}{R_p^2} e^{-\frac{E_a}{RT}} \{x^* - x\}, \quad (35)$$

where D_{so} defines a pre-exponential factor of the efficient water diffusivity in the adsorbent, E_a represents the activation energy, R is the universal gas constant and R_p is the average radius of the adsorbent grains. Kinetic data were taken from [28, 29]. Hence the adsorption uptake at equilibrium condition is expressed as a function of pressure (P) and temperature (T). The authors have measured the isotherms of water adsorption on silica gel of type RD, type A [30] and on SWS-1L [31, 32]. These experimentally measured data are fitted using the Tóth's equation [33], i.e.,

$$x^* = \frac{x_m K_o \cdot \exp\{\Delta H_{ads}/(R \cdot T)\} \cdot P}{[1 + \{K_o \cdot \exp(\Delta H_{ads}/(R \cdot T)) \cdot P\}^{t_1}]^{1/t_1}}, \quad (36)$$

where x^* is the adsorbed adsorbate at equilibrium conditions, x_m denotes the monolayer capacity, ΔH_{ads} the isosteric enthalpies of adsorption, K_o the pre-exponential constant, and t_1 is the dimensionless Tóth's constant. These values are furnished in Table 4.

Table 4. Adsorption isotherms of silica gel-water systems

Type	K_o (Pa ⁻¹)	ΔH_{ads} (kJ/kg)	x_m (kg kg ⁻¹)	t_1
RD (Tóth isotherm)	7.3×10^{-13}	2800	0.4	8
SWS-1L (Tóth isotherm)	2×10^{-12}	2760	0.8	1.1
Type	a	b	$c \times 10^9$	ΔF kJ/mol
SWS-1L (polynomial equation)	2.83378 5.80313	-3.0133×10^{-4} -0.00119	7.46702 69.9054	1-5 5-9

The most significant difference between these two adsorbents (silica type RD and SWS-1L) lies in their water vapor uptake characteristics. From Table 4, one could observe that the water vapor uptake capacity of SWS-1L is higher than that of type RD. On the other hand, the adsorption uptake of water vapor on SWS-1L is expressed in terms of mole/mole by the polynomial equation, i.e., $x^* = \exp(a + b\Delta F + c\Delta F^2)$ [28, 32], where ΔF indicates the Polanyi adsorption potential and is represented by $\Delta F = -RT \ln(P/P_s)$. The values of the adjustable coefficients a, b and c that provide the best approximation of the two segments of the temperature-independent curve of sorption of water by SWS-1L composite [28, 32] are also furnished in Table 4. It should also be noted here that the values of D_{so} , E_a and R_p are found same for both RD silica gel-water and SWS-1L-water systems, i.e., the adsorption/desorption rate for both systems are nearly same but the difference between the two systems are occurred due to their different uptake capacities.

Bed

As the evaporated refrigerant is associated onto the solid adsorbent by the flow of cooling fluid at ambient conditions during adsorption period, and the desorbed refrigerant is dissociated from the solid adsorbent by the flow of heating fluid during desorption period. The heat energy is exchanged between cooling/heating fluid and the adsorption bed. A schematic of the adsorption bed with heat exchanger is shown in Figure 1. The energy balance for the heat transfer fluid is given by

$$\frac{\partial T_f^j}{\partial t} = -u_f^j \frac{\partial T_f^j}{\partial z} + \frac{\lambda_f^j}{\rho_f^j c_{p,f}^j} \frac{\partial^2 T_f^j}{\partial z^2} - \frac{h_{f-m}^j A_f^j}{\rho_f^j c_{p,f}^j V_f^j} (T_f^j - T_m), \quad (37)$$

where u defines the flow rate of cooling/heating fluid, j indicates heating or cooling for desorption or adsorption, h_{f-m}^j represents the heat transfer coefficient. The boundary condition for fluid flow becomes

$$\text{during adsorption: } T_f^j(z=0, t) = T_f^{cool, in} \text{ and } \frac{\partial T_f^j}{\partial z}(z = L^{tube}, t) = 0,$$

$$\text{during desorption: } T_f^j(z=0, t) = T_f^{hot, in} \text{ and } \frac{\partial T_f^j}{\partial z}(z = L^{tube}, t) = 0.$$

The energy balance of the metal tube that contains heat transfer fluid is written as

$$\begin{aligned} \frac{\partial T^{tube}}{\partial t} = & \frac{\lambda^{tube}}{\rho^{tube} c_p^{tube}} \frac{\partial^2 T^{tube}}{\partial z^2} - \frac{h_{f-m}^j A^{tube}}{\rho^{tube} c_p^{tube} V^{tube}} (T^{tube} - T_f^j) - \frac{h_{m-s} A^{tube}}{\rho^{tube} c_p^{tube} V^{tube}} (T^{tube} - T^{sg}) \\ & - \zeta \frac{A^{tube}}{\rho^{tube} c_p^{tube} V^{tube}} \lambda^{fin} \frac{\partial T^{fin}}{\partial r} \end{aligned} \quad (38)$$

Here the value of ζ is equal to 1 when any fin is attached with the tube, otherwise $\zeta = 0$. The boundary conditions of the heat exchanger tube inside the adsorber are $\frac{\partial T^{tube}}{\partial z}(z=0, t) = 0$ and $\frac{\partial T^{tube}}{\partial z}(z = L^{tube}, t) = 0$, respectively.

The fin thickness is very small and the heat transfer in the fin is assumed to be one dimensional in the radial direction. The energy balance equation of the fin is given by

$$\frac{\partial T^{fin}}{\partial t} = \frac{\lambda^{fin}}{\rho^{fin} c_p^{fin}} \frac{\partial \left(\frac{\partial T^{fin}}{\partial r} r \right)}{r \partial r} - \frac{h_{fin-s} A^{fin}}{\rho^{fin} c_p^{fin} V^{fin}} (T^{fin} - T^{sg}). \quad (39)$$

The boundary conditions are $T^{fin}(r = r_o) = T^{tube}$ and $\frac{\partial T^{fin}}{\partial r}(r = r^{fin}) = 0$.

The energy balance of the adsorbent control volume can be written as (heat flow is considered both in r and z direction)

$$\begin{aligned} (\rho^{sg} c_p^{sg} + \rho^g x c_p^a) \frac{\partial T^{sg}}{\partial t} = & \nabla \cdot (\lambda^{eff} \nabla T^{sg}) + \rho^{sg} \Delta H_{ads} \frac{dx}{dt} - \frac{h_{fin-s} A^{fin}}{V^{fin}} (T^{fin} - T^{sg}) \\ & - \frac{h_{m-s} A^{tube}}{V^{tube}} (T^{tube} - T^{sg}) \end{aligned} \quad (40)$$

where the specific heat capacity of the adsorbed phase is given by [34]

$$c_p^a = c_p^l + \Delta H_{ads} \left\{ \frac{1}{T^{sg}} - \frac{1}{v^g} \frac{\partial v^g}{\partial T^{sg}} \right\} - \frac{\partial(\Delta H_{ads})}{\partial T^{sg}}. \text{ The first term in the right hand side}$$

indicates the specific heat capacity at liquid phase, and the other terms occur due to the non ideality of gaseous phase, which incorporate two additional inputs from the properties of adsorbent + adsorbate system, namely the ΔH_{ads} and the isotherms (P - T - x) data [35]. On the other hand, the effective thermal conductivity of the adsorbed phase is

$$\lambda^{eff} = \lambda^g \left/ \left(\phi + 2/3 \frac{\lambda^g}{\lambda^{sg}} \right) \right. [36], \text{ where } \phi \text{ indicates the porosity of bed. Here } \lambda^{eff} \text{ is defined}$$

as the total thermal conductivity of adsorbent particles stacked together in the adsorber. The

$$\text{boundary condition at radial direction becomes } -\lambda^{eff} \frac{\partial T^{sg}}{\partial r} \bigg|_{r=r_o} = h_{m-s} (T^{tube} - T^{sg}) \text{ and}$$

$$\frac{\partial T^{sg}}{\partial r} \bigg|_{r=r_{fin}} = 0.$$

Condenser

After desorption, the desorbed refrigerant is delivered to the condenser as latent heat and this amount of heat is pumped to the environment by the flow of external cooling fluid. In the modelling, we assume that the condenser tube bank surface is able to hold a certain maximum amount of condensate. Beyond this the condensate would flow into the evaporator via a U-bend tube. This ensures that the condenser and the desorber are always maintained at the saturated pressure of the refrigerant. The energy balance of the condenser is expressed as

$$(\rho c_p)_{eff}^{cond} \frac{\partial T^{cond}}{\partial t} \left(\frac{d_{con,o}^2 - d_{con,i}^2}{4} \right) = \lambda^{cond} \frac{\partial^2 T^{cond}}{\partial z^2} \left(\frac{d_{con,o}^2 - d_{con,i}^2}{4} \right) + d_{con,i} h_{con,i} (T^{cond} - T^{cool}) \quad (41)$$

where $(Mc_p)_{eff}^{cond}$ is the sum of all mass capacities of the condenser. The first term on the right hand side defines the latent heat of condensation, the second term is the enthalpy of liquid condensate and the last term denotes the sensible cooling of the condenser.

$$\text{Temperature boundary conditions are } \frac{\partial T^{cond}}{\partial z} \bigg|_{z=0} = 0 \text{ and } \frac{\partial T^{cond}}{\partial z} \bigg|_{z=L^{cond}} = 0.$$

The energy balance equation of the cooling water control volume is written as

$$\rho_f^{cool} c_{p,f}^{cool} \frac{\partial T_f^{cool}}{\partial t} = -u_f^{cool} \rho_f^{cool} c_{p,f}^{cool} \frac{\partial T^{cool}}{\partial z} + \lambda_f^{cool} \frac{\partial^2 T^{cool}}{\partial z^2} - \frac{(UA)^{cool}}{V_f^{cool}} (T^{cool} - T^{cond}) \quad (42)$$

The boundary conditions of the cooled water tube are $T^{cool}(z=0, t) = T^{cool, in}$ and $\frac{\partial T^{cool}}{\partial z}(z = L^{tube}, t) = 0$.

Mass Balance

The mass balance of refrigerant in the adsorption chiller is expressed by

$$\frac{dM_{ref}}{dt} = -M^{sg} \left\{ \frac{dx_{des}^{bed}}{dt} + \frac{dx_{ads}^{bed}}{dt} \right\}, \quad (43)$$

where M^{sg} is the mass of adsorbents packed in each of the two adsorbent beds, and M_{ref} is the mass of refrigerant in liquid phase.

The roles of the beds (containing the adsorbent) are refreshed by switching which is performed by reversing the direction of the cooling and the heating fluids to the designated sorption beds and similarly, the evaporator and condenser are also switched to the respective adsorber and desorber.

It is noted that during switching interval, no mass transfers occur between the hot bed and the condenser or the cold bed and the evaporator.

The cycle average cooling capacity Q^{chill} , heating capacity $Q^{heating}$ and COP are, respectively calculated as

$$Q^{chill} = \rho_f^{chill} u_f^{chill} A_f^{tube, chill} c_{p,f}^{chill} \int_0^{t_{cycle}} \frac{T_f^{chill, in} - T_f^{chill, out}}{t_{cycle}} dt, \quad (44)$$

$$Q^{heating} = \rho_f^{heating} u_f^{heating} A_f^{tube, bed} c_{p,f}^{heating} \int_0^{t_{cycle}} \frac{T_f^{heating, in} - T_f^{heating, out}}{t_{cycle}} dt, \quad (45)$$

$$\text{and } COP = \frac{Q^{chill}}{Q^{heating}}. \quad (46)$$

4.2. Discussion

The adsorption bed design incorporates a circular finned tube heat exchanger. The values for the parameters used in the present model are furnished in Table 5. Figure. 5 features the temperature histories at the outlets of the type RD silica gel (red lines in Figure 5) and SWS-1L based chiller system (thick black lines in Figure 5) and these are compared with experimental data (thick blue lines and circles) of RD silica gel and water based adsorption chiller. Due to the positioning of the temperature sensors, the experimentally measured outlet temperatures are affected by the time constant of downstream mixing valves in the pipeline. It

is evident that our present simulation results exhibit a sufficiently good agreement with the experimental data stemming from a distributed parameter model. Figure 5 also shows the temperature histories at the outlets of the condenser and chilled water. It should be noted here that the delivered chilled water temperature is slightly lower for adsorption chiller employing SWS-1L as can be seen in Figure 5.

Table 5. Values adopted for adsorption chiller simulation used in the present model [37]

D_{so}	$2.54 \times 10^{-4} \text{ m}^2/\text{s}$ for SWS-1L and RD silica gel
E_a	$4.2 \times 10^4 \text{ J/mol}$ for SWS-1L and RD silica gel
R_p	$1.7 \times 10^{-4} \text{ m}$ for type RD and $1.74 \times 10^{-4} \text{ m}$ for SWS-1L
c_p^{sg}	924 J/(kg K)
h_{m-s}	$36 \text{ W/(m}^2 \text{ K)}$ [16]
h_{fin-s}	$36 \text{ W/(m}^2 \text{ K)}$ [16]
$(UA)^{chill}$	$(2557 \text{ W/(m}^2 \text{ K)} \times 1.37 \text{ m}^2)$
$(UA)^{cond}$	$(4115 \text{ W/(m}^2 \text{ K)} \times 3.71 \text{ m}^2)$
$(Mc_p)_{eff}^{evap}$	$(8.9 \text{ kg} \times 386 \text{ J/(kg K)} + 40 \text{ kg} \times c_{p,water} \text{ J/(kg K)})$
$(Mc_p)_{eff}^{cond}$	$(24 \text{ kg} \times 386 \text{ J/(kg K)} + 5 \text{ kg} \times c_{p,water} \text{ J/(kg K)})$
r_i	7.94 mm
$A^{tube} = 2\pi r_o L^{tube}$	$r_o = 8.64 \text{ mm}$, $L^{tube} = 1 \text{ m}$
$V_f^{chill} = \pi r_o^2 L^{evap}$	$L^{evap} = 2.1 \text{ m}$
$V_f^{cool} = \pi r_o^2 L^{cond}$	$L^{cond} = 2.34 \text{ m}$
$V^{fin} = \pi N h (r_{fin}^2 - r_o^2)$	$N = 100$, $h = 0.1 \text{ mm}$, $r_{fin} = 22 \text{ mm}$
u_f^{chill}	0.18 m/s
u_f^{cool}	0.198 m/s
$u_f^{heating}$	0.14 m/s
M^{sg}	20 kg
$T_f^{cool,in}$	$31 \text{ }^\circ\text{C}$
$T_f^{hot,in}$	$85 \text{ }^\circ\text{C}$
$T_f^{chill,in}$	$14.8 \text{ }^\circ\text{C}$

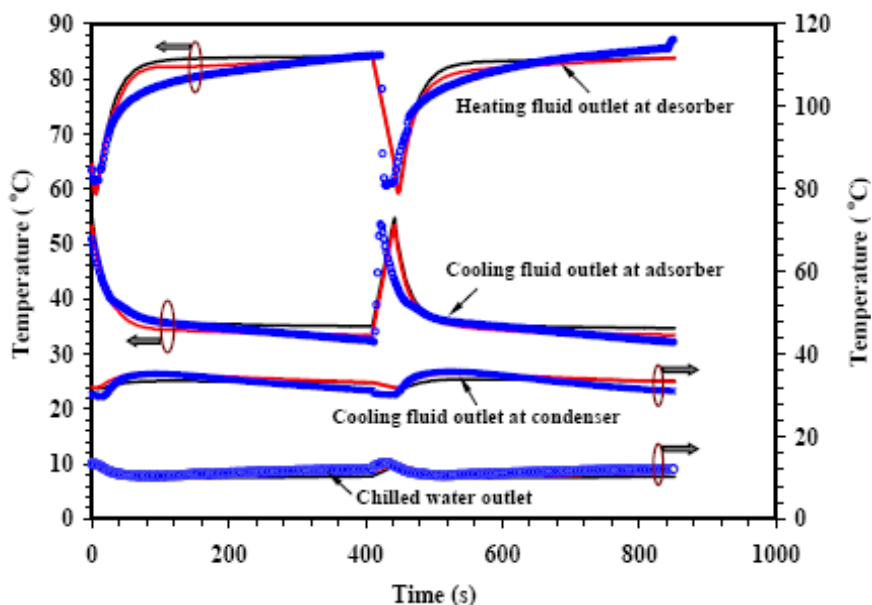


Figure 5. Simulated (black for SWS-1L-water system; red line for type RD silica gel-water system) and experimental (blue circles for type RD silica gel-water based adsorption system) heating fluid and cooling fluid outlet temperatures from the adsorption chiller system. Simulated and experimentally (for type RD silica gel only) measured fluid outlet temperatures from the condenser and evaporator are also shown here.

Figure 6 (a) presents the simulated Dühring diagram of the cyclic steady state condition of an entire bed comprising SWS-1L, from which one observes that during cold-to-hot thermal swing of the bed, momentary adsorption takes place although heating source has already been applied to heat up the bed in pre-heating mode. The entire bed is observed to be essentially following an isosteric path (constant x) during switching. In contrast, the local spatial points in the bed are not evolving in an isosteric manner, which is confirmed by the present analysis. This shows that while some parts of the bed may continue to adsorb, other parts desorb, resulting in the entire bed following an isosteric path. At the end of hot-to-cold thermal swing, there is a pressure drop in the bed. This causes the adsorbate in the cool bed to desorb momentarily and condense into the evaporator. The P - T - x diagram for adsorption bed employing RD type silica gel during steady state is also imposed in Figure 6 (b) for comparison.

Figure 7 presents the effects of cycle time on COP and cycle average chiller cooling capacity for type RD and SWS-1L based adsorption chiller systems. It is clearly seen that the COP increases monotonically with the cycle time. The reason is that with a longer cycle time, the relative time frame occupied bed switching which involves a significant sensible heat exchange is reduced vis-à-vis that of a shorter cycle time. This will lead to a favorable effect on the COP. The variation of cooling capacity is not monotonic. For SWS-1L based adsorption chiller, the cooling power increases steeply up to 500 s, and it begins to decrease with a similar slope at the cycle time of over 500 s. Lower cooling capacity under a relative shorter cycle time is caused by a reduced extent of adsorption, which is also related to a reduced extent of desorption due to the insufficient heating of the desorber. At a certain cycle time, the maximum adsorption/ desorption capacity is achieved at the prevailing heating and

cooling source temperatures. Extending the cycle time further brings forth unfavorable effect on useful cooling as the cycle average cooling capacity decreases. For the SWS-1L - water based pair, cycle times longer than 300 s can be realized with the higher cooling power and COP as compared to the adsorption cooling system based on RD silica gel-water pair.

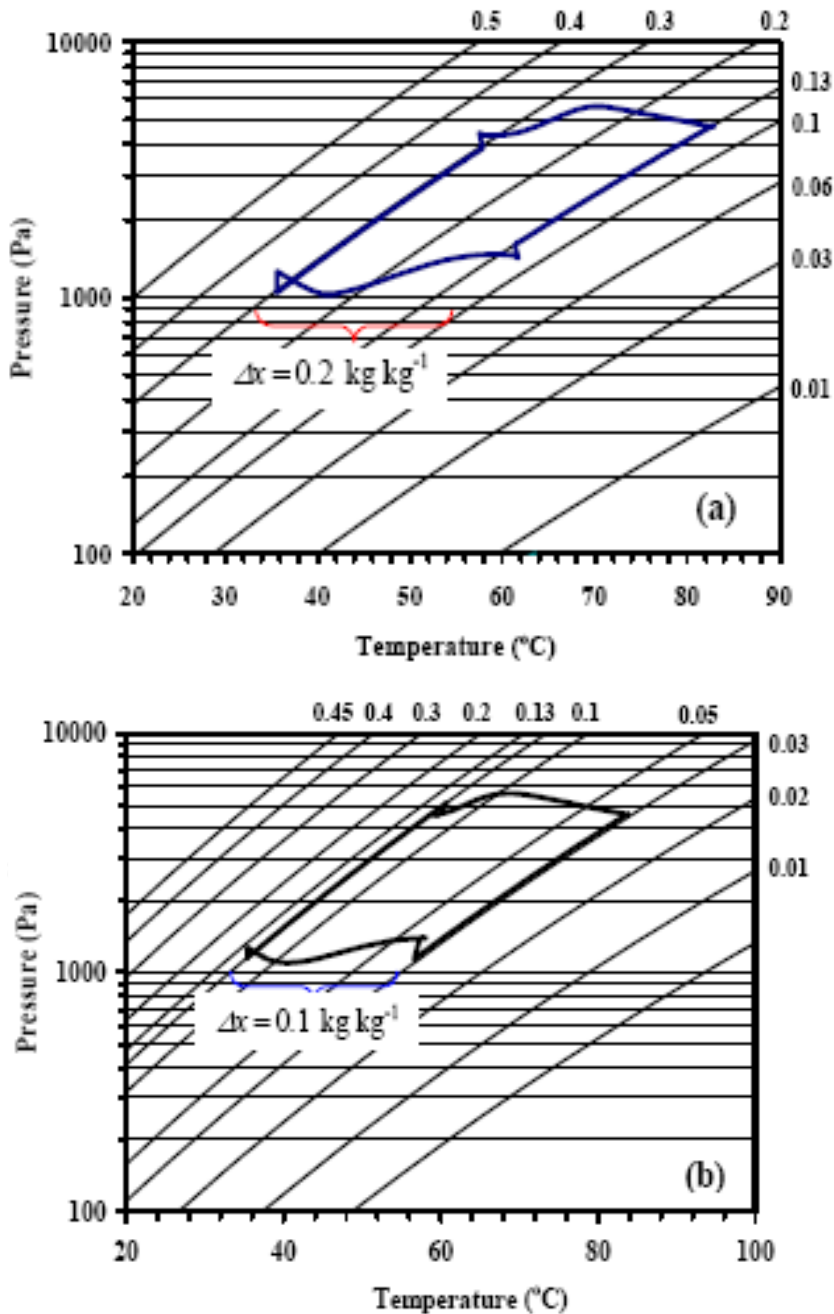


Figure 6. Dühring diagram of the whole bed under cyclic steady state condition for (a) SWS-1L and water based adsorption chiller, (b) type RD silica gel and water based adsorption cooling cycle.

Figure 7 presents the effects of cycle time on COP and cycle average chiller cooling capacity for type RD and SWS-1L based adsorption chiller systems. It is clearly seen that the COP increases monotonically with the cycle time. The reason is that with a longer cycle time, the relative time frame occupied bed switching which involves a significant sensible heat exchange is reduced vis-à-vis that of a shorter cycle time. This will lead to a favorable effect on the COP. The variation of cooling capacity is not monotonic. For SWS-1L based adsorption chiller, the cooling power increases steeply up to 500 s, and it begins to decrease with a similar slope at the cycle time of over 500 s. Lower cooling capacity under a relative shorter cycle time is caused by a reduced extent of adsorption, which is also related to a reduced extent of desorption due to the insufficient heating of the desorber. At a certain cycle time, the maximum adsorption/ desorption capacity is achieved at the prevailing heating and cooling source temperatures. Extending the cycle time further brings forth unfavorable effect on useful cooling as the cycle average cooling capacity decreases. For the SWS-1L - water based pair, cycle times longer than 300 s can be realized with the higher cooling power and COP as compared to the adsorption cooling system based on RD silica gel-water pair.

The system performance at different driving heat source temperatures in case of optimum conditions [(i) cycle time 420 s, switching time 30 s for type RD silica gel-water system, and (ii) cycle time 630 s, switching time 30 s for SWS-1L – water system] is shown in Figure 8 for the same heat sink temperature of 31 °C.

For type RD silica gel-water system the COP reaches the maximum value of 0.35 at $T = 75\text{--}80\text{ }^{\circ}\text{C}$. For SWS-1L - water system at this temperature range the COP is larger (0.42-0.45) and remains almost constant at higher T .

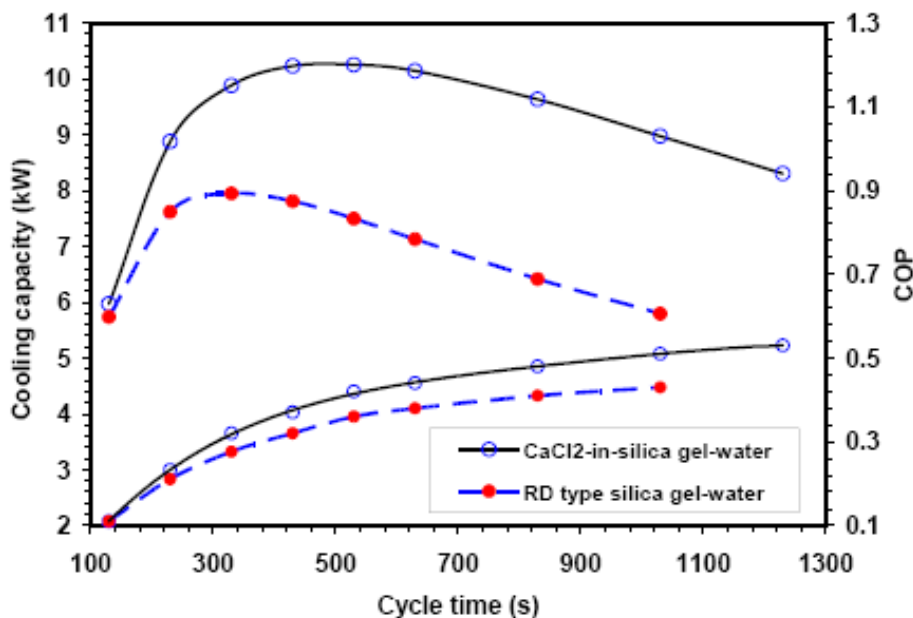


Figure 7. Effect of cycle time on COP and cycle average cooling capacity.

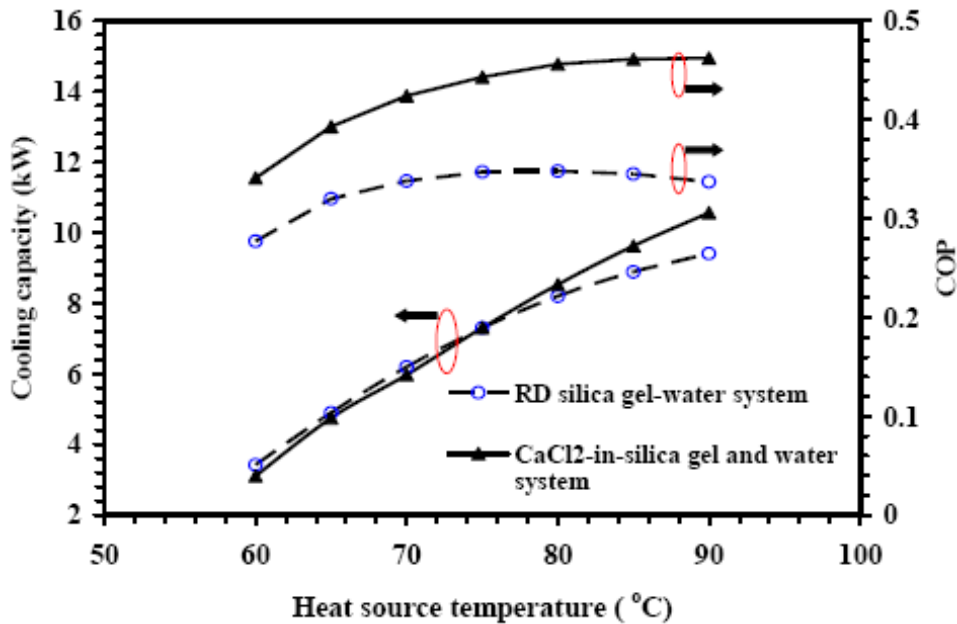


Figure 8: Influence of driving heat source temperature on cyclic average cooling capacity and COP.

The COP of SWS-1L - water system is higher than that of RD-water system because of high cooling and less driving heat generation powers, which may occur due to larger Δx for the same heat source and heat sink temperatures. This much larger COP shows significant advantage of the new working pair as compared with the conventional unit. Thus, from the present simulation results, it is found that the newly SWS-1L based adsorption chiller provides a promising unit for cooling applications. This theoretical conclusion should be confirmed practical testing of the new adsorbent in the optimized ADC configuration.

4.3. Summary of Section 4

We have successfully modeled and predicted the performances of SWS-1L and water based adsorption chiller using a simplified distributed approach such that both the transient and steady state behaviors of ADC can be captured. It is found that the performances of ADC incorporating SWS-1L as adsorbents, in terms of cooling capacity, coefficient of performance and peak chilled water temperature, are better than those of the commercial available silica gel-water based adsorption chiller. An optimum switching time of 30 s is obtained for both cycles and the cycle performance improves with increasing hot water inlet temperature.

5. MACRO AND MICRO THERMOELECTRIC COOLERS

The reversible thermoelectric effects are the Seebeck, Peltier and Thomson effects [38]. These are related to the transformation of thermal into electrical energy, and vice versa. The physical nature of the thermoelectric effects is not well explained in the literature, as well as

the dependence of Seebeck coefficient on temperature and materials. From the electron theory, the absorption of Thomson heat in the interior of a thermally non-uniform conductor has been reported to be the additive superposition of two effects: Firstly, a part of Thomson effect is the internal Peltier effect which is caused by the non-equilibrium electron distribution functions in a thermally non-uniform conductor. Secondly, the other part is heat absorbed due to current flow against the drift potential difference. These effects are assumed to be reversible and hence, the sign of the Thomson heat changes with the reversal of current direction. The thermoelectric effects in semi-conductors are stronger than those found in metals. This is attributed to the fact that electron gas in semi-conductors is far from being degenerated and obeys the classical Boltzmann statistics. The non-equilibrium changes in the distribution function are more noticeable than in a degenerated gas and this affects the magnitude of the thermoelectric effects. The magnitude of non-equilibrium change in the distribution function (and consequently the magnitudes of the thermoelectric effects) depends on the relative importance of the factors (such as electric field, thermal non-uniformity) that are responsible for the departure from equilibrium, as well as the mechanism for re-establishing the equilibrium. When an electric field is applied to a thermoelectric device, the following irreversible processes are deemed to occur in each elemental volume:

- (i) Electric conduction (electric current due to an electric potential gradient).
- (ii) Heat conduction (heat flow due to a temperature gradient).
- (iii) A cross effect (electric current due to a temperature gradient)
- (iv) The appropriate reciprocal effect (heat flow due to an electric potential gradient).

The last two belongs to a new class of irreversible process [14].

The organization of this section is as follows:

Section 5.1 describes the thermodynamic modelling of the bulk thermoelectric cooler and in addition, the entropy analysis of a transient thermoelectric cooler is also discussed. The thermodynamic behavior of a pulse thermoelectric cooler is investigated in section 5.2. The governing equations employed in this section are derived from the Boltzmann Transport Equation (BTE) that is reported in the previous section.

5.1. Thermoelectric Cooling

The refrigeration capability of a semiconductor material depends on parameters such as the Peltier effect, Joule heat, Thomson heat and material's physical properties over the operational temperatures between the hot and cold ends. A thermoelectric device is composed of p-type and n-type thermoelements such as Bi_2Te_3 and they are connected electrically in series and thermally in parallel. These thermoelectric elements are sandwiched between two ceramic substrates. As shown in Figure 9, thermoelectric cooling is generated by passing a direct current through one or more pairs of n and p-type thermoelements, the temperature of cold reservoir decreases because the electrons and holes pass from the low energy level in p-type material through the interconnecting conductor to the higher energy level in the n-type material.

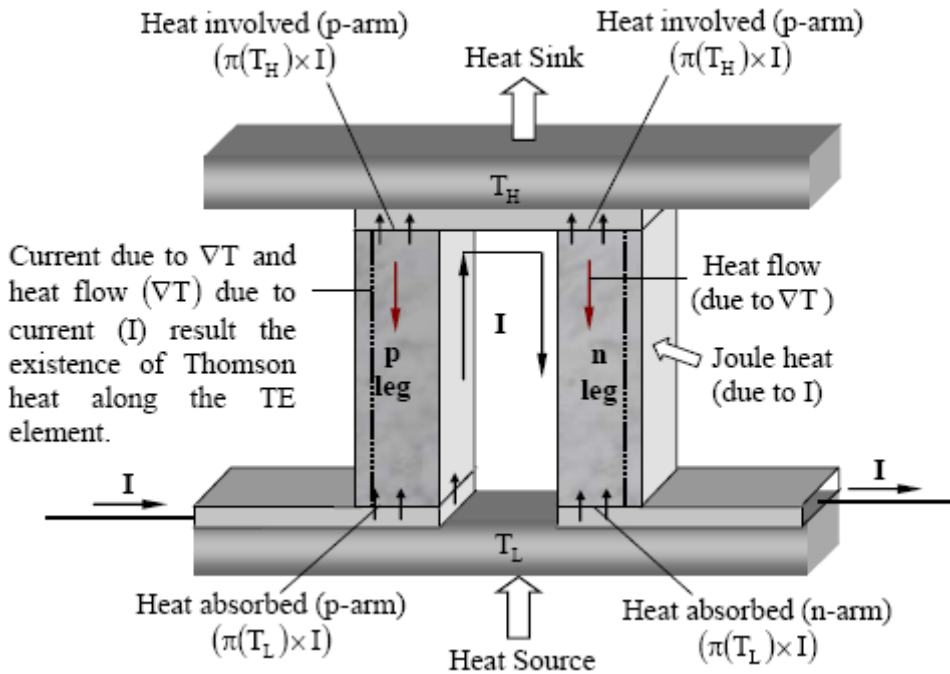


Figure 9. The schematic view of a thermoelectric cooler.

Similarly, the arrival of electrons and holes in the opposite end results in an increase in the local temperature forming the hot junction.

When a temperature differential is established between the hot and cold junctions, a Seebeck voltage is generated and the voltage is directly proportional to the temperature differential. The amount of heat absorbed at the cold-end and dissipated at the hot end depends on the product of Peltier coefficient (π), Fourier effect (λ_{te}) and the current (I) flowing through the semiconductor material, whilst the heat generation due to the Thomson effect occurs along the thermoelectric element. Thermoelectric effects are caused by coupling between charge transport and heat transport and from which the basic mass, energy and entropy equations can be formulated to form a thermodynamic framework.

5.1.1. Energy Balance Analysis

The Peltier and the Thomson effects enhance the cooling effect in thermoelectric materials. The Thomson effect is a function of the gradients from the Seebeck coefficient and the temperature in an operating thermoelectric pallet or element. The energy balance equation of the thermoelectric cooler, as shown in Figure 9, follows the methodology of the Boltzmann transport equation which has been discussed in the previous section, namely:

$$\frac{\partial(\rho u)}{\partial t} = -\nabla \cdot (\rho u \mathbf{v} + \mathbf{J}_q) - \mathbf{P} : \nabla \mathbf{v} + \mathbf{J} \mathbf{E} + \left. \frac{\partial(\rho u)}{\partial t} \right|_{\text{colli}}, \quad (47)$$

where u is the internal energy per unit mass, ρ is the density, $\mathbf{v}$ defines velocity, $\mathbf{J}_q$ indicates the heat flow, $\mathbf{P}$ represents the pressure and $\mathbf{J} \mathbf{E}$ is the energy field term.

For the bulk thermoelectric material analysis, the contributions from the collision terms are deemed negligible and can be neglected;

$$\frac{\partial(\rho_{te}u)}{\partial t} = -\nabla \cdot (\rho_{te}u\mathbf{v} + \mathbf{J}_q) - \mathbf{P} : \nabla \mathbf{v} + \mathbf{J}E. \quad (48)$$

Hence the subscript $_{te}$ indicates the thermoelectric cooler. As there is no velocity and pressure fields in a thermoelectric device,

$$\rho_{te} \frac{\partial u}{\partial t} = -\nabla \cdot \mathbf{J}_q + \mathbf{J}E \quad (49)$$

Invoking the definition of enthalpy;

$$h = u + pV \Rightarrow \frac{\partial h}{\partial t} = \frac{\partial u}{\partial t} + \frac{\partial(pV)}{\partial t} = \frac{\partial u}{\partial t}$$

$$h = h(T, p) \Rightarrow \frac{\partial h}{\partial t} = \left(\frac{\partial h}{\partial T_{te}} \right)_p \frac{\partial T_{te}}{\partial t} + \left(\frac{\partial h}{\partial p} \right)_{T_{te}} \frac{\partial p}{\partial t} = c_{p,te} \frac{\partial T_{te}}{\partial t}$$

where the pressure gradient term is zero.

The first term of right hand side of equation (3.1) is the heat current density, $\mathbf{J}_q$ (in W/m^2), and the second term is the electric current field, $\mathbf{J}E (= J \nabla \phi)$ (in W/m^3). Using the thermodynamic-phenomenological treatment [39], the heat current density

$$\mathbf{J}_q = -\frac{Q_o}{F} J - \lambda_{te} \nabla T, \quad (50)$$

where J (in amp/m^2) denotes the electric current density, Q_o indicates the heat transport of electrons/ holes, λ_{te} defines the thermal conductivity of the bulk thermoelectric element and F is the Faraday constant and the electric current density can be expanded as

$$J = \sigma'_{te} \nabla \phi + \frac{\sigma'_{te} Q_o}{FT_{te}} \nabla T_{te}, \quad (51)$$

where σ'_{te} defines the electrical conductance and ϕ is the electrical potential.

Equation (51) is re-arranged as,

$$\nabla \phi = \frac{J}{\sigma'_{te}} - \frac{Q_o}{FT_{te}} \nabla T_{te} \quad (52)$$

$$\text{Hence, } -\nabla \cdot \mathbf{J}_q + \mathbf{J}E = \nabla \cdot (\lambda_{te} \nabla T_{te}) + \frac{J^2}{\sigma'_{te}} + \frac{J}{F} T_{te} \nabla \left(\frac{Q}{T_{te}} \right)$$

where $\left(\frac{Q}{T_{te}} \right)$ is equivalent to the entropy term.

Now, substitute all these relations into equation (49), the expression becomes [40]

$$\rho_{te} c_{p,te} \frac{\partial T_{te}}{\partial t} = \nabla \cdot (\lambda_{te} \nabla T_{te}) + \frac{J^2}{\sigma'_{te}} + \frac{JT_{te}}{F} \left(\frac{\partial s_{te}}{\partial T_{te}} \right)_p \nabla T_{te}, \quad (53)$$

where s_{te} introduces the transported entropy of the bulk thermoelectric arms. Defining the Thomson coefficient (Γ) as [41],

$$-\Gamma \equiv \frac{T_{te}}{F} \left(\frac{\partial s_{te}}{\partial T_{te}} \right)_p,$$

the governing thermal transport in the bulk semiconductor arms is given by

$$\rho_{te} c_{p,te} \frac{\partial T_{te}}{\partial t} = \nabla \cdot (\lambda_{te} \nabla T_{te}) + \frac{J^2}{\sigma'_{te}} - \mathcal{J}T \nabla T_{te} \quad (54)$$

Using the Kelvin relations [17],

$$\Gamma = -\frac{\pi}{T_{te}} - \left(\frac{\partial \pi}{\partial T_{te}} \right), \text{ where } \pi (= \alpha T) \text{ is the Peltier coefficient.}$$

Equation (54) can now be written as (derivations are shown in Appendix),

$$\rho_{te} c_{p,te} \frac{\partial T_{te}}{\partial t} = \lambda_{te} \nabla^2 T_{te} + \frac{J^2}{\sigma'_{te}} + \mathcal{J}T \nabla \alpha|_{T_{te}} - \mathcal{J}T \left(\frac{\partial \alpha}{\partial T} \right) \nabla T_{te} \quad (55)$$

5.1.2. Entropy Balance Analysis

The basic entropy balance equation has been introduced in the previous chapter, as shown below:

$$\begin{aligned}\rho \frac{ds}{dt} &= -\nabla \cdot \mathbf{J}_s + \sigma \\ \frac{\partial(\rho s)}{\partial t} &= -\nabla \cdot (\mathbf{J}_s + \rho s \mathbf{v}) + \sigma\end{aligned}\quad (56)$$

Introducing the phenomenological relations:

$$\mathbf{J}_{s,te} + \rho_{te} s_{te} \mathbf{v} = -\frac{\lambda_{te}}{T_{te}} \nabla T_{te} + \frac{\pi}{T_{te}} \mathbf{J}, \quad (57)$$

and invoking the Kelvin laws, one could observe

$$T\alpha = \pi. \quad (58)$$

Assuming only the bulk thermoelectric materials, the collision terms are usually neglected and the entropy source strength is given by (as discussed in the previous sections);

$$\sigma = -\frac{1}{T^2} \mathbf{J}_q \cdot \nabla T - \frac{1}{T} \sum_{k=1}^n \mathbf{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} \right) + \frac{1}{T} \mathbf{J} \cdot \mathbf{E}$$

Hence, the entropy generation of thermoelectric arm can now be modified into a form that is inclusive of the Peltier coefficient and the local temperature as [17]

$$\sigma = -\frac{1}{T_{te}} \left(-\frac{\lambda}{T_{te}} \nabla T_{te} + \frac{\pi}{T_{te}} \mathbf{J} \right) \cdot \nabla T_{te} + \frac{1}{T_{te}} \mathbf{J} \cdot (\alpha \nabla T_{te} + \mathbf{J} / \sigma'_{te})$$

Finally, the entropy balance equation (56) becomes;

$$\frac{\partial(\rho_{te} s_{te})}{\partial t} = \frac{\nabla \cdot (\lambda_{te} \nabla T_{te})}{T_{te}} - \nabla \cdot \frac{\pi \mathbf{J}}{T_{te}} + \frac{J^2}{T_{te} \sigma'_{te}} \quad (59)$$

The first term on the right-hand side of equation (59) represents the change of entropy due to heat conduction; the second term indicates the entropy flux due to Seebeck effect and the last term is the entropy generation due to Joule heat.

A more elegant method of writing the entropy fluxes of thermoelectric arm is to express them in terms of (i) the heat and carrier fluxes, (ii) the internal dissipation, and (iii) the entropy generation that comes from conduction and Joulean heat transfer:

$$\frac{\partial(\rho_{te} s_{te})}{\partial t} = \overbrace{\nabla \cdot \left(\frac{\lambda_{te} \nabla T_{te}}{T_{te}} - \frac{\pi J}{T_{te}} \right)}^{\text{entropy flux}} + \left\{ \overbrace{-\lambda_{te} \nabla T_{te} \cdot \nabla \left(\frac{1}{T_{te}} \right)}^{\text{internal dissipation}} + \overbrace{\frac{J^2}{T_{te} \sigma'_{te}}}^{\text{entropy source strength due to Joulean heat}} \right\} \quad (60)$$

where the units of entropy flux is in W/m² K and it is given by,

$$S_{flux} = \frac{\lambda_{te} \nabla T_{te}}{T_{te}} - \frac{\pi J}{T_{te}}, \quad (61)$$

and entropy generation per unit volume is in W/m³ K which is expressed as:

$$S_{gen} = -\lambda_{te} \nabla T_{te} \cdot \nabla \left(\frac{1}{T_{te}} \right) + \frac{J^2}{T_{te} \sigma'_{te}}. \quad (62)$$

Equation (62) is always a positive term.

5.1.3. Temperature-Entropy Plots of Bulk Thermoelectric Cooling Device

From the work of Carnot and Clasius, Kelvin deduced that the reversible heat flow discovered by Peltier must have entropy associated with it. It has been shown that the coefficient discovered by Seebeck was a measure of entropy associated with electric current [41]. A temperature-entropy (T-s) has been proven to be a pedagogical tool in analyzing the performance of thermoelectrics undergoing both reversible and irreversible processes. The parameters used in the computation are listed in Table 6.

Table 6. Physical parameters of a single thermoelectric couple

Property	value
Hot junction temperature, T_H	300 K
Cold junction temperature, T_L	270 K
Thermoelectric element length, L	1.15×10^{-3} m *
Cross-sectional area, A	1.96×10^{-6} m ² *
Electrical conductivity, σ'	97087.38 ohm ⁻¹ .m ⁻¹ *
Seebeck coefficient α (V/K) $\alpha(T) = \alpha_o + \alpha_I \ln(T/T_o)$	$\alpha_o = 210 \times 10^{-6}$ V/K, $\alpha_I = 120 \times 10^{-6}$ V/K $T_o = 300$ K (Seifert et al., 2002)
Thermal conductivity, λ	1.70 W/m K *

*Melcor thermoelectric catalogue, Melcor Corporation, 1040 Spruce Street, Trenton, NJ 08648, USA. Web site: www.melcor.com.

For an ideal thermoelectric device, the Seebeck (α) coefficient is constant and the heat flux at the hot and cold junctions are given by $\alpha J T_i$ where the subscript i refers either to the hot or cold junction. Thus, the temperature Seebeck coefficient (T - α) plot is simply a simple rectangle. However, the temperature effect on the Seebeck (α) coefficient induces the dissipative losses along the p and n legs of thermoelectrics and an indication of these losses are shown by the shaded area on the T - α plot, as shown in Figure 10, in which the physical properties of the Bismuth Telluride thermoelectric pairs are used.

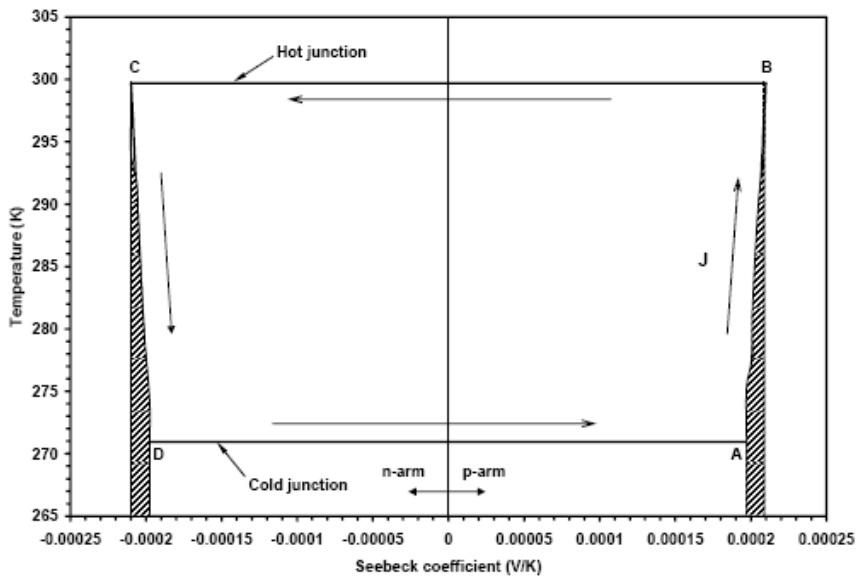


Figure 10. T - α diagram of a thermoelectric pair. The shaded areas indicate dissipative losses along p and n legs.

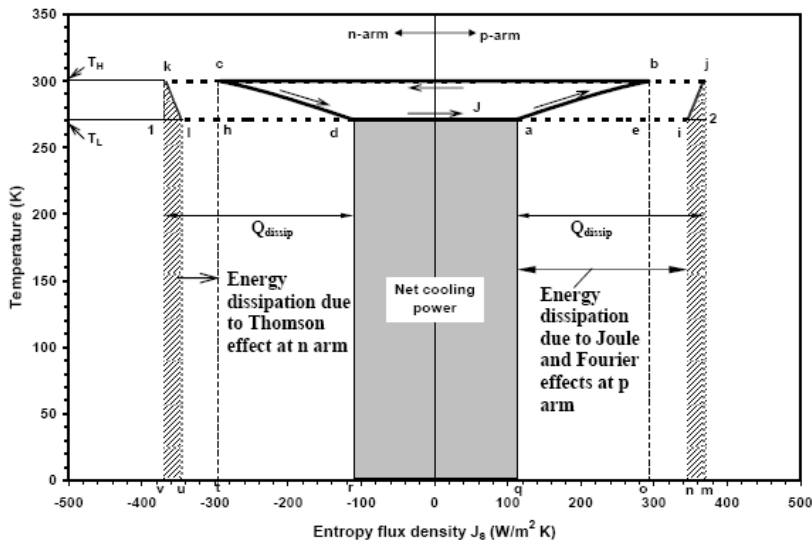


Figure 11. Temperature-entropy flux diagram for the thermoelectric cooler at the maximum coefficient of performance identifies the principal energy flows.

The two isotherms are the hot and cold junctions whilst the inclined lines indicate the effect of temperature on the α values when the current (I) travels along the p- and n-legs.

For thermodynamic consistency, the temperature-entropy (or temperature-entropy flux) diagram is. In an optimum current operation of the thermoelectric cooler, the presence of entropy loss (due to conduction heat transfer and Joule heat) along the p-n legs is given by $K\nabla T/T_i$ and they are manifested by enclosed areas “k-i-u-r-d-c-k” and “j-i-n-q-a-b-j” of Figure 11. Both mentioned dissipative losses have the consequence of reducing the cooling effect, represented by area “a-d-r-q”. Within the internal framework (adiabatic chiller), the cycle “a-b-c-d” operates in an anti-clockwise manner with process with two isotherms b-c and d-a, as well as two non-adiabats a-b and c-d. Details of these processes are described in Table 7. Thus, the T-s diagram provides an effective means of analyzing how the real chiller cycle of thermoelectrics is inferior to the ideal Carnot cycle by capturing the key losses and useful effects in the cycle.

From temperature-entropy flux diagram, the thermodynamic performance variables can be easily tallied with the enclosed rectangles. The heat fluxes at the cold (process d-a) and hot (process b-c) reservoirs are as follows (for details please see Appendix)

$$Q_L = \text{Area}(adrq) = T_L |J_{S,pn}| = T_L \left(\alpha I - \frac{\lambda \nabla T|_{cj}}{T_L} \right) = \alpha I T_L - \lambda \nabla T|_{cj} \quad (63)$$

$$= \underbrace{\alpha I T_L}_{\text{Peltier cooling}} - \underbrace{\frac{1}{2} I^2 R}_{\text{Joule heat}} - \underbrace{\frac{K \Delta T}{K \Delta T}}_{\text{conduction heat}} - \underbrace{\frac{1}{2} I \tau \Delta T}_{\text{Thomson heat}}$$

$$Q_H = \text{Area}(bcto) = T_H |J_{S,pn}|_{hj} = T_H \left(\alpha I - \frac{\lambda \nabla T|_{hj}}{T_H} \right) = \alpha I T_H - \lambda \nabla T|_{hj} \quad (64)$$

$$= \underbrace{\alpha I T_H}_{\text{Peltier heat}} + \underbrace{\frac{1}{2} I^2 R}_{\text{Joule heat}} - \underbrace{\frac{K \Delta T}{K \Delta T}}_{\text{Conduction loss}} + \underbrace{\frac{1}{2} I \tau \Delta T}_{\text{Thomson heat}}$$

where ΔT is the temperature difference across the hot and cold junctions. The first term of right hand side of both equations (63) and (64) indicates Peltier cooling and heating, the second term is the Joule heat, the third term represents heat conduction between hot and cold junctions and the heat absorbed by the Thomson effect.

The Thomson heat is transmitted by thermal conduction across the thermo-element and this effect is not reversible. From the first law of thermodynamics, the required electrical power input is given by,

$$\begin{aligned} P &= \text{Area}(bcto) - \text{Area}(adrq) = T_H |J_{S,pn}|_{hot} - T_L |J_{S,pn}|_{cold} \\ &= \overbrace{\alpha I T_H + \frac{1}{2} I^2 R - K \Delta T + \frac{1}{2} I \tau \Delta T}^{Q_u} - \overbrace{\alpha I T_L + \frac{1}{2} I^2 R + K \Delta T + \frac{1}{2} I \tau \Delta T}^{Q_L} \\ P &= \alpha I (T_H - T_L) + I^2 R + I \tau \Delta T \end{aligned} \quad (65)$$

The equivalent cycle at the same T_H and T_L is denoted by a rectangle 1-2-j-k (see Figure 11), for which $COP_{carnot} = Area(1vm2)/[Area(kvmj) - Area(1vm2)]$ or $COP_{carnot} = Area(1vm2)/Area(12jk) = T_L/\Delta T$.

Table 7. Description of close loop a-b-c-d-a (Figure 11)

Process	Description
a--b	This process is developed along P-arm of the thermoelectric pair. Points a and b are the states at the ends of the thermoelement of which the temperatures are T_L and T_H respectively (as current J flows from P-arm to N-arm). The process a-b can not be adiabatic because it absorbs heat due to the Thomson effect which depends on the Seebeck coefficient of the thermoelectric element. The areas beneath the a-b process represent dissipation due to heat conduction, and heat absorbed by the Thomson effect. Area 2-i-j represents the energy dissipation due to Seebeck coefficient, which varies along the thermoelectric p-arm.
b--c	This process represents the heat exchange between system and medium (environment) which occurs at the union between P-arm and N-arm at temperature T_H .
c--d	The process c-d is developed along N-arm, where points c and d are at the ends of the thermo-element whose temperature are T_H and T_L . The areas beneath c-d process indicate heat losses due to dissipation. If this process is adiabatic, the Thomson effect would be null. Area 1-l-k indicates the energy losses due to Seebeck effect along the n-arm.
d--a	This process represents the heat exchange between the system and the heat load at isothermal condition; however it occurs in the physic union between thermoelectric elements at temperature T_L .

The irreversibility is the heat dissipation, which is shown in Figure 11, occurs due to the Joule heat and to the heat conduction along the thermoelectric arm.

5.2. Transient Behavior of Thermoelectric Cooler

The performance of a Peltier or thermoelectric cooler can be enhanced by utilizing the transient response of a current pulse [42-45]. At fast transient, a high but short-period (4 seconds) current pulse is injected so that additional Peltier cooling is developed instantly at the cold junction: The joule heating developed in the thermoelectric element is a slow phenomenon as heat travels slowly over the materials and could not reached the cold junction in the short transient. Hence, the cold junction temperature is at the lowest possible value and heat flows only from the source to the cold junction. An example of such an application of the short transient cooling is an infrared detector operating in a ‘winking mode, which needs to be super cold only during the wink. Figure 12 shows the schematic diagram of a current “pulse train” thermoelectric cooler with the p- and n- doped semiconductor elements are electrically

connected in series and are thermally in parallel. The hot side of the device is mounted directly onto a substrate to reject heat to the environment and the thermal contact between the cold junction of thermoelectric device and the cold substrate (load) is made periodically. There are two periods of operation: Firstly, an “open contact” period with t_{no} and current flow J_{np} to maintain the lowest temperature T_{min} at the cold junction but the cold substrate (load) is not connected with the cold junction. Secondly, a large current pulse J_p (where $J_p = MJ_{np}$, $M > 1$) is applied for a duration t_p and concomitantly, the cold substrate makes contact with the cold junction. Intense Peltier cooling is achieved during t_p , which reduces the cold junction temperature below T_{min} . However, Joule and Thomson heating are developed in the bulk thermoelectric module and diffuse towards the hot and cold ends of the device. Thermal contact of the cold substrate with the cold end of the thermoelectric module is maintained over the short current pulse period but these surface break contact before the cooling could be degraded by the conduction heat.

In the open contact manner, the cold substrate temperature could reach below that of the cold junction temperature under the normal thermoelectric operation. The total operation consists of two periods; one is the normal thermoelectric operation and the other is the pulse or effective operation. The cycle of (normal operation + pulse operation) is repeated such that the device is continuously produced cooling.

This section formulates a non-equilibrium thermodynamic model to demonstrate the energy and entropy balances of a transient thermoelectric cooler. In analyzing the fast transient cycle in the classical T - s plane, one distinguishes the entropy fluxes of the working fluid (which is the current flux J) from the external entropy fluxes in the hot and cold reservoirs and at the interface with the reservoirs. The T - s relation is formulated that identifies the key heat and work flows, the heat conduction and electrical resistive dissipative losses.

5.2.1. Derivation of the T - S Relation

The methodology of energy and entropy balances of the commercial available thermoelectric device has been discussed briefly in the previous sections. Starting from the general entropy balance equation, it can be expressed in terms of the key parameters such as Peltier effect (π), electrical conductivity (σ'), current density (J) and Fourier effect (λ), as shown below [46]:

$$\frac{\partial(\rho_p s_p)}{\partial t} = \overbrace{\nabla \cdot \left(\frac{\lambda_p \nabla T_p}{T_p} - \frac{\pi J_p}{T_{p,te}} \right)}^{\text{entropy flux}} + \overbrace{\left\{ -\lambda_p \nabla T_p \cdot \nabla \left(\frac{1}{T_p} \right) + \frac{J_p^2}{T_p \sigma'_p} \right\}}^{\text{entropy generation}}, \quad (66)$$

hence the subscript p defines the pulsed thermoelectric cooler, the first term of the right hand side indicates the entropy flux in a given control volume and the second terms represent the total entropy generation. The total entropy flux density (in $\text{W}/\text{m}^2 \text{K}$) is expressed by

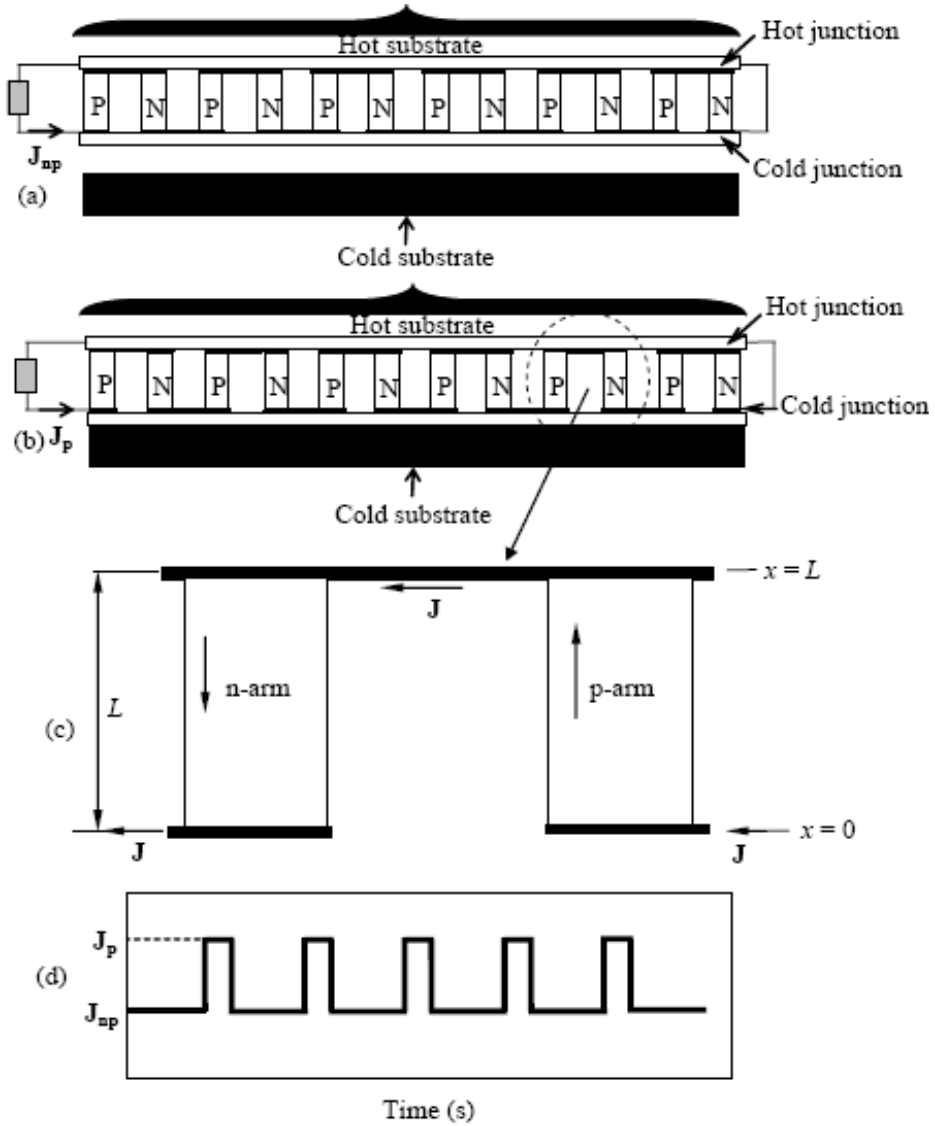


Figure 12. Schematic diagram of the first transient thermoelectric cooler. (a) indicates the normal operation and cold substrate is out of contact, (b) defines the thermoelectric pulse operation and cold substrate is in contact with the cold junction, (c) shows the thermoelectric couple consisting of p and n arms, (d) indicates that the pulse current is applied to the device.

$$\mathbf{J}_{s,tot}|_p = \frac{\lambda_p \nabla T_p}{T_p} - \alpha J_p, \quad (67)$$

and the entropy generation (in $\text{W/m}^3 \text{ K}$) is written as

$$\sigma_{p,tot} = -\lambda_p \nabla T_p \cdot \nabla \left(\frac{1}{T_p} \right) + \frac{J_p^2}{T_p \sigma'_p}. \quad (68)$$

The energy conservation equation is as follows

$$\rho_p c_p \frac{\partial T_p}{\partial t} = \lambda_p \nabla^2 T_p + \frac{J_p^2}{\sigma'_p} + J_p T_{p,te} \nabla \alpha|_{T_p} - J_p T_p \left(\frac{\partial \alpha}{\partial T_p} \right) \nabla T_p. \quad (69)$$

To solve the problem, two boundary conditions are defined: Firstly, during the normal (open-contact) operation, there is only Peltier cooling at the cold junction

$$\left. \frac{\partial T_p}{\partial x} \right|_{atcj} = \frac{\alpha J T_{cj}}{\lambda_p}, \quad (70)$$

and at hot junction, a hot side heat sink is represented by, $T_p|_{athj} = T_{hj}$. But during the pulse (close-contact) operation, at the cold junction the boundary condition becomes

$$\left. \frac{\partial T_p}{\partial x} \right|_{atcj} = \frac{\alpha J T_{cj}}{\lambda_p} + \frac{q_{subs}}{\lambda_p}, \quad (71)$$

where q_{subs} is the cooling load of the cold substrate.

5.2.2. Discussion

Figure 13 shows the transient behavior of the pulsed thermoelectric cooler where the hot junction is assumed to be constant at $T_{hj} = 308$ K. Based on the physical properties of a thermoelectric cooler, as tabulated in Table 6, the simulations with an initial current density of $J_{np} = 0.675$ A/mm² yield an exponential decrease of the cold junction temperature to $T_{c,A} = 240$ K (denoted by point A'), and beyond which a pulsed current density of $J_p = 2.025$ A/mm² for a duration of 4 s is applied for the pulsed or contact mode. The high pulsed current in the thermoelectrics produces instantaneous Peltier cooling, as shown by the decrease in the cold junction temperature to point B. Concomitantly, the pulsed current generates the Joule and Thomson heating within the p-n legs and this is reflected by the rise of cold junction temperature from point B to C. As no cooling could be achieved by the cold substrate, the cold junction breaks contact with it at point C. However, the residual heat transfer from the mentioned effects is generally a slower phenomenon as compared to Peltier cooling, the temperature of the cold junction continues to rise until the cooling by J_{np} overcomes the residual heat within the legs, culminating in a maxima for the temperature of the cold junction, as depicted by point B'.

For the non-contact duration, the energy flows in the thermoelectric device can best be followed by tracking the temperature versus entropy fluxes along the p-leg in a anti-clockwise direction, i.e., points "a" to "g" of Figure 14: Point "a" denotes the cold junction temperature and the entropy flux here is taken to be zero or the datum. As holes migrate along the p-leg,

both entropy flux and temperature increase with the spatial length until point “g” is reached, due primarily to the property changes with the local temperature of Bi_2Te_3 materials such as the electrical resistivity (ohm-cm), Seebeck coefficient (V/K) and thermal conductivity (W/cm K).

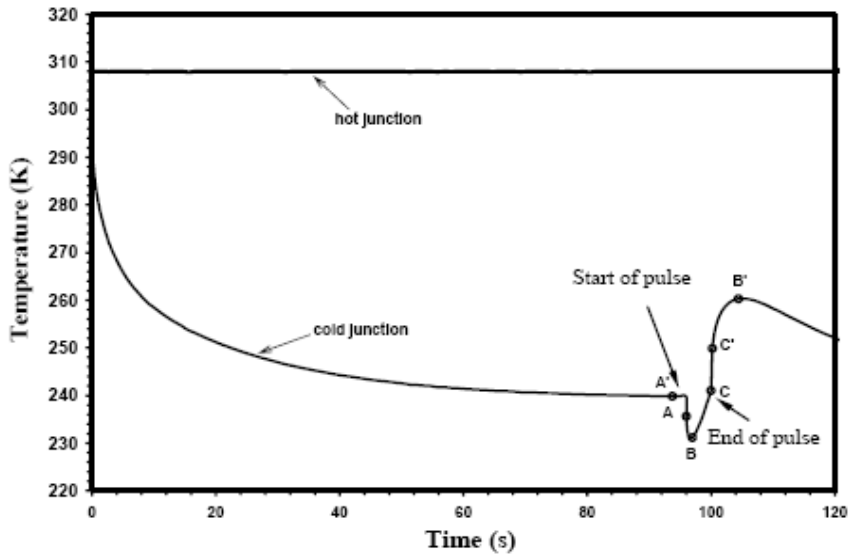


Figure 13. The transient temperature-time trace of cold reservoir temperature of a pulsed thermoelectric cooler. Point “A” indicates the beginning of pulse period, “B” denotes the lowest temperature reached by the cooler and “C” represents the end of pulse period, “C” “ shows the beginning of non-contact period, “B” “ indicates maximum temperature rise due to energy balance between the residual heat from the pulsed period and the steady state cooling.

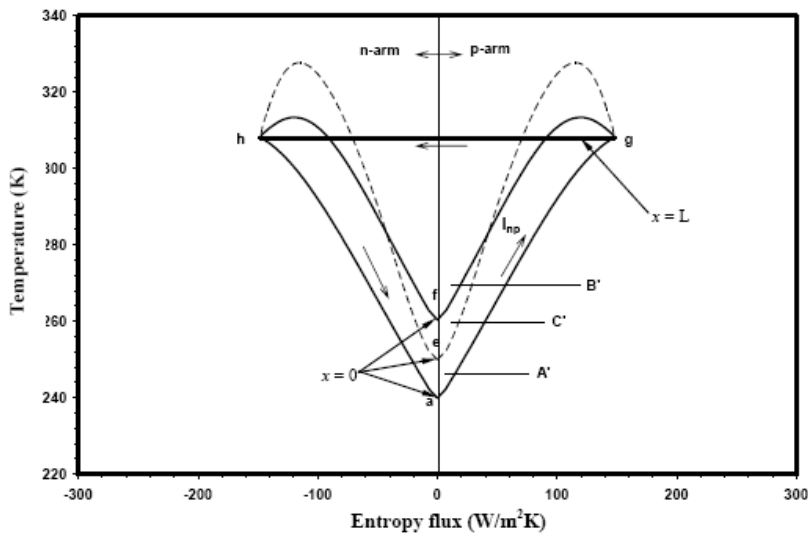


Figure 14. Temperature-entropy flux (T-s) diagram showing the anti-clockwise loop of a pulsed thermoelectric cooler for the non-pulse duration for three operation points [46].

As opposed to the non-contact duration, the cold junction on the T-s plot has an isotherm path, and the area enclosed below the isotherm a-a' indicates the amount of cooling produced at point A of the contact operation. Similar isotherms c-c' and d-d' correspond to the points B and C during the transients. Although the enclosed area for point C is slightly larger than that of point B, but the cold junction temperature of point C is found to be higher, caused by the diffusion of Joule heat from the legs of the thermoelectrics.

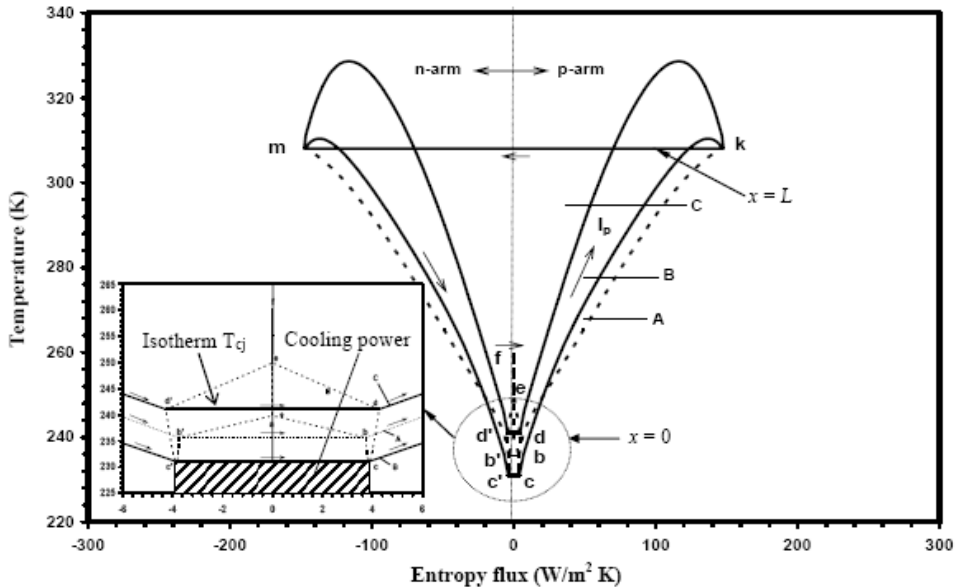


Figure 15. Temperature-entropy flux (T-s) diagram showing the energy flow details of a pulsed period of thermoelectric cooler. Cycles A to C refer to the beginning of cooling, the lowest temperature reached and the maximum cooling power by the cooler. The details of the processes within the cold junction of thermoelectrics are shown by the small insert, denoted correspondingly by “a” to “c”. The enclosed area below T_c isotherms in the T-s diagram indicates the cooling power.

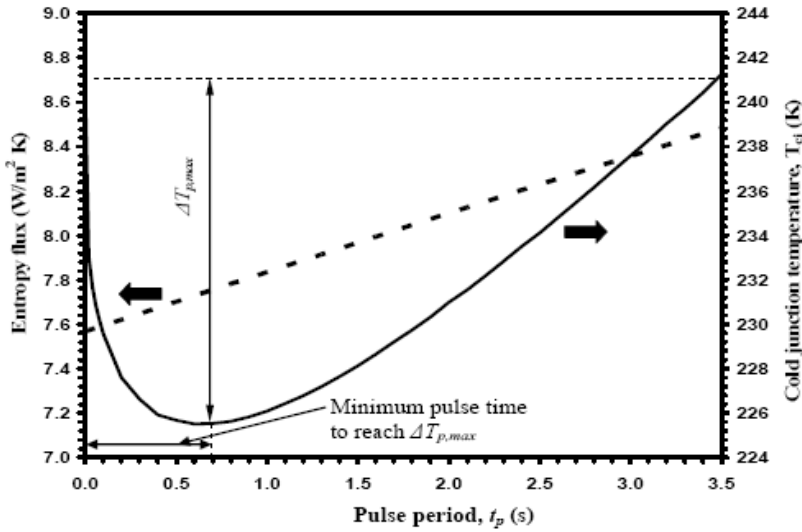


Figure 16. The effects of pulse periods on entropy flux and the cold junction temperature subjected to a step current pulse of magnitude $M = 4$.

No cooling power is developed during non-contact period but the cooling power is generated during pulse period. Figure 16 shows the time evolution of entropy flow and temperature at the cold junction and calculates the minimum time to reach the maximum temperature difference between the super-cooling and the steady state or $\Delta T_{p,max}$. The characteristics time, entropy flux and cold end temperature as shown in Figure 16 may be used to characterize the pulse cooler as functions of length of pulse t_p , pulse factor M , and pulse current density, J_p . This graph is helpful to design a cooler where the user would easily calculate the amount of increasing cooling, cooling behaviors, the needed pulse current and the time between pulses.

The effects of pulse factors on entropy flux at cold end and the maximum temperature drop or $\Delta T_{p,max}$ are shown in Figure 17 and the optimization is obtained at pulse factor 4 [46].

5.2.3. Summary of Section 5.2

We have successfully plotted the T-s diagrams for the transient features of a pulsed thermoelectric cooler. The thermodynamic formulation (based on the Gibbs law) provides the necessary expression for the entropy flux that is expressed in terms of the basic variables describing the device, namely, the current density, Seebeck coefficient, the local temperature and temperature gradient. Using the T-s diagram, the process paths of the pulsed and non-pulsed operations of thermoelectric cooler are accurately mapped and it has immense pedagogical value for cycle evaluation, depicting the useful energy flows and “bottlenecks” of cycle operation.

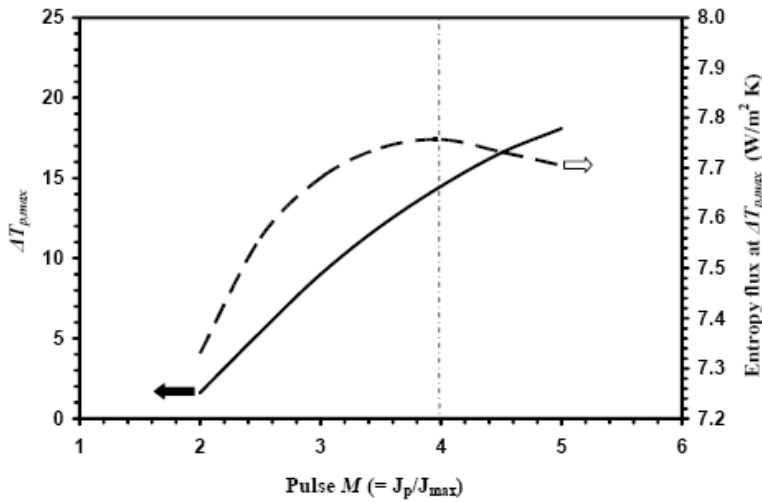


Figure 17. Maximum pulse cooling difference in temperatures and entropy fluxes as a function of pulse factor, exhibits the optimization.

5.3. Microscopic Analysis: Super-Lattice Type Devices

The development of semi-conductor materials for cooling and heating applications has made steady progress with the thermoelectric (TE) coolers being made of the Bismuth-Telluride (Bi_2Te_3), Antimony-Telluride (Sb_2Te_3), and Silicon-Germanium (SiGe) materials [47]. Two factors, however, limit the wide spread application of such coolers, namely (i) the low efficiency or coefficient of performance (COP) at higher temperature differential across the cold and hot junctions, and (ii) the cost of the semi-conductor devices per unit cooling capacity. The cooling efficiency of TE elements, comprising the p-n layers of semi-conductors, is characterized by the dimensionless ZT parameter: T is the absolute operational temperature and the thermoelectric figure of merit Z is given by $\alpha^2/\rho\lambda$ where α is the Seebeck coefficient, ρ is the density and λ is the thermal conductivity. The best thermoelectric materials available, hitherto, have a $ZT \approx 0.9$, but for commercial viability as cooling devices at ambient conditions, the ZT value should exceed a value 3. Recently, there were reports of semi-conductor materials with multi-quantum well materials [48], PbSeTe-based quantum dot superlattice structures [49] and thin-film $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ -based superlattice thermoelectric element for both refrigeration and power generation applications [50, 51]. Thin-film thermoelectric coolers using silicon materials such as $\text{Si}/\text{Si}_{0.8}\text{Ge}_{0.2}$, have been fabricated by alternating barrier and conducting layers which generate the quantum wells and increase the electron mobility. The procedures of making thermoelectric modules with p and n-type ($\text{Si}/\text{Si}_{0.8}\text{Ge}_{0.2}$) superlattices have been reported [52].

The size of thermoelectric device characterizes the transport of electrons, holes and phonons. In a very thin film with a thickness less than mean free path, electrons go through the film ballistically and experience little or no collision [53]. Scattering or collision dominates the transport process of electrons, holes and phonons in thick films or bulk materials. In case of bulk thermoelectric material such as Bi_2Te_3 , SiGe , SbTe , the limiting speed of thermoelectric element responses from milliseconds to a few second, so the energy

dissipation due to collisions of electrons, holes and phonons is not significant and heat transport is purely diffusive [54]. The reduction of device sizes to the sub-micrometer range not only increases the device switching speed from nano-second to pico-second but also increases the local rate of heat generation due to electron-phonon interactions or hole-phonon interactions [54, 55].

The motivation of this section is to model the thin-film thermo-electric cooling devices [50] as shown in Figure 18 using the BTE where both macro and micro phonological dissipations are rigorously captured at the micro-scaled dimensions. The present model treats the non-equilibrium transport of electrons-phonons (in case of n-type such as $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Te}_{2.83}\text{Se}_{0.17}$ thin film thermoelectric element) and holes-phonons (for p-type such as $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ thin film thermoelectric element), and their non-equilibrium coupling or the collision contributions at different electric fields using the practical temperature-entropy (T-s) diagrams.

This T-s diagram quantifies the net useful cooling effects at the cold junction and the COP. The proposed model of the thin film thermoelectric cooler that accounts for the collision contributions is validated with a recently published experimental data [50].

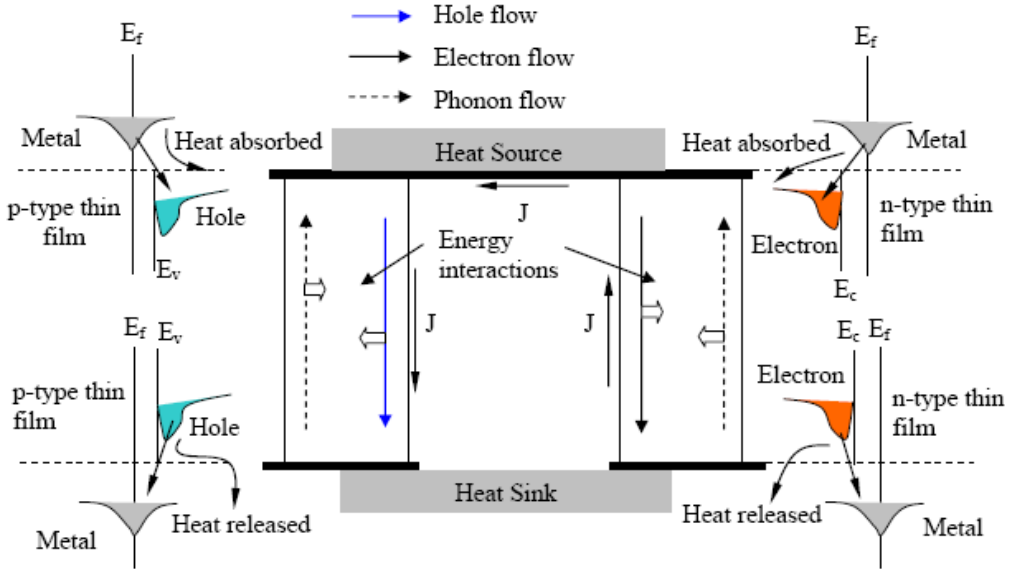


Figure 18. Schematic diagram of a thin film thermoelectric couple.

5.3.1. Thermodynamic Modeling for Thin-Film Thermoelectrics

The interactions of electrical and thermal phenomena are important to simulate the superlattice thermoelectric element. The most important thermal effect is the thermal runaway, in which the electrical dissipation of energy causes an increase in temperature which in turn causes a greater dissipation of energy. Without repeating the basic derivation (as derived in section 2), a complete model of electron, hole and phonon conservation equations for a thin film thermoelectric element is summarized in Table 8.

Table 8. The balance equations

Particles		Equations
Electrons	mass	$\frac{\partial n_e}{\partial t} = -\nabla(v_e n_e) + \frac{\partial n_e}{\partial t} \Big _{\text{colli}} \quad (72)$
	energy	$\frac{\partial u_e}{\partial t} = -\nabla \cdot \mathcal{Q}_e + \mathbf{JF} \Big _e + \frac{\partial u_e}{\partial t} \Big _{\text{colli}} \quad (73)$
	entropy	$\frac{\partial s_e}{\partial t} = \nabla \cdot J_{se} + \sigma_{\text{irr},e} + \sigma_{\text{colli},e-h} + \sigma_{\text{colli},e-g} \quad (74)$
Holes	mass	$\frac{\partial n_h}{\partial t} = -\nabla(v_h n_h) + \frac{\partial n_h}{\partial t} \Big _{\text{colli}} \quad (75)$
	Energy	$\frac{\partial u_h}{\partial t} = -\nabla \cdot \mathcal{Q}_h + \mathbf{JF} \Big _h + \frac{\partial u_h}{\partial t} \Big _{\text{colli}} \quad (76)$
	entropy	$\frac{\partial s_h}{\partial t} = \nabla \cdot J_{sh} + \sigma_{\text{irr},h} + \sigma_{\text{colli},h-e} + \sigma_{\text{colli},h-g} \quad (77)$
Phonons	energy	$\frac{\partial u_g}{\partial t} = -\nabla \cdot \mathcal{Q}_g + \frac{\partial u_g}{\partial t} \Big _{\text{colli}} \quad (78)$
	entropy	$\frac{\partial s_g}{\partial t} = \nabla \cdot J_{sg} + \sigma_{\text{irr},g} + \sigma_{\text{colli},g-e} + \sigma_{\text{colli},g-h} \quad (79)$
Combined (Electron + Hole + Phonon)	energy	$\frac{\partial u}{\partial t} = -\nabla \cdot \mathcal{Q} + \mathbf{JF} + \frac{\partial u}{\partial t} \Big _{\text{colli}} \quad (80)$
	entropy	$\frac{ds}{dt} = \nabla \cdot J_s + \sigma \quad (81)$

As seen in Table 8, the Boltzmann Transport Equation is employed together with the phenomenological relationship [14]. The energy balance equations for electrons, holes and phonon are computed using Gibbs law. Based on these formulation, the entropy flux and entropy generation for electrons, holes and phonons in the well and barrier of the superlattice thermoelement are developed and they are summarized in Table 9.

5.3.2. Discussion

The simulation results presented herein are for the transient heat transport in the direction of hot and cold junctions of $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ thin-film thermoelectric element. Venkatasubramanian et al. [50] reported the properties and dimensions of a prototype superlattice, and the values are tabulated in Table 10. In the presence of high electric fields within the thin film structure, lesser equilibrium between electrons-phonons or holes-phonons is expected. Thus, the collision effect from electrons and phonons is increased.

Following the classical T-s diagram methodology, which demarcates accurately how energy input to a device is consumed in overcoming the dissipative and finite-rate heat

transfer losses, the Figures 19 (a) and 19 (b) show the temperature and entropy fluxes of electrons, holes and phonons for a set of cold and hot temperatures of 270K and 300K, respectively. As can be seen, the electrons flow in n-type element (cold to hot junctions or negative Seebeck coefficient) which is opposite to the current flow, whilst the holes flow through the p-type element (cold to hot junctions or positive Seebeck coefficient) in the same direction of current flow. As the electrons of n-type thin film and holes of p-type thin film are known to have lesser dissipative losses, the based area of cold reservoir is larger, i.e. $T_L \times AD$ [in Figure 19 (a)], reflecting a larger potential for cooling.

However, the accompanying phonons, which have larger internal and dissipative losses, reduce the cooling capacity, i.e., $(T_L \times OE)$ at the p-arm and $(T_L \times OH)$ at the n-arm, as shown in Figure 19 (a).

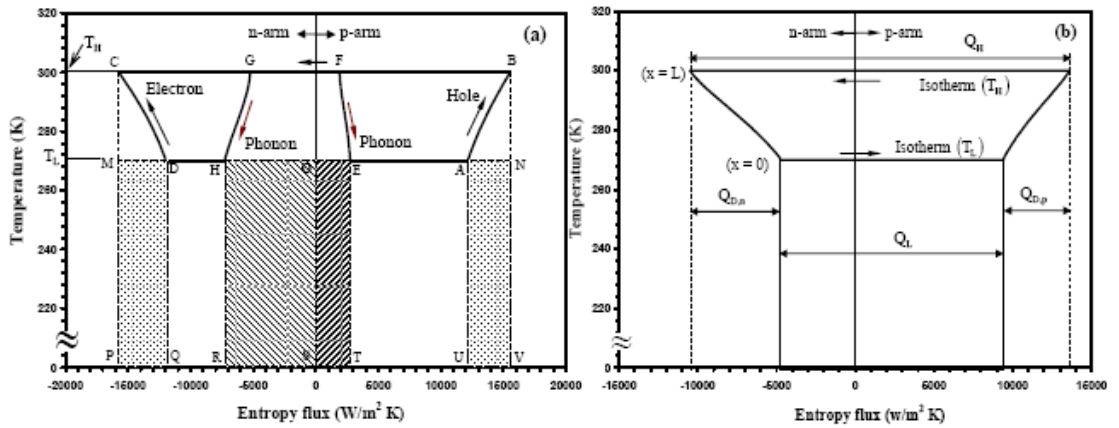


Figure 19. The temperature-entropy diagram of a thin film thermoelectric couple (both the p and n-type thermoelectric element are shown here) at optimum cooling capacity or maximum COP.

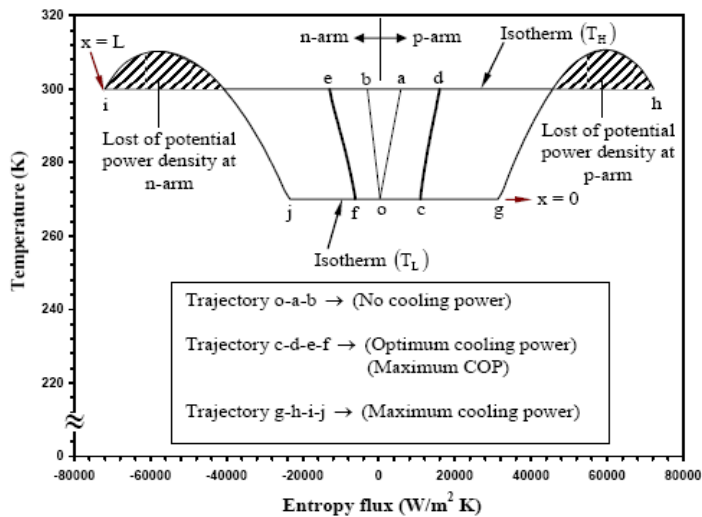


Figure 20. Temperature-entropy flux (T-J_s) diagrams for the thin film thermoelectric cooler at three operating points.

Table 9. The energy, entropy flux and entropy generation equations of the well and the barrier [4]

well			
Particles	Energy balance	Entropy flux W/m ² K	Entropy generation W/m ³ K
Electron	$c_w \frac{\partial T_{w,e}}{\partial t} = \nabla \cdot (\lambda_{w,e} \nabla T_{w,e}) + \frac{J_{w,e}^2}{\sigma'_{w,e}} + c_w \left. \frac{\partial T_{w,e}}{\partial t} \right _{colli}$	$-\frac{\lambda_{w,e} \nabla T_{w,e}}{T_{w,e}} + \frac{\pi_e J_{w,e}}{T_{w,e}}$	$-\lambda_{we} \nabla T_{we} \cdot \nabla \left(\frac{1}{T_{we}} \right) + \frac{J_{we}^2}{T_{we} \sigma'_{we}} + \frac{c_w}{T_{we}} \left. \frac{\partial T_{we}}{\partial t} \right _{colli}$
Hole	$c_w \frac{\partial T_{w,h}}{\partial t} = \nabla \cdot (\lambda_{w,h} \nabla T_{w,h}) + \frac{J_{w,h}^2}{\sigma'_{w,h}} + c_w \left. \frac{\partial T_{w,h}}{\partial t} \right _{colli}$	$-\frac{\lambda_{w,h} \nabla T_{w,h}}{T_{w,h}} + \frac{\pi_h J_{w,h}}{T_{w,h}}$	$-\lambda_{wh} \nabla T_{wh} \cdot \nabla \left(\frac{1}{T_{wh}} \right) + \frac{J_{wh}^2}{T_{wh} \sigma'_{wh}} + \frac{c_w}{T_{wh}} \left. \frac{\partial T_{wh}}{\partial t} \right _{colli}$
Phonon	$c_w \frac{\partial T_{w,g}}{\partial t} = \nabla \cdot (\lambda_{w,g} \nabla T_{w,g}) + c_w \left. \frac{\partial T_{w,g}}{\partial t} \right _{colli}$	$-\frac{\lambda_{w,g} \nabla T_{w,g}}{T_{w,g}}$	$-\lambda_{wg} \nabla T_{wg} \cdot \nabla \left(\frac{1}{T_{wg}} \right) + \frac{c_w}{T_{wg}} \left. \frac{\partial T_{wg}}{\partial t} \right _{colli}$
Combined	$c_w \frac{\partial T_w}{\partial t} = \nabla \cdot (\lambda_w \nabla T_w) + \frac{J_w^2}{\sigma'_w} + c_w \left. \frac{\partial T_w}{\partial t} \right _{colli}$	$-\frac{\lambda_w \nabla T_w}{T_w} + \frac{\pi J_w}{T_w}$	$-\lambda_w \nabla T_w \cdot \nabla \left(\frac{1}{T_w} \right) + \frac{J_w^2}{T_w \sigma'_w} + \frac{c_w}{T_w} \left. \frac{\partial T_w}{\partial t} \right _{colli}$
barrier			
	Energy balance	Entropy flux	Entropy generation
Electron	$c_b \frac{\partial T_{b,e}}{\partial t} = \nabla \cdot (\lambda_{b,e} \nabla T_{b,e}) + c_b \left. \frac{\partial T_{b,e}}{\partial t} \right _{colli}$	$-\frac{\lambda_{b,e} \nabla T_{b,e}}{T_{b,e}}$	$-\lambda_{be} \nabla T_{be} \cdot \nabla \left(\frac{1}{T_{be}} \right) + \frac{c_b}{T_{be}} \left. \frac{\partial T_{be}}{\partial t} \right _{colli}$

Particles	Energy balance	Entropy flux W/m ² K	Entropy generation W/m ³ K
Hole	$c_b \frac{\partial T_{b,h}}{\partial t} = \nabla \cdot (\lambda_{b,h} \nabla T_{b,h}) + c_b \left. \frac{\partial T_{b,h}}{\partial t} \right _{colli}$	$-\frac{\lambda_{b,h} \nabla T_{b,h}}{T_{b,h}}$	$-\lambda_{bh} \nabla T_{bh} \cdot \nabla \left(\frac{1}{T_{bh}} \right) + \frac{c_b}{T_{bh}} \left. \frac{\partial T_{bh}}{\partial t} \right _{colli}$
Phonon	$c_b \frac{\partial T_{b,g}}{\partial t} = \nabla \cdot (\lambda_{b,g} \nabla T_{b,g}) + c_b \left. \frac{\partial T_{b,g}}{\partial t} \right _{colli}$	$-\frac{\lambda_{b,g} \nabla T_{b,g}}{T_{b,g}}$	$-\lambda_{bg} \nabla T_{bg} \cdot \nabla \left(\frac{1}{T_{bg}} \right) + \frac{c_b}{T_{bg}} \left. \frac{\partial T_{bg}}{\partial t} \right _{colli}$
Combined	$c_b \frac{\partial T_b}{\partial t} = \nabla \cdot (\lambda_b \nabla T_b) + c_b \left. \frac{\partial T_b}{\partial t} \right _{colli}$	$-\frac{\lambda_b \nabla T_b}{T_b}$	$-\lambda_b \nabla T_b \cdot \nabla \left(\frac{1}{T_b} \right) + \frac{c_b}{T_b} \left. \frac{\partial T_b}{\partial t} \right _{colli}$

Table 10. The thermo-physical properties of thin film thermoelectric element

Sample	Electrical resistivity Ω-m	Seebeck coefficient μV/°C	Phonon Thermal conductivity W/m K	Electron Thermal conductivity W/m K
Bi ₂ Te ₃ /Sb ₂ Te ₃ (P-arm) [50]	1.2×10 ⁻⁵	238	0.22	0.37
Bi ₂ Te ₃ /Bi ₂ Te _{2.83} Se _{0.17} (n-arm) [50]	1.23×10 ⁻⁵	-238	0.58	0.37

Taking the phonon losses into account, the combined diagram gives the flow of current density, J , from p to n arms, as given by the close loop “a-b-c-d-a” which establishes the T-s diagram (denoted by the full lines) and this is shown in Figure 19 (b). Thus, the cooling capacity is given by the area, $T_L \times (ad)$, and the heating power is given by $T_H \times (bc)$, and power input is the area bounded by their differences, i.e., $T_H \times (bc) - T_L \times (ad)$. The net coefficient of performance (COP) is the ratio of useful effect to energy input which is simply given by $T_L \times (ad) / [T_H \times (bc) - T_L \times (ad)]$.

Figure 20 constitutes the temperature-entropy flux plots for different electric fields of the thin film thermoelectric cooler, where the close loop o-a-b-a defines zero cooling capacity and zero COP at very low electric field (0.05 A). The close loop c-d-e-f-c represents the maximum COP or the optimum cooling capacity at high electric field (6 A). The close loop g-h-i-j-g indicates the T-s diagram for the maximum cooling capacity.

The effect of collisions arising from electrons and phonons (n-arm) and holes and phonons (p-arm) is compared with the same cycle without the collision terms for different currents and these simulation results are tabulated in Table 11. For a given dimensions of thin film thermoelectric element [50] and a current range of 1 - 10 A [50], the contribution of collision dissipation is found to be less than 7.4% of the total energy input. It is noted that the COP increases with the current density increases in the thin-films, reaching an optima at 2 A when the energy lost to collision effect is 11.8%. However, at higher input current densities, the cooling capacity of the thin-films decreases to near zero due to three key effects, namely (i) the Joulean heat loss, (ii) the Fourier loss and (iii) the collision loss. The contribution from collisions becomes increasing important at these high current densities, reaching as high as 32% of the input power.

As depicted on a T-s diagram, the comparative results are shown in Figure 21. Cycle A-B-C-D-A is without collision terms and the cycle is superimposed onto the cycle A'-B'-C'-D'-A' that includes collision effect.

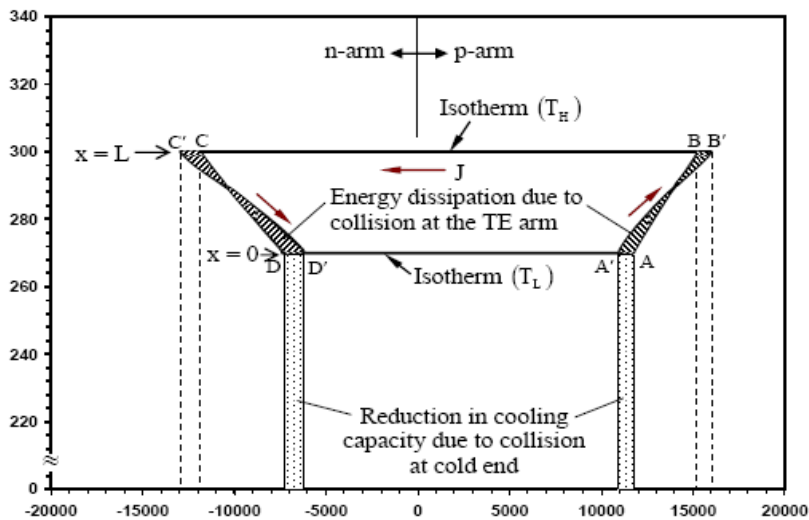


Figure 21. The temperature-entropy diagrams of p and n-type thin film thermoelectric elements. The close loop A'-B'-C'-D' shows the T-s diagram when the collision terms are taken into account and the close loop A-B-C-D indicates the T-s diagram when collisions are not included. Energy dissipation due to collisions is shown here.

Table 11. Performance analysis of the thin film thermoelectric cooler (excluding collisions effect and including collisions effect) [56]

I kA/cm ²	With out collision effects			With collision effects			Input energy loss due to collisions (%)
	J _{s, hj} W/cm ² K	J _{s, cj} W/cm ² K	COP	J _{s, hj} W/cm ² K	J _{s, cj} W/cm ² K	COP	
40	0.55	0.281	0.85	0.57	0.28	0.78	7%
60	1.62	0.96	1.14	1.70	0.95	1.0	12%
72	2.30	1.47	1.35	2.41	1.42	1.13	16%
80	2.75	1.80	1.40	2.89	1.72	1.15	18%
100	3.91	2.56	1.43	4.13	2.43	1.12	22%
120	5.16	3.40	1.45	5.44	3.08	1.04	27%
160	7.85	5.10	1.40	8.20	4.19	0.85	35%
240	13.4	7.60	1.04	14.41	5.56	0.53	45%
For the case of optimum operation 2 A, the area under the T-s diagram are (Figure 6)							
Q _{H, ncolli}			200 mW		Q _{H, colli}		208 mW
Q _{L, ncolli}			120 mW		Q _{L, colli}		112 mW
P _{input, ncolli} = Q _H - Q _L			80 mW		Pinput, colli = Q _H - Q _L		96 mW
Loss due to collisions Q _{colli} = 16 mW							

At the optimal conditions, the net heat dissipation at the hot junction with and without collisions are computed to be 208 mW and 200 mW, respectively, whilst the corresponding cooling capacities are 112 mW and 120 mW, respectively. The effect of collision reduces the COP of the thin film thermoelectrics by 20%. This increase is attributed to two effects, namely, (i) the reduction of cooling power as indicated by the shaded area, $T_L \times (AA' + DD')$, and secondly, (ii) the energy input is increased by shaded area, $T_H \times (CC' + BB')$.

All results presented herein are the predictions of the performances of next generation solid state micro-coolers. As it is beneficial to compare the predictions with experiments, the measured ΔT across the hot and cold junctions of a *p-type* thin film superlattice [50] is depicted against the imposed current density, as shown in Figure 22. For this comparison, the thermophysical properties of the thin film thermoelectric element are extracted from Table 9. As seen from comparison, the proposed BTE model with the collision effect shows good agreement with the experimental data whilst the conventional thermoelectric model [1, 21] over predicts the absolute cooling power and could not capture the true behaviors of thin-films.

5.3.3. Summary of Section 5.3

This section presents the uniquely combined conservations laws where the classical irreversible (Joule heat and conduction) and electrons/holes-phonons collision losses are captured. A finite difference code for solving the BTE for finite time collisions of the particles within the thin-film super-lattice thermo-electric cooler has been demonstrated. For a

broad range of current densities, the dissipative contributions from both the electron-phonons and holes-phonon collisions within the thin-film, have been derived theoretically with BTE approach and the actual data from literature were incorporated here for analysis.

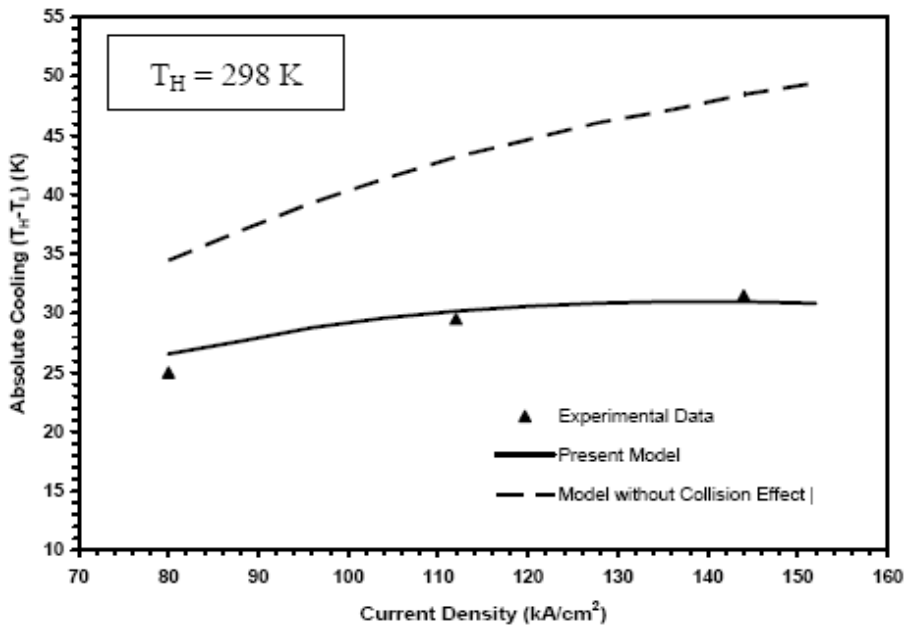


Figure 22. Absolute cooling ($T_H - T_L$) as a function of current density in a p-type thin film superlattice. Hence ($\blacktriangle$) defines the experimental data for p-type superlattice device [6], ($\bullet$) represents the simulation of present modelling for p-type superlattice, where the energy transports between holes and phonons are taken into account and (—) depicts the simulation of p-type thin film superlattice without energy transfer between phonons and holes.

Given a finite dimension of the thermo-element, the COP exhibits an optimal behaviour at medium current density level where the collision dissipation is about 10% of the power input, and increasing the current densities beyond the optimum point would accelerate the increase in the dissipative losses from collision and mitigates the COP values to naught. The practical and pedagogical values of a novel Temperature-entropy flux diagram for thin film thermoelectrics have also been demonstrated. To predict the performance of the thin film thermoelectric device, it is important to understand the thermal behavior, which occurs in nanosecond range. This is also useful to design a micro-structure and understand the mechanisms of phonon transport.

CONCLUSIONS

In this chapter, a universal thermodynamic framework for both the macro and micro scale modeling of both adsorption and thermoelectric coolers has been derived and their applications have been demonstrated. It is based on the Boltzmann Transport Equation (BTE) approach, incorporating the classical Gibbs law and the energy conservation equation where their amalgamation yields the form of the temperature-entropy flux (T-s) formulation. This T-

s formulation demonstrates the energy flows of adsorption and thermoelectric cooling systems and their transformation into useful and dissipative effects. The modeling is also applied to the energy flows and performance investigation of the solid state cooling devices such as the thermoelectric coolers, the pulsed-mode thermoelectric coolers and the thin-film superlattice thermoelectric device. It demonstrates the regimes of entropy generation that are associated to irreversible transport processes arising from the spatial thermal gradients, as well as the contributions from the collisions of electrons, phonons and holes in a micro-scaled type solid state cooler. The pedagogical value of the general temperature-entropy flux diagram is also demonstrated. The area under the process paths of a thermoelectric element indicates how energy input has been consumed by the presence of both the reversible (Peltier, Seebeck and Thomson) and the irreversible (Joule and Fourier) effects.

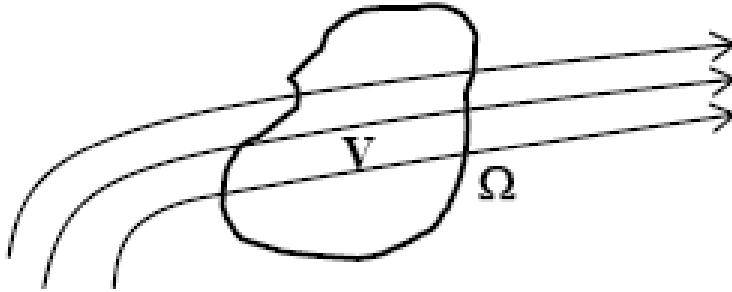
APPENDIX.

GAUSS THEOREM APPROACH

V is the volume of an element (solids, liquids, viscoelastic materials and rigid bodies) which is bounded by a closed surface Ω . The differential element of the volume and surface area is written as dV and $d\Omega = n d\Omega$ respectively, where n is the unit normal to Ω and is defined as pointing out of V . with this notation the Gauss' Theorem is written as,

$$\int_V \nabla \cdot \mathbf{X} dV = \int_{\Omega} \mathbf{X} \cdot \vec{n} d\Omega = \int_{\Omega} \mathbf{X} \cdot d\mathbf{\Omega} \quad (A1)$$

where $\mathbf{X}$ is any sufficiently smooth vector field and is defined on the volume V and the boundary surface Ω as shown below.



Balance equations represent the fundamental physical laws and these include the conservation of mass, momentum, energy and some form of the second law of thermodynamics, entropy. At any instant, the mass is taken to occupy the volume V and has a bounding surface given by Ω . The general form of the conservation laws is given by,

The time rate of change of a quantity = actions of the surroundings on the surface of V + the actions of the surroundings on the volume itself.

The word “actions” means the change of quantity. Logically, the general form of the conservation principle always include all possible ways to influence the time rate of change of the quantity of interest.

The Thomson effect in equation (55)

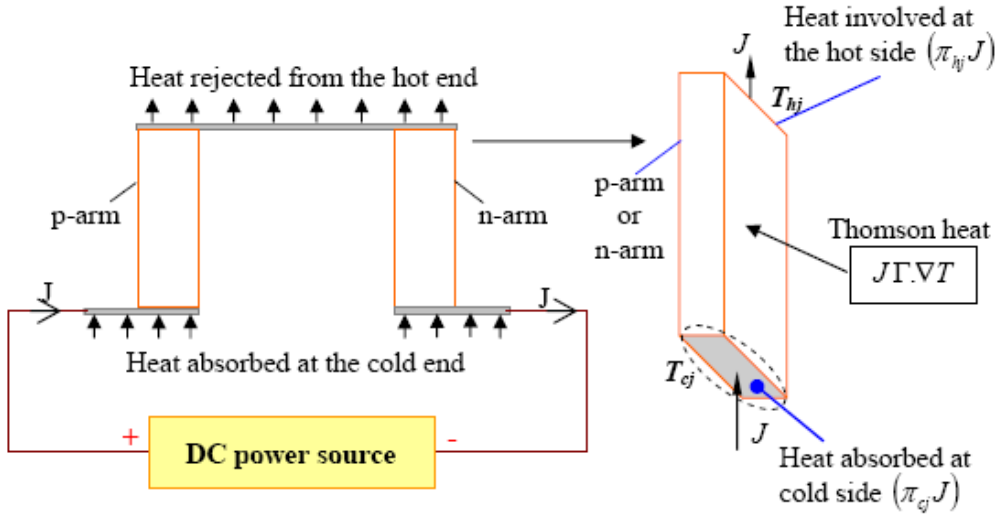


Figure B1. A thermoelectric element showing the transportation of heat and current.

The electrical and thermal currents are coupled in a thermoelectric device. The Peltier coefficient of the junction is a property depends on both the materials and is the ratio of power evolved at the junction to the current flowing through it. When current is applied to a thermoelectric element, thermal energy is generated or absorbed at the junction due to Peltier effect. The Seebeck coefficient depends on temperature and this is different at different places along the TE material. So the thermoelectric element is thought of as a series of many small Peltier junctions and each of which is generating or absorbing heat. This is called Thomson power evolved per unit volume $(J \nabla T)$.

In a Thomson effect, heat is absorbed or evolved when current is flow in a thermoelectric element with a temperature gradient. The heat is proportional to both the electric current and the temperature gradient. The proportionality constant is known as Thomson coefficient.

If the heat current density of a thermoelectric element is only a result of temperature gradient and the electric current density occurs due to electric potential gradient. Then, $\mathbf{J}_q = -\lambda \nabla T$ and $\mathbf{J} = \sigma \nabla \phi$. Using equation (3.1) the energy balance equation of a thermoelectric element is obtained.

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + \frac{J^2}{\sigma'} \quad (\text{B1})$$

The first term of right hand side of equation (B1) is Fourier conduction term and the second term indicates the Joule heat. But in a thermoelectric cooling device, the junctions are

maintained at different temperatures and an electromotive force will appear in the circuit. This flow of heat has a tendency to carry the electricity along the thermoelectric arm.

When two or more irreversible processes take place in a thermodynamic system, they may interfere with each other. A completely consistent theory of thermoelectricity has been developed using the Onsager symmetry relationship (Onsager, 1931). When a current is applied to a thermoelectric device, the heat current of TE arm is developed as a result of electric current and temperature gradient (cross flow) and the electric current is generated due to electric potential and the temperature gradient.

Using the thermodynamic-phenomenological treatment, the heat current density is

$$\mathbf{J}_q = -\frac{Q_o}{F} J - \lambda \nabla T, \text{ and the electric current density in amp per m}^2 \text{ becomes}$$

$$J = \sigma' \nabla \phi + \frac{\sigma' Q_o}{FT} \nabla T$$

$$\nabla \phi = \frac{J}{\sigma'} - \frac{Q_o}{FT} \nabla T$$

Equation (55) now becomes

$$\begin{aligned} \rho c_p \frac{\partial T}{\partial t} &= -\nabla \cdot \left(-\lambda \nabla T - \frac{Q_o}{F} J \right) + J \left(\frac{J}{\sigma'} - \frac{Q_o}{FT} \nabla T \right) \\ &= \nabla \cdot (\lambda \nabla T) + \frac{J}{F} \nabla Q_o + \frac{J^2}{\sigma'} - \frac{J Q_o}{FT} \nabla T \\ &= \nabla \cdot (\lambda \nabla T) + \frac{J^2}{\sigma'} + \frac{JT}{F} \nabla \left(\frac{Q_o}{T} \right) \\ \rho c_p \frac{\partial T}{\partial t} &= \nabla \cdot (\lambda \nabla T) + \frac{J^2}{\sigma'} + \frac{JT}{F} \nabla \left(\frac{Q_o}{T} \right) \end{aligned} \quad (\text{B2})$$

Hence the third term $\frac{JT}{F} \nabla \left(\frac{Q_o}{T} \right)$ occurs due to current flow for temperature gradient (cross flow) and heat flow for the electric potential gradient (reciprocal effect). This term indicates the least dissipation of energy [14]

$\frac{JT}{F} \nabla \left(\frac{Q_o}{T} \right) = \frac{JT}{F} \nabla(s)$, where $s \left(= \frac{Q_o}{T} \right)$ is the entropy (in J/mol.K) along the thermoelectric arm.

Hence

$$\begin{aligned}
 \frac{JT}{F} \nabla \left(\frac{Q_o}{T} \right) &= \frac{JT}{F} \nabla(s) \\
 &= \frac{JT}{F} \frac{\partial s}{\partial T} \cdot \nabla T \\
 &= J \left(\frac{T}{F} \frac{\partial s}{\partial T} \right) \cdot \nabla T
 \end{aligned}$$

The Thomson heat is defined as

$$\begin{aligned}
 Q_T &= J \left(\frac{T}{F} \frac{\partial s}{\partial T} \right) \cdot \nabla T, \\
 Q_T &= J(-\Gamma) \nabla T
 \end{aligned}$$

where Thomson coefficient $-\Gamma = \frac{T}{F} \frac{\partial s}{\partial T}$.

The temperature gradient is bound to cause a certain degradation of energy by conduction of heat. The electric potential gradient must cause an additional degradation of energy, making the total rate of increase of entropy along the thermoelectric arm.

So the electric current due to temperature gradient (cross flow) and the heat current due to electric potential gradient (reciprocal effect) indicate the Thomson effect, which will be discussed in the following section. Without Thomson effect, the physics of thermoelectricity is not completed.

Derivation of equation (55)

The energy balance of the thermoelectric arm is

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + \frac{J^2}{\sigma'} - \mathcal{I} \nabla T \quad (B3)$$

Expression of the third term

$$\text{Using Kelvin relations } \left[\Gamma = \frac{\pi}{T} - \frac{\partial \pi}{\partial T}, \text{ and } \pi = \alpha T \right]$$

$$\mathcal{I} \nabla T = J \left(\frac{\pi}{T} - \frac{\partial \pi}{\partial T} \right) \cdot \nabla T \quad (B4)$$

$$\nabla \pi = \nabla \pi|_T + \frac{\partial \pi}{\partial T} \cdot \nabla T \quad (\text{de Groot and Mazur, 1962})$$

From equation (B4) we have

$$\begin{aligned}
J\Gamma\nabla T &= J\frac{\pi}{T}\cdot\nabla T - J\frac{\partial\pi}{\partial T}\cdot\nabla T \\
&= J\frac{\pi}{T}\cdot\nabla T - J(\nabla\pi - \nabla\pi|_T) \\
&= J\frac{\pi}{T}\cdot\nabla T - J\nabla\pi + J\nabla\pi|_T \\
&= J\alpha\nabla T - J\nabla(\alpha T) + JT\nabla\alpha|_T \\
&= J\alpha\nabla T - J\alpha\nabla T - JT\frac{\partial\alpha}{\partial T}\cdot\nabla T + JT\nabla\alpha|_T \\
&= -JT\frac{\partial\alpha}{\partial T}\cdot\nabla T + JT\nabla\alpha|_T
\end{aligned}$$

Equation (B3) is now written as

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + \frac{J^2}{\sigma'} - JT \frac{\partial\alpha}{\partial T} \cdot \nabla T + JT \nabla\alpha|_T \quad (\text{B5})$$

Equation (B5) is same as equation (55).

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Chapter 4

MICROBES AND BUILDING MATERIALS

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ABSTRACT

Microbes – including bacteria, fungi, algae and lichen – are successful invaders of all types of building materials in indoor and outdoor environment on modern and historic buildings. With respect to the numerous problems caused by biogenic spoilage and deterioration of building materials our contribution will present (a) the most important groups of chemoheterotrophic and chemolithotrophic bacteria, cyanobacteria, fungi and lichens occurring on rock, plaster, mortar, paint coatings, plaster board and other building materials; (b) the mechanisms and destruction phenomena caused by microbes ranging from mere esthetical spoilage to significant material losses (c) the environmental factors – humidity, ventilation, nutrient availability - enhancing or inhibiting microbial growth, (d) the state of the art methods for detection and analysis of biodeteriorative organisms and processes especially highlighting the molecular techniques as e.g. genetic fingerprinting of microbial communities and single microbial species (DGGE, RFLP) or quantification of microbes in materials by real time PCR, (e) possible strategies for antimicrobial treatments and preventive measures with focus on pros and cons of hydrophobic treatments, nano-technology based paint coatings and novel disinfectants. The contribution will aim to researchers in the fields of material sciences and building physics as well as to practitioner of building industries, thus descriptions on microbiology and molecular techniques will be given on a high quality but generally understandable level.

1. INTRODUCTION

Substrates used for building materials as stones, stuccos, mortars, plasters, frescoes and ceramic products, all of them employed in architecture, are subjected to biodeterioration, thus

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causing irreparable loss to our cultural heritage (Koestler 2000). Besides chemical and physical factors, microorganisms play a major role in building materials decay. They can modify the rates and mechanisms of chemical and physical weathering of stones and other exposed materials. Through the recognition and understanding of the microorganisms involved in biodeterioration as well as the deterioration processes induced by microorganisms themselves, it will be possible to prevent and/or solve some of the associated problems and thereby to avoid further damage to building materials and monuments.

With this goal, there is a need to collect detailed information about the identity of microorganisms colonizing building materials as well as about the type, intensity and extend of weathering damage caused by or in relation with the colonization of the detected microorganisms. However, this information is difficult to collect and catalogue, since there are a huge number of studies reporting on the deterioration of many different building substrata under different climatic conditions. Furthermore, one has to summarize results obtained by using many different techniques, i.e. cultivation-dependent and -independent methodologies, microscopy, etc, which are not always delivering coherent data.

In this contribution we summarize the most important groups of microorganisms occurring on rock, plaster, mortar, paint coatings, plaster board and other building materials; the mechanisms and destruction phenomena caused by microbes ranging from mere esthetical spoilage to significant material losses; the environmental factors enhancing or inhibiting microbial growth; the state of the art methods for detection and analysis of biodeteriorative organisms and processes, and last but not least the possible strategies for antimicrobial treatments and preventive measures. The contribution will aim to researchers in the fields of material sciences and building physics as well as to practitioner of building industries.

2. MICROORGANISMS COLONIZING ROCK, PLASTER, MORTAR, PAINT COATINGS, PLASTER BOARD AND OTHER BUILDING MATERIALS

Inorganic substrates are preferentially colonized by autotrophic microorganisms. Nevertheless, inorganic materials are not completely lacking organic substances. The presence of organic matter on the surface of the substrates is very common, especially if the objects are exposed to open air. Atmospheric pollution, pollen, previous biological colonization, old treatments (waxes, oils casein, glues, etc) or new ones (protective coatings, consolidants) and the contribution by animals (birds, insects) favor the development of heterotrophic microflora. For this reason the dogma of primary colonization by phototrophic organisms is not longer valid. Especially on surface with low water availability fungi may well be the first colonizers able to stand desiccation and low nutrient availability.

2.1. Scenario of Microbial Settlement in Building Materials and Monuments

Stone and related building materials provide a variety of ecological niches, allowing colonization by photoautotrophic and chemolithotrophic microorganisms as well as heterotrophic fungi and bacteria. Nutrients for heterotrophic bacteria are available from

metabolites of autotrophic bacteria, from airborne organic contamination and dripping water, from animal feces and from organic compounds sometimes present in the substrates themselves. Concerning wall paintings, pigments are often suspended in water or organic binders as oil, casein, skin glue, mostly together with organic binders such as casein, egg yolk and milk before application on the damp lime plaster.

2.2. Bacteria

Among the first colonizers on mineral materials are chemolithotrophic bacteria (which use inorganic and/or organic substrates indifferently) that induce biological corrosion of the building material by the release of acids (Karpovich-Tate and Rebrikova, 1991). The occurrence of chemoorganotrophic bacteria has also been investigated for their capacity to produce organic acids that solubilize the mineral components of the materials and affect the colour of the substrate surface (Urzi et al. 1991; Tiano 1998). They are commonly found on inorganic substrates containing traces of organic compounds which settle on the masonry surface (Saiz-Jimenez, 1995, 1997; Zanardini et al. 2000). Heterotrophic bacteria include a variety of genera such as *Alcaligenes*, *Arthrobacter*, *Bacillus*, *Paenibacillus*, *Flavobacterium*, *Pseudomonas*, *Micrococcus*, *Staphylococcus*, *Nocardia*, *Mycobacterium*, *Streptomyces* and *Sarcina*, which are the most frequent species isolated from wall paintings (Bassi et al. 1986; Heyrman et al. 1999; Saiz Jimenez, 1997; Ciferri, 1999; Pepe et al. 2008; Suihko et al. 2007). Recently, the use of a polyphasic approach for the detection and identification of the bacteria isolated from biodeteriorated frescoes, as well as the study of the microbial community by molecular techniques, highlighted several new genera previously not detected with conventional methods, indicating the large biodiversity found in such inorganic substrates (Rölleke et al. 1996; 1998; 2000; Gurtner et al. 2000; Daffonchio et al. 2000; Saiz-Jimenez and Laiz, 2000; Schabereiter-Gurtner et al. 2001a, 2001b; Imperi et al. 2007; Portillo et al. 2008).

The alterations produced by bacteria are no different from those of purely chemical origin: black crust, powdering, exfoliation, patinas, production of crystals.

2.3. Fungi

Fungi cause staining on and within stones, mortar, plaster and mural paintings, frequently with dark spots. Fungi with dark melanized cell walls are the most harmful microorganisms associated with stone and monuments biodeterioration. Species belonging to the genera *Coniosporium*, *Sarcinomyces*, *Trimmatostroma*, *Hortaea*, *Cladosporium*, *Exophiala*, *Capnobotryella* and *Alternaria* are commonly isolated from sun-exposed surfaces, where they are associated to biological alterations (Sterflinger 1995; Sterflinger and Krumbein, 1997a; 1997b; Sterflinger, 2000; Sterflinger and Prillinger 2001; Urzi et al. 1998). They can remain metabolically active for long periods of time, even if low amounts of nutrients are available (Sterflinger, 1998). The staining caused by these fungi is due to melanins encrusting the cell wall. The mycelium penetrates deeply inside the plasters of wall paintings and can cause loss of cohesion and detachment of paint layers. In calcite stones, hyphae penetrate the calcite crystals, not only along the crystal planes, and the stone surfaces appear clearly etched when

observed under SEM. Some fungi are endolithic and produce pitting phenomena, and the filamentous structure of hyphae makes their penetration into fissures and pores easier. The main deterioration of building materials caused by fungi is caused by chemical actions, as solubilization correlated with a decrease in pH, due to the production of acids. Fungi can produce carbonic acid and many organic acids as citric, oxalic, gluconic, glucuronic, tartaric, malic and fumaric acid (Braams, 1992).

2.4. Cyanobacteria and Algae

Cyanobacteria colonize a wide variety of terrestrial habitats, including rocks, hot and cold desert crusts, as well as modern and ancient buildings. The role of cyanobacteria in the deterioration of surfaces of historic buildings has been the subject of several recent studies (Gaylarde and Gaylarde, 2000; Crispin and Gaylarde, 2005). The most important factors conditioning the establishment of algae are light intensity, humidity, temperature and pH. Cyanobacteria (or blue-green algae) are often the first colonizers of stone because they need only light, few inorganic compounds, prefer an alkaline substrate (with a pH in between 7 and 8) and are adapted to changing conditions of humidity and complete desiccation (Ortega-Calvo et al. 1991). Many Cyanobacteria are surrounded by gelatinous sheath able to absorb and retain water for a long time. Algae contribute to stone deterioration by respiration processes, by retaining water which expands in freeze-thaw cycles or by releasing acids or chelating compounds.

Depending on the relation with the substrate, algae and other microorganisms can be divided into two groups. The first group consists of the epilithic microorganisms, which are able to grow on exposed surfaces. They form patinas or sheets of different thickness, consistency and colour. The second group consists on the endolithic microorganisms, colonizing the interior of substrates, as stones, mortar, brick and plaster. The endolithic group of microorganisms includes: a) the chasmoendolithic, living inside preformed fissures and cavities open to the stone surface (Ascaso et al. 1998); b) the cryptoendolithic, colonizing structural cavities within the porous rocks and forming a coloured layer parallel to the surface at a depth of some millimeters. They have been described as occurring under extreme environmental conditions, but have been found also in monuments and marbles in quarries suggesting a greater widespread of these microorganisms (Saiz-Jimenez et al. 1990); c) the euendolithic, actively penetrating into the substrate (De los Rios et al. 2004). They are able to actively dissolve carbonates, penetrating into the substrate and forming microcavities.

2.5. Lichens

Lichens are regarded as primary colonizers and very aggressive agents in biodeterioration of stone and man-made substrata as glass, plaster or roof tiles (Gehrmann et al. 1992; Krumbein et al. 1998; Lisci et al. 2003). They are able to survive at varying water content, and this enables them to live in extreme environments. Lichens growing on stone are called *saxicolous*. They can penetrate into stone (several millimeters) with all hyphae of the lower cortex or with their attachment organs (holdfast and rhizines). They can be epilithic or endolithic. Lichens exert a physical force on the substrate by contraction and expansion of

their thalli under succession of dry-wet periods. They can also produce chemical damage by the generation of carbonic acid, the excretion of oxalic acid and the production of lichen compounds with chelating abilities (Oksanen, 2006).

3. MECHANISMS AND DESTRUCTION PHENOMENA CAUSED BY MICROBES RANGING FROM MERE ESTHETICAL SPOILAGE TO SIGNIFICANT MATERIAL LOSSES

Microbial-induced deterioration processes cause structural as well as aesthetic damage to building materials. The formation of pigmented biofilms, biomineralisation, the dissolution of metals by acids and chelating agents, the degradation of organic binders and consolidants, and the degradation and discoloration of pigments are some of the damaging phenomena triggered by microbial growth. Figure 1 shows some examples of deteriorative phenomena caused by microorganisms.

Bacteria and fungi produce a wide variety of pigments ranging from light yellow, orange, deep purple and green to dark brown and black. The orange and red colors are due to the formation of carotenes sheltering the cell against high UV-radiation and salt stress. Pink to violet stains frequently occur on salty walls – e.g. semi-basements – because the bacteria that are salt-loving or highly salt tolerant typically produce those pigments. Orange stains of sandstone or marble macroscopically resemble iron oxide and a microbiological and chemical analysis is needed to clarify their origin (Sterflinger et al. 1999). The biogenic pigments are very stable over long periods of time if they are incorporated into the calcium matrix of stone and are still visible after the organism itself has died due to changing environmental conditions or biocide treatments. Orange pigments often occur in combination with crusts made of calcium oxalate (whewellite and weddellite), the latter being the result of oxalate excretion by bacteria, lichen or fungi.

Many fungi produce melanin (mainly DHN melanin) that does not only protect against UV-radiation but also against desiccation, chemical attack or salt stress and that plays a major role for their ability to penetrate hard substrates. The dark and rigid crusts are optically similar to black gypsum crust that frequently occurred on old monuments and facades in industrial areas with high SO₂ pollution. Also algae and cyanobacteria, normally appearing green due to the photosynthetic pigment chlorophyll can appear dark brown or even black when their biofilms are completely dry. However, after re-wetting such biofilms become deeply green again and the organisms gain full physiological activity within a few minutes.

The formation of biofilms on and within building material, however, is not only an esthetical problem for the monuments. As mentioned above bacteria and fungi are able to produce a wide range of organic acids that attack carbonate and dissolve metal ions leading to significant material loss or diagenesis of minerals. Not only carbonated rocks but also granite, feldspar, aluminosilicates and silicates, quartz and glass are attacked their organic acids (Sterflinger, 2000). Inorganic acids are produced by chemolithotrophic bacteria that derive their energy from oxidation of ammonium or reduced sulfur compounds resulting in the formation of nitric and nitrous and sulfuric and sulfur acids which are highly corrosive for natural stone as well as concrete and cement.



Figure 1. Examples of deteriorative phenomena caused by microorganisms.

Moreover, the biogenic formation of hygroscopic salts – e.g. ammonium salts – increases the water uptake of the material thus enhancing physical and chemical weathering processes. The formation of extracellular polymers (EPS) in which bacterial cells embed themselves when forming biofilms also increases water retention inside of materials and hampers water diffusion. As a consequence the material retains water for a longer period of time and biological growth is even enforced. The gel-like EPS layers formed by bacteria and also by

algae can also exhibit a mechanical stress on paint layers or within stone and plaster because they reflect changing water availability by shrinking and swelling. High pressure can be exhibited by micro-colonial fungi growing inside of crystalline rock (granite or marble) leading to detachment of single crystals and finally to significant material loss (Sterflinger and Krumbein, 1997a). Chipping and exfoliation of large areas of rock material can well be the consequence of internal surface parallel biofilms. Especially algae and cyanobacteria form such biofilm inside of the materials – under plaster but also inside of natural stone.

Material alteration and final loss of material always is a combination of physical chemical and biological processes influencing each other. A clear separation is not possible and synergistic effects have to be taken into account.

4. ENVIRONMENTAL FACTORS – HUMIDITY, VENTILATION, NUTRIENT AVAILABILITY - ENHANCING OR INHIBITING MICROBIAL GROWTH

There is no natural or man made surface on earth that is free of micro-organisms. Microbes have a 3.8 billions years evolution and learned to adapt to all substrates in the most harmful environments (Bunyard, 1996). However, the type of microorganisms, the amount of biomass developed and the diversity of microorganisms inhabiting a facade, a building, an indoor wall, is determined by the environmental factors. Micro organisms are influenced by many factors such as relative ambient humidity, material humidity, temperature fluctuations, light, the nature of nutrients on the material, physical properties of the surface of the object, moisture adsorption-emission mechanisms in the support, pH, dust, oxygen and carbon dioxide concentration in the atmosphere, and the presence of microclimates that may induce condensation (Valentin, 2003).

The most decisive factor for microbial growth is the availability of water. For this reason the control of the water content of a building material is most important to keep the development for microbes at a minimum. Porous building materials that are able to take up a lot of water and to keep it for long periods of time are easy inhabited by a wide variety of bacteria and fungi. Materials that are breathable and easily dry after rain events are more difficult to inhabit and the time needed for primary colonization is prolonged, the amount of biomass and the species diversity are more restricted. Bacteria generally need high water activities ($a_w > 0.98$) and fungi are able to germinate and to grow at much lower water activities ($a_w > 0.65$). Bacteria on the other hand are able to tolerate high salt concentrations on and inside of building materials. For this reason, very humid and salty environments as e.g. basements built of brick, semi-basements on exterior facades are often inhabited by salt tolerating bacteria but nearly free of fungal growth. Facades that are exposed to sun and are affected by changes of humidity during rain events and complete dryness usually are inhabited by black fungi and by cyanobacteria forming dark green and brown crust on and within plaster and natural stone. Algal films are common in very humid semi-basements, on pavement and terraces. Light is a necessary prerequisite for growth of these photosynthetic organisms.

Microorganisms differ widely in their nutrient demands. What holds true for nearly all of them is nitrogen, being an important growth promoting element. Possible nitrogen sources

affection building materials may be defect wastewater drains, N-containing additives in consolidants but also fertilization of the lawn affecting the pavement and semi-basements of the buildings. In indoor environments as private homes or working places the relative humidity usually does not allow bacterial or algal growth on the surfaces due to low relative humidity. However, fungi are a common problem resulting from lack of aeration and condensation effects on walls with wrong or missing thermal insulation (Flannigan et al. 2002).

In addition to the physical properties of the building and materials their chemical composition are decisive for growth of the fungi. Many paint coatings contain high amounts of organic additives as modified cellulose, latex or silicone. All these substances can be degraded by the fungi and thus their growth is supported by the use of such paints. For this reason mere mineral coatings should always be preferred in indoor environments.

5. STATE OF THE ART: METHODS FOR DETECTION AND ANALYSIS OF BIODETERIORATIVE ORGANISMS, ESPECIALLY HIGHLIGHTING THE MOLECULAR TECHNIQUES

5.1. Culture-Dependent Strategy

Traditionally, microbiology research carried out in the field of microbial biodeterioration of building materials was mainly based on classical cultivation methods. To evaluate the danger to historical buildings, monuments or statues from biodeterioration it is essential to identify, and if possible, to quantify these microorganisms. Enumeration is usually done by plate count and most probable number (MPN) techniques, which are based on the cultivation of microorganisms on selective media. Culture-based approaches, while extremely useful for understanding the physiological potential of isolated organisms, do not necessarily provide comprehensive information on the composition of microbial communities. It is generally accepted that cultivation methods recover less than 1% of the total microorganisms present in environmental samples (Ward et al. 1990). In addition, cultivation strategies require a relatively high amount of sample material, and are quite time-consuming requiring 1-6 weeks of incubation. Due to suboptimal culture conditions and methodological limitations, the cell numbers are usually underestimated. An overview of destructive and non-destructive methods used to study the stone-inhabiting microflora in rocks and building stones was reported by Hirsch et al. (1995).

Nevertheless, the use of conventional culture techniques and the developing of new culture media are encouraged due to the advantages of having pure isolates to perform physiological and metabolic studies. Combining both, molecular analysis and enrichment culture techniques, it is possible to characterize the microbial diversity and culture characteristics of the isolated microorganisms in different environments, allowing a more complete picture. The phylogenetic information obtained by using molecular techniques about the identity of the microorganism desirable to be cultivated can be a very useful tool for the specific design of appropriate culture media (Piñar et al. 2001a). Figure 2 shows an overview of the protocol used for the analyses of microbial communities colonizing building materials and Cultural assets by combining culture-dependent and –independent techniques.

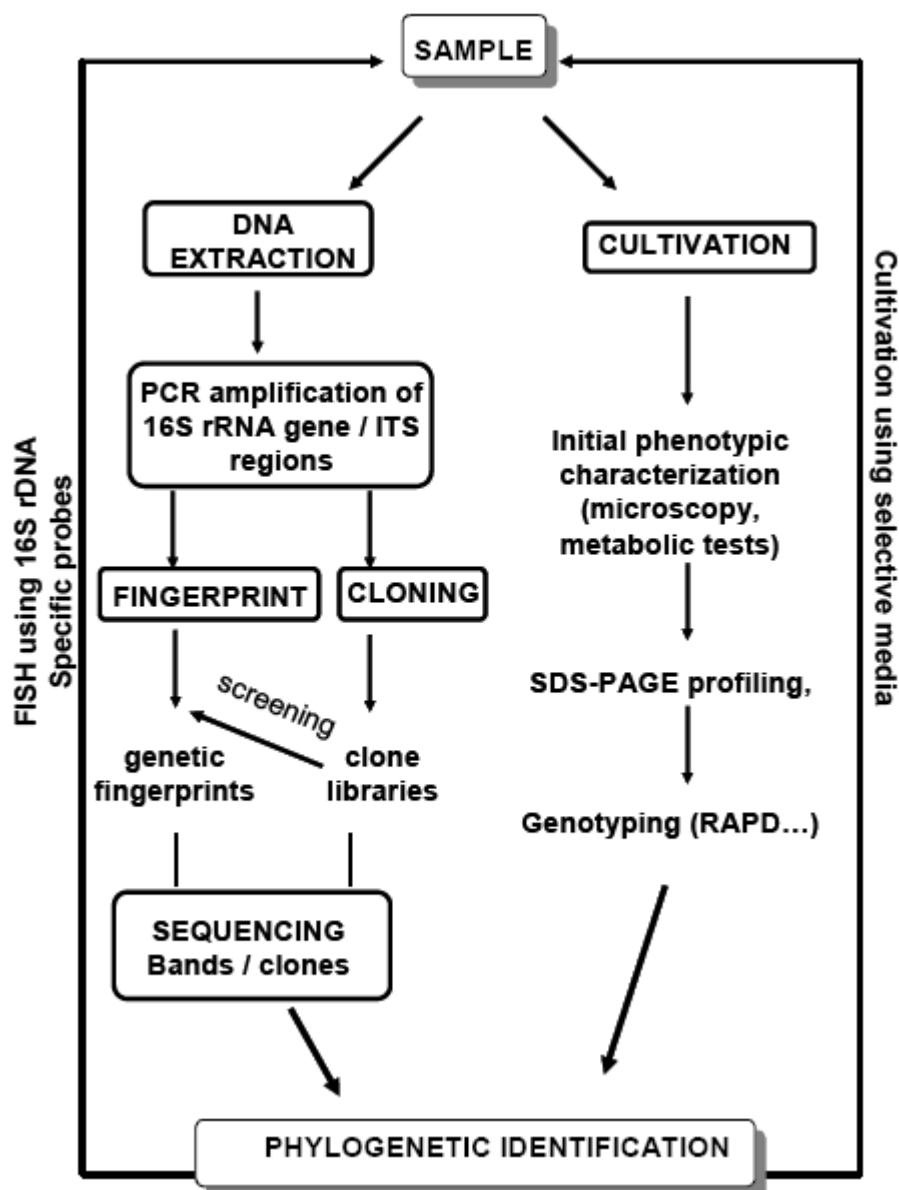


Figure 2. Outline of a standard protocol combining culture-dependent and -independent techniques for the study of microbial communities colonizing building materials and cultural assets.

5.1.1. Microscopy Techniques

Several microscopy techniques have been used to study the interaction microorganisms-substrata. The first investigations of microorganisms-stone relationship using non-destructive techniques were carried out with light microscopy (Ascaso et al. 1990) and light microscopy combined with scanning electron microscopy (Ascaso et al. 1991). At the early 1990s, with the development of scanning electron microscopy in back-scattered mode (SEM-BSE) technique (Wierchos and Ascaso, 1994), started a detailed study of the interactions between

microorganisms and rock lithic substrates, since this technique allowed the jointly analysis of organic and mineral phases (*in situ*) with good resolution.

In SEM-BSE, fixed rock fragments containing biological material embedded in resin and then polished are analyzed. It is worth noting that the microorganisms involved in the deterioration of rock monuments are not only those externally recognized on the monument rock (epilithic) but also those present inside the rock (endolithic). As with light microscopy, SEM-BSE technique allows the examination of an area of several square centimeters, but with a higher resolution, more similar to that of transmission electron microscopy (TEM). The increased resolution allows epilithic and endolithic microorganisms as well as nearby minerals to be simultaneously visualized (de los Rios and Ascaso, 2005).

Recently, SEM-BSE was complemented with other *in situ* microscopy techniques, such as low-temperature SEM (LTSEM) and confocal scanning laser microscopy (CSLM), which have allowed compilation of a complete picture showing all aspects of the colonizing microbial communities involved in biodeterioration processes (Ascaso et al. 2002; Barker et al. 1998). Fluorescence signals can be measured by the digital image analysis system which allows semi-automatic counting of microorganisms in stone materials (Bartosch et al. 1996). However, many fluorescence dyes including DAPI which is widely applied to study bacteria in natural samples proved to be unsuitable, as these dyes bind to the stone material and cause strong background fluorescence which hinders visualization of microorganisms. Staining by means of acridine orange (AO) has been shown to be suitable to visualize microorganisms on and in natural stone (Quader and Bock, 1995). After dye application the green fluorescing microorganisms can be easily distinguished from the red fluorescing mineral components. However, with AO staining, it is not possible to distinguish between active and inactive microorganisms (Bartosch et al. 2003).

For assessment and monitoring of the risk of biodeterioration of a historical building, it may be necessary to know the *in situ* activity of microorganisms. Tetrazolium salts have been used to analyze the activity of natural populations. They act as artificial electron acceptors within functional electron transport system (e.g. respiratory) or for certain active dehydrogenases.

The tetrazolium salts 2,3,5-triphenyltetrazolium chloride (TTC) (Warscheid et al. 1990) and 2-(p-iodophenyl)-3-(p-nitrophenyl)-5-phenyltetrazolium chloride (INT) (Taylor and May, 1995; 2000) have been used to investigate microbial activity in stone materials. A recent work reported on the use of tetrazolium salt 5-cyano-2,3-ditolyltetrazolium chloride (CTC) to visualize and quantify *in situ* the actively respiring microorganisms in natural stones. In contrast to TTC and INT, the formazan crystals formed by CTC reduction (CTF) show red fluorescence and CTC is therefore more suitable for the visualization of microorganisms in stone by using confocal laser scanning microscopy (Bartosch et al. 2003).

5.2. Molecular Strategy

5.2.1. Extraction of Nucleic Acids from Collected Samples

Generally, the first step in the molecular detection of microorganisms consists on the extraction of nucleic acids from collected samples. Samples collected from cultural assets are usually very small (often less than 1 mg), which makes analyses difficult. Most studies dealing with molecular strategies applied in this field have followed the basic protocol

described by Schabereiter-Gurtner et al. (2001a) showed in figure 2. In general, the selected DNA extraction protocol has to be usually adapted and optimized depending on the kind of material to be investigated. Thereafter, the detection of microorganisms is mainly based on the sequences of the small subunit (16S for prokaryotes and 18S for eukaryotes) ribosomal RNA (rRNA) genes. This is a universal gene present in every living organism. Recently, the Internal Transcribed Spacers (ITS regions), which are nested in the nuclear rDNA repeat, have been selected to investigate the fungal diversity of fungi on building materials (Sterflinger and Prillinger, 2001). The ITS regions possess a high variation between taxonomically distinct fungal species and even within the species. Different primers have been published to analyze these regions (Martin and Riguewicz, 2005)

The existence of complete DNA databases for rRNA genes guarantees optimal identification of the microorganisms detected through their sequences and the possibility of carrying out phylogenetic analysis with their closest relatives. rRNA genes are highly conserved and contain a level of divergence that allows microorganisms to be differentiated.

5.2.2. PCR Amplification of Target Genes

The main problem when dealing with samples collected from cultural assets is the limitation in sampling size, which makes many forms of analyses difficult, or even impossible to carry out. In the basic molecular protocol (Figure 2), specific target genes (rRNA genes, ITS regions) are PCR-amplified in order to obtain a large number of copies of these DNA fragments (Schabereiter-Gurtner et al. 2001a). The PCR technique requires two gene-specific primers and is carried out through 25–35 thermal cycles consisting of a denaturation step, annealing of the primers, and extension of the newly synthesized DNA fragment. In the current literature there are available primers described able to target any class of microorganism within a microbial community, such as Bacteria, Archaea, or Eukarya. Furthermore, the range of microorganisms to be detected can be restricted to group-specific amplifications, e.g. sulfate-reducing bacteria (Daly et al. 2000), nitrate-reducing bacteria (Petri and Imhoff, 2000), and even to a unique and specific microorganism.

5.2.3. Genotyping Techniques-Fingerprinting

PCR amplification products can be processed to obtain a microbial community fingerprint. The amplified rRNA genes (Schabereiter-Gurtner et al. 2001a) or ITS sequences (Michaelsen et al. 2006) from different microorganisms reveal different electrophoretic patterns of migration. As a consequence, the microbial community of a sample can be visualized by its electrophoretic profile, the so-called microbial community fingerprint. This allows the analysis of the microbial diversity of a specific sample, its comparison with the fingerprint from other samples, and the evaluation and/or monitoring of sites, or temporal series (Gonzalez and Saiz-Jimenez, 2004).

The community fingerprint or profile can be obtained from a variety of available techniques, such as Denaturing Gradient Gel Electrophoresis (DGGE), Temperature Gradient Gel Electrophoresis (TGGE), terminal-restriction fragment length polymorphisms (t-RFLP), single strand conformational polymorphisms (SSCP), and others. An ideal fingerprinting technique should be able to differentiate highly similar DNA fragments even if showing minimal differences. Sequences with single nucleotide differences can be discriminated by using some of these methodologies.

- a) Denaturing gradient gel electrophoresis (DGGE) and Temperature gradient gel electrophoresis (TGGE)

Separation of DNA fragments in DGGE and TGGE is based on differences in migration of the molecules with different sequences that have a different melting behavior in polyacrylamide gel containing a linear gradient of DNA denaturants or a linear temperature gradient (Muyzer et al. 1993; Muyzer and Smalla, 1998). For studies of microbial communities colonizing building materials and artworks, DGGE is the technique most often used (Rölleke et al. 1996; 1998; Piñar et al. 2001a, 2001b, 2001c; Schabereiter-Gurtner et al. 2001a, 2001b, Gonzalez and Saiz-Jimenez, 2004; Cappitelli et al. 2007a; Miller et al. 2008; Portillo et al. 2008). Figure 3A shows an example of the DGGE community-fingerprints derived from microbial communities colonizing ornamental carbonated stones.

Other techniques, such as analysis of terminal restriction fragment length polymorphisms (t-RFLP), have been frequently used in molecular surveys of microbial communities in ecological studies.

- b) Terminal restriction fragment length polymorphism (t-RFLP) technique.

Terminal restriction fragment length polymorphism (t-RFLP) is a method that has been frequently used to survey the microbial diversity of environmental samples and to monitor changes in microbial communities. T-RFLP is a highly sensitive and reproducible procedure that combines a PCR with a labeled primer, restriction digestion of the amplified DNA, and separation of the terminal restriction fragment (t-RF). The reliable identification of t-RF requires the information of nucleotide sequences as well as the size of t-RF. However, it is difficult to obtain the information of nucleotide sequences because the t-RFs are fragmented and lack a priming site of 3'-end for efficient cloning and sequence analysis (Lee et al. 2008).

- c) Single Strand Conformation Polymorphism (SSCP)

Single Strand Conformation Polymorphism (SSCP) is an electrophoresis technique which was developed, like others, for detection of mutations (Orita, et al. 1989). Under non-denaturing conditions, single stranded DNAs will fold into secondary structure or specific conformations depending on their nucleotide sequences and the physicochemical conditions such as temperature and ionic strength. The electrophoretic mobility of the DNA in a gel is dependent not only on its length and molecular weight, but also on its shape. Due to the differential electrophoresis mobility of these structures, these conformations can be separated by non-denaturing polyacrylamide gel electrophoresis producing a fingerprint. This technique has been applied for the analyses of microbial communities on natural environments (Lee et al. 1996) and attempts have been done with this method for screening of clone libraries of samples obtained from building materials (non-published data).

- d) Random Amplification of Polymorphic DNA (RAPD)

This genotyping method uses an oligonucleotide of arbitrarily chosen sequence to prime DNA synthesis from pair of sites to which it is matched or partially matched, and results in strain-specific profiles of DNA products (Wehls and McClelland 1990; Williams et al. 1990). This molecular method has been adapted for the genetic typing of microorganisms isolated from building materials and monuments (Urzi et al. 1999, Ripka et al. 2006, Suihko et al. 2007). Figure 3B shows an example of RAPD analysis as a high discriminative typing method for differentiating halobacilli strains isolated from building materials (Ripka et al.

2006). The discriminatory potential of RAPD-PCR can be attributed to its ability to determine polymorphisms in the entire bacterial genome.

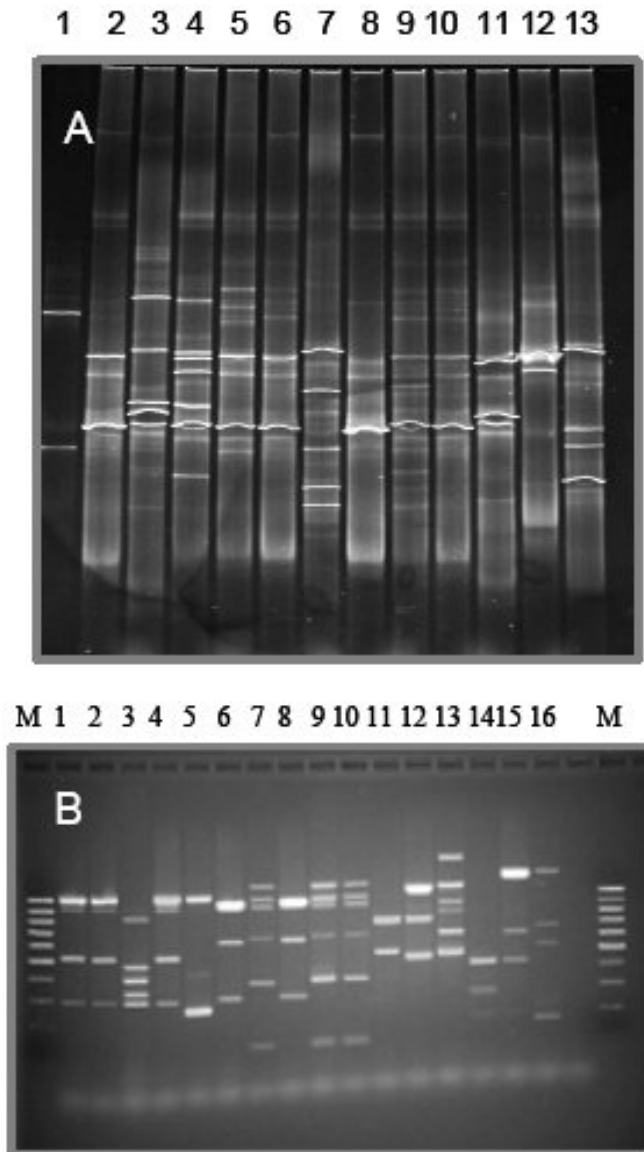


Figure 3. A) DGGE community-fingerprints of DNA fragments coding for 16S rRNA amplified from ornamental carbonate stone samples. Numbers indicate different sampling sites. B) RAPD-PCR analyses of *Halobacillus* species isolated from wall paintings and building materials. RAPD profiles were generated with the ~17 nt primer D14216. Lanes indicate the number of different *Halobacillus* strains tested, lane M: 100-bp ladder.

5.2.4. Creation of Clone Libraries and Sequence Analysis

Microorganisms forming a microbial community must be further phylogenetically identified. Cloning and sequencing can complement the information obtained from a

community fingerprinting of the investigated sample by allowing a precise identification of the microorganisms corresponding to the detected target DNA sequences. This is done by constructing a 16S rDNA library and then following a generally time-consuming screening, using electrophoresis analyses (e.g., DGGE) process for the analysis of individual clones to select different clones while avoiding replicated copies (Schabereiter-Gurtner et al. 2001a). Gonzalez et al. (2003) have recently developed a screening procedure highly efficient allowing to save time and costs of up to 90%. The process consists on the processing of clones in groups. The clones are initially organized in sets (generally 10 clones per set), which are then PCR-amplified and analyzed by DGGE. Once a set includes the clone of interest is detected, clones forming this set are analyzed individually.

The information contained in any 16S rRNA gene sequence is enough to obtain an unambiguous identification of a microorganism at the genus level. A homology search of the sequence against DNA databases provides information on the taxonomic and phylogenetic lineage of the microorganism corresponding to that sequence. The most commonly used homology search algorithm is Blast (Altschul et al. 1997), which is available online at the US National Center for Biotechnology Information [<http://www.ncbi.nlm.nih.gov/BLAST/>].

5.2.5. *In Situ-Hybridization Analysis*

Fluorescence in situ hybridization (FISH) is a rapid and highly valuable tool for the cultivation-independent identification of individual microbial cells from environmental samples using rRNA-targeted oligonucleotide probes (Amann et al. 1990). Since then, the scientific literature witnesses the description and application of a broad battery of taxon-specific oligonucleotide probes (Amann et al. 1995; 2001) for rapid determination of organisms which are difficult to either differentiate by traditional criteria or to obtain pure cultures. Design of new probes for specific taxa of microorganisms thus allows the application of a top-to-bottom approach for the characterization of the microbial community structure.

In recent years, FISH has also been applied in the field of building materials and historical monuments to study bacteria, archaea and fungi involved in the biodeterioration of surfaces (Sterflinger and Hain, 1999; Piñar et al. 2001a; 2002; 2003; Urzi and Albertano, 2001; Urzi et al. 2003; 2004; Capitelli et al. 2007). Furthermore, the application of FISH directly on adhesive tape strips added another advantage to this non-destructive sampling method: the identification “*in situ*” of the microorganisms present on a given area, without the destruction of the valuable surfaces and with little biofilm disturbance (La Cono and Urzi, 2003).

Since FISH, using DNA probes, is often hampered by rigid fungal cell wall, only recently peptide nucleic acid (PNA) were applied for fluorescent in-situ detection of filamentous fungi (Teertstra et al. 2004). PNA probes are synthetic DNA mimics, where the negatively charged DNA backbone is replaced by a neutral polyamid backbone (Stender et al. 2002). Due to this, PNA probes have better binding features to complementary targets and penetrate fungal cell walls more easily. This method could be a promising tool for specific detection and visualization of fungi on and in building materials.

5.2.6. *RNA-Based Molecular Analyses*

Recent improvements in molecular studies have shown the advantages of RNA-based molecular analyses (Gonzalez, 2003). RNA-based analyses require the synthesis of a DNA

(cDNA) complementary to the RNA extracted from the studied samples. The cDNA is obtained by a reaction using an inverse transcriptase and either a single 16S rRNA-specific primer or a random-hexamers priming alternative (Ausubel et al. 1992). In an RNA-based approach, not only the presence of a species of microorganism but also its metabolic activity can be determined, since the levels of RNA in a cell are proportional to the need of that cell for synthesizing proteins required for metabolism. This type of microbial community survey thus provides information on the fraction of the microbial community actually involved in the metabolic activity of a given sample. Consequently, microorganisms comprising that community are the ones directly responsible for any biodeterioration processes occurring on the artwork under study. RNA-based studies have been carried out to investigate the yellow and grey colonizations on the walls of Altamira Cave, Spain (Portillo et al. 2008). RNA-based fingerprints simplify the study, since the number of active microorganisms is generally much lower than the total number of microorganisms present in a sample. The drawback to RNA-based molecular detection of microorganisms is that, since RNA is very labile due to the omnipresence of RNases, the procedure is complicated and requires the use of extremely clean facilities and extra care in sample handling and amplification.

5.3. Culture-Dependent Versus Culture-Independent Techniques

Molecular, culture-independent methods are now well established for the study of microbial communities colonizing cultural assets and in the field of monument conservation and assessment (Gonzalez and Saiz-Jimenez 2005). There are several works focusing on the study of microbial communities colonizing wall paintings, monuments and building materials employing culture-independent techniques (Rölleke et al. 1996; 1998; Schabereiter-Gurtner et al. 2001a; 2001b; Piñar et al. 2001b, 2001c; Laiz et al., 2003; Gonzalez and Saiz-Jimenez, 2004; 2005; Imperi et al. 2007). They have shown that the cultivable microorganisms do not account for the high molecular diversity found in the samples. Furthermore, the use of culture-dependent and -independent methodologies generally delivers disparity of results (Laiz et al. 2003). While culturing methods just give information on the microorganisms able to grow on the culture media used in the experiment (Roszak and Colwell, 1987), molecular techniques provide with an estimate of the sequences of DNA extracted and amplified from the samples (Amann et al. 1995). At present, there is no consensus on how to relate and complement these results. Culturing techniques are unable to provide with the whole microbial community in a sample for a number of reasons and among them one could underline that (i) we do not know every microbial species present in a sample, (ii) the ideal conditions allowing growth of each of the microorganisms in a sample is also unknown, and (iii) some of the microbes in a sample could be in dormant physiological stages and might not show growth using standard culturing procedures. Culturing-independent techniques ideally can allow us to know the microbial community present in a sample, which clearly complements culturing techniques. However, molecular methods do not provide any information on the physiological stage of the detected microbes; these microorganisms could be actively growing, viable, dormant, or they could have even died and their DNA might still be present in the sample. Besides, culture-independent techniques require optimization in order to obtain a maximum of information from the processed samples.

Taking all these data together, the current knowledge of the microbial diversity colonizing monuments and building materials has moved away from the obsolete classical vision that only few groups of microorganisms can grow on cultural assets. This new knowledge required to be carefully understood in order to design appropriate strategies for controlling the parameters affecting the microbial interaction with monuments.

6. POSSIBLE STRATEGIES FOR ANTIMICROBIAL TREATMENTS AND PREVENTIVE MEASURES WITH FOCUS ON PROS AND CONS OF HYDROPHOBIC TREATMENTS, NANO-TECHNOLOGY BASED PAINT COATINGS AND NOVEL DISINFECTANTS

Considering biogenic alterations and presence of micro-organisms has direct implications for the cleaning, consolidation and exposition of objects as follows (Sterflinger and Sert, 2006).

6.1. Cleaning and Biocide Treatments

In all fields of restoration practice cleaning of objects including the removal of patinas and crusts belongs to the first steps of restoration measures. In most instances the appropriate cleaning method is determined by the chemical composition and strength of the material itself and by the chemical quality of other than biogenic patinas. Figure 4A shows an example of a desalination treatment using cellulose compresses embedded in water for the treatment of salt attacked stones.

In the case that an object suffers from strong biogenic contamination, the following considerations should be taken into account for cleaning: Algal and cyanobacterial layers and crusts should be completely dry before cleaning. Dry crusts often readily detach from the material and can be removed mechanically using brushes or sandblasting. In contrast, humid layers of algae are densely attached to the material and trying to remove them mechanically results in a mucilaginous smear that will be pressed forward even deeper into porous material. Cleaning porous material with high pressure or superheated steam should be avoided because it pushes organisms and water deep into the material. As a consequence microbial growth will not only be faster afterwards but colonization will also take place deeper inside the material (Warscheid and Braams, 2000). Care has to be taken with the use of laser-cleaning on darkly pigmented lichen or fungal crusts. Melanins and carotenes are bio-pigments that can be burned into the crystal matrix by the heat of the laser and the resulting black stain is even more difficult to remove. Here, sandblasting – either with sand or with nutshell – can be a suitable alternative. Velvety or powdery surfaces of mould colonies occurring in indoor environments indicate heavy sporulation. Because these spores are easily transferred by the air they are sources of contamination for other rooms and for furniture. Moreover, their allergenic potential is a health risk for the restorer. Therefore, spores should be removed by a vacuum cleaner that must be equipped with a HEPA filter. In case this equipment is not available wet cleaning using cotton swabs soaked with 70% ethanol is recommended. Dry

cleaning with small brushes or paint-brush will disperse the spores and thus should be avoided at all means.

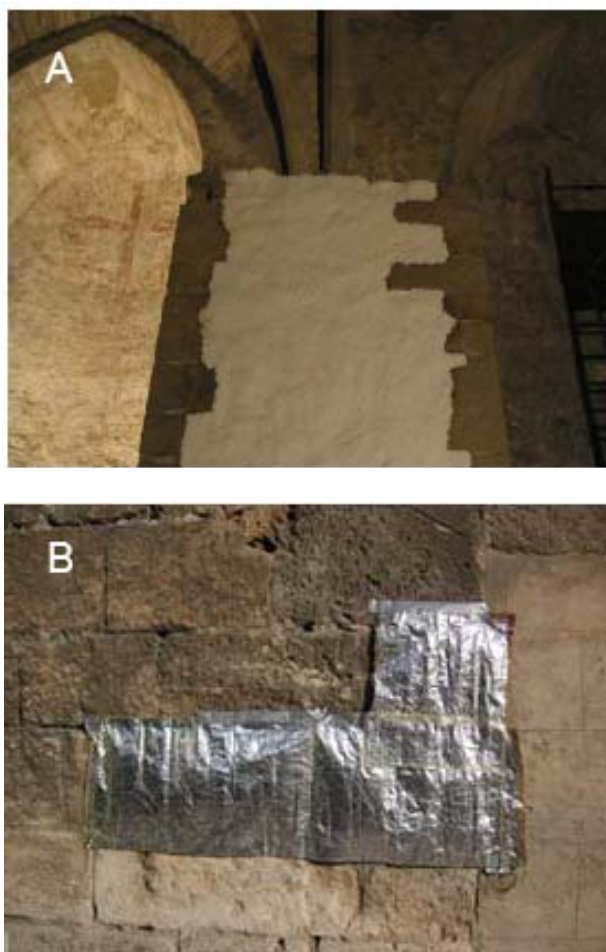


Figure 4. A) Desalination treatment using cellulose compresses applied on salt-attacked stone at the Chapel of St. Virgil, Vienna, Austria. B) Bacterially induced calcium carbonate precipitation applied to the restoration of ornamental calcareous stone on a building in Granada, Spain. Treated area is covered during the treatment to avoid direct UV radiation and desiccation of the applied calcium carbonate producing -bacteria (in this case *Myxococcus xanthus*).

Bioremediation of artworks is also based on the use of sulfate-reducing bacteria, which reduce sulfate to gaseous hydrogen sulfide (Cappitelli et al. 2007b), and nitrate-reducing bacteria, which reduce nitrates to gaseous nitrogen and nitrous oxide (Saiz-Jimenez, 1997).

Having thoroughly removed all macroscopically visible micro-flora from an object, a biocide treatment can be considered. There are some indications for the application of biocides in conservation and refurbishment: Biogenic layers or colonies are often located inside the material: organisms penetrate pores, fissures, grow under exfoliating crusts and between paint layers. Therefore, micro-organisms can often not be reached mechanically and residues in form of single viable cells or whole colonies are a source for rapid recurrence of fouling-processes. Here, a careful infiltration with biocide substances can avoid intrinsic

recurrence. Often, contaminated objects as figures, sculptures, relieves or columns cannot be stored or exposed in a way that microbial growth is confined to absolute minimum. This is the case for most outdoor monuments but also for objects stored in depots and for pieces made of organic materials that would suffer from low relative humidity. In such cases biocide treatments should be considered because on the accident of an climatic event – for example a temporal breakdown of the climate-condition and dehumidifiers – the micro-flora present inside the material in a kind of dormant state can be active within a few hours and can cause high damage even before the climate change is detected by the museum personnel. If restorers made the decision for a biocide treatment, the choice for the appropriate active component should best be based on preliminary micro-biological studies that focus on the object-specific micro-flora and conditions. These studies should include the analysis of the microorganisms present, counts of viable microbial cells and analysis of microbial activity before and after the biocide treatment. The choice of the toxic agent is somehow restricted by the European Biocide directive (<http://ec.europa.eu/environment/biocides/index.htm>). For this reason highly toxic organic-tin or -mercury and other heavy-metal components will no longer be used in restoration. Albeit a variety of biocides are available on the market with effects on different groups of organisms (Bagda, 2000), in restoration practice substances effective against a broad spectrum of organisms are needed.

Two substance groups are approved to be effective against fungi, bacteria, algae, moss and lichen, because they affect very general cellular processes: (1) Products containing formaldehyde releasers and (2) products containing the so called quaternary ammonium salts (benzalconium chloride). Also Dithiocarbamates (Ziram, Thiram) have a broad spectrum but are only stable in a pH range from pH 7-10, which can be problematic in combination with highly alkaline materials, e.g. lime-slurries, plaster or mortar. Triazoles (for example Preventol A8) are also in use but they have a selective spectrum within the fungi and are not effective against algae. To combat the most destructive indoor fungus *Serpula lacrymans* borates and quaternary ammonium-salts are used in combination.

Most ready to use paints and plasters available from do-it-yourself stores contain biocides. These, however, aim to conserve the product during shelf-life but are not suitable to prevent a wall against microbial growth for longer than a few months.

The choice of the right biocide has to be complemented by the appropriate application. In field studies carried out on stone facades and figures we found out that biocides have to be applied at least two times in daily periods to achieve an effective killing of the organisms. In case of lichen crusts a three time application on physiologically active lichens is necessary. In general, a physiologically active biofilm is much more vulnerable against biocides than dried cells or dormant states are. For this reason we recommend to keep surfaces humid several hours before the biocide is applied. For the application compresses soaked with biocide are optimal but also flooding is appropriate.

It is important to keep in mind that none of the biocides currently available on the market has any long-term preventive effect against re-colonization. Thus, controlling the humidity, temperature, light, nutrients and combinations of these environmental parameters is the only way to suppress microbiological contamination and to prevent re-infection. In case those parameters cannot be controlled due to conditions given by the object or because the necessary architectural measures and changes of building physics can not be realized, maintenance agreements including control and cleaning in regular terms should be concluded between authorities/sponsors and restorers. Restorers should keep in mind and put into

writing in their contracts that they cannot guarantee for the long term development of microbes in case the owner/sponsor does not agree with architectural, building physics and climatic measures necessary to prevent microbial growth.

6.2. Consolidants, Coatings and Hydrophobic Treatment

The fact that most synthetic polymers – e.g. acrylate as Paraloid B-72 or Primal AC33 and polyvinyl-acetates as Mowilith 20 - used for consolidation or as additives for filling material and mortars are degradable by fungi and bacteria has been widely discussed as an argument against their use (Heyn et al. 1996). However, while using those substances on the object their portion in total microbial nutrient supply is relatively low in most cases because - and this holds true especially for the outdoor exposition - organic pollutants are available in high amounts and most of them – also carbon hydroxides, aromates and some PAHs - are much easier degraded by micro-organisms than synthetic polymers are. In contrast, organic binders and consolidants as skin-glue, casein, methyl-cellulose, egg, linseed-oil etc. are beneficial for microbes and provoke rapid colonization and biogenic degradation. The same holds true for or synthetic substances containing nitrogen sources because these are kind of fertilizers for organisms.

Irrespectively of the chemical composition of the polymer used for consolidation and coating, the decisive factor promoting microbial growth is the change of the physical properties and the resulting micro-climate created by the polymer coatings. On porous material, especially on rock, superficial consolidation or coating with polymers often leads to water accumulation inside the material. This is because films of polymers are really impermeable only for the first yeast after application, then first fissures occur due to loss of flexibility and water permeates through those fissures. However, because the major proportion of the surface is still coated with polymer the diffusion of vapor is hampered and water accumulates inside the rock. The high and constant humidity favors microbial growth inside the material and this leads to contour scaling and finally to loss of material. Effects similar to those described for the synthetic resins can be caused by hydrophobic treatments if their application has a sealing effect.

6.3. Cementations, Fillings, Substitutes, Artificial Material

In restoration of stone monuments fillings are frequently necessary. Mud-mortars are often used for gap-fillings, for consolidating fissures and cracks and for small substitutions. Mud mortars mostly consist of sand and lime and are often bound with synthetic resins – e.g. acryl-dispersions. Microbiological studies have shown that the use of artificial binders containing nitrogen sources as e.g. Primal should be avoided. Nevertheless, the physical parameter as roughness, pore space and water absorption are far more important for the speed of microbial development and for the absolute amount of microbial biomass inside and on the material.

Specific metabolic activities have been employed to develop new bioremediation method based on the use of microbial cells and enzymatic activity to remove organic material (Ranalli et al. 2000; 2005; Beutel et al. 2002; Antonioli et al. 2005) or bio-induce calcite precipitation

using specific bacteria for monumental stone reinforced (Castanier et al.1999; Tiano et al. 1999; Rodriguez-Navarro et al. 2003; Fernandes 2006, Jimenez-Lopez et al. 2007; 2008). Figure 4B shows an example of the restoration of ornamental calcareous stone by the application of calcium carbonate producing-bacteria.

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Chapter 5

DETERMINATION OF MOISTURE TRANSPORT AND STORAGE PROPERTIES OF BUILDING MATERIALS

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1. INTRODUCTION

Moisture accumulation within the material of a building envelope can lead to poor thermal performance of the envelope, degradation of organic materials, metal corrosion and structure deterioration (Künzel, 1995; Pel, 1995; Qin et al. 2007, 2008a). In addition to the building's construction damage, moisture migrating through building envelopes can also lead to poor interior air quality as high ambient moisture levels result in microbial growth, which may seriously affect human health and be a cause of allergy and respiratory symptoms. Also, human perception of air quality and the transport of volatile and semi-volatile organic compounds through building materials depend largely on the relative humidity. Therefore, the investigation of heat and moisture transfer in porous building materials is important not only for the characterization of behavior in connection with durability, waterproofing and thermal performance, but also building energy efficiency and avoiding health risk due to the growth of microorganisms.

Moisture problems in building materials are results of simultaneous heat and moisture transfer in building envelopes and indoor air. During the past decades, numerous models have been developed to calculate the hygrothermal transfer in building materials (Qin et al. 2006, 2007). However, accurate moisture properties and transport coefficients required by many models are still lacking. The scope of this study is to develop a series of experimental methods to determine the moisture transport and storage properties of building materials.

In the Chapter, four experimental methods have been proposed. Firstly, a gravimetric sorption-desorption method for evaluating the moisture diffusion coefficient of concrete and

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cement mortar is presented. The test was carried out in LEPTAB, France (Belarbi et al. 2006; Qin, 2007). It can also be used to determine the moisture distribution inside the material. The moisture diffusion coefficients calculated by this method fit some published experimental data (Janz, 2000). Secondly, the temperature gradient coefficient ε (Qin et al. 2006) has been determined experimentally (Qin et al. 2008a). The test is based on a modified cup method and was carried out in DBM, Lund University, Sweden. Meanwhile, the classic cup method for evaluating the moisture diffusivity and the climate box method for the determination of the sorption isotherms of certain building materials have also been presented in the chapter.

2. DETERMINATION OF MOISTURE DIFFUSIVITY

Most methods for determining moisture diffusivity are based on the analysis of moisture profiles (Drchalova, 1998; Kaspar, 1984). For this analysis, a sufficient number of measured points forming the moisture profile are necessary. These experiments are always complicated and normally employ enough deep samples for the moisture profile measurements. There are also some advanced and precise methods, such as NMR (Pel, 1995; Kopinga, 1994), microwave reflection or transmission (Mouhasseb, 1995; Maierhofer, 1997) or γ -ray attenuation (Kumaran, 1989), which give accurate quantitative information with high spatial resolution.

Measured transient moisture profiles reveal much about the moisture behavior of a material or combination of materials. They can be used to calibrate models of moisture transport or, as shown above, the moisture diffusivity can be determined from the measured profiles. Several different methods of determining moisture profiles exist. An overview of these methods is given below.

2.1. Slice-Dry-Weigh Method

In order to measure the moisture profile, the specimen that has been exposed to unidirectional water uptake or drying is rapidly sliced into discs that are weighed, dried, and weighed again. The water in the disc evaporates during the drying and the water content in mass by mass can be calculated from the weight loss. The drying procedure can be executed in several different ways, depending on the material tested and its ability to resist heat. The quickest and most common way is to use an oven at 105°C. Materials that cannot resist heat can be dried in some other way, for example, in an exsiccator with a drying agent like silica gel or sulfuric acid. This procedure is rather time-consuming.

This method has several disadvantages. One major problem is that it is destructive; for one specimen is destroyed each time the moisture profile is measured. Consequently many specimens are required. It may even be impossible to get sufficient specimens if they have to be taken from an existing building. The slicing itself presents further problems. It cannot be done by sawing as this would generate heat, or would involve adding water to the specimen. Splitting is thus the only option. However, it is difficult to get a specimen to split perfectly parallel to the surface exposed to water or the drying climate. A parallel split is essential to avoid an error in the x-coordinate of the disc. It can be also be difficult to split a specimen

into discs thin enough for use when evaluating a very steep moisture front. Finally, this method is only suitable when water and non-volatile fluids are used for the absorption experiment. It cannot be used with volatile fluids, as these would evaporate from the disc during the splitting process.

Provided that the slicing can be done accurately, this method is the most accurate because the amount of water in the specimen is measured. It can therefore be used to calibrate and verify all the other methods described below.

2.2. Gamma-Ray Attenuation

Gamma-ray attenuation is a non-destructive method of measuring water content. If two different gamma-ray sources are used, both the water content and the material density can be measured. The gamma rays (photons) interact with the orbital electrons in the material and are absorbed or scattered. The intensity of a narrow beam of gamma rays passing through a material can be expressed by the following formula (Descamps, 1990):

$$I = I_0 e^{-\mu \rho x}$$

where, I is the gamma-ray intensity after passing through the material (counts s^{-1}); I_0 is the intensity without absorbing material (counts s^{-1}); μ is the mass absorption coefficient of the material ($\text{m}^2 \text{kg}^{-1}$); ρ is the density of the material (kg m^{-3}), x is the thickness of the material (m).

In order to measure the moisture profile, a gamma-ray source and a detector are needed. The source can be buried in the material with the detector on the surface, or, more commonly, the specimen can be placed between the source and the detector. A simplified scheme of the gamma-ray attenuation system is present in Figure 1.

Disadvantages of this method are that the gamma-ray equipment must be calibrated for specific material being studied and that the equipment is rather expensive. Gamma rays should not be used if the material structure changes over time (e.g. during the hydration process of young concrete).

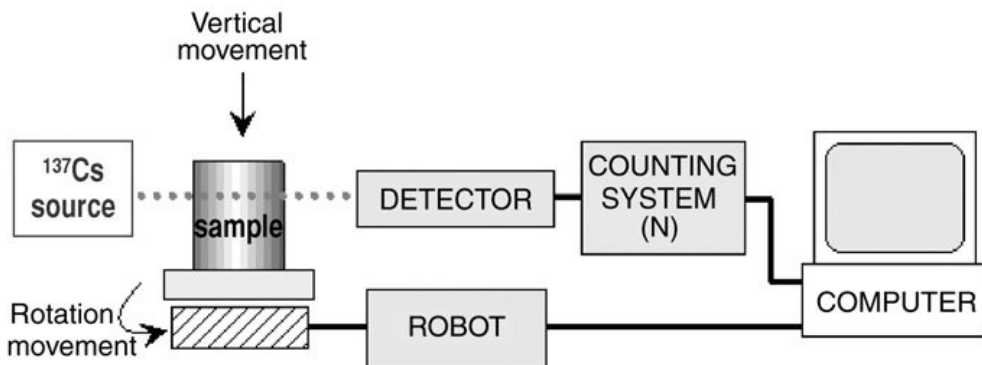


Figure 1. Simplified scheme of the gamma-ray attenuation measurement system (Baroghel-Bouny, 2007).

The reason is that hydration reduces the moisture content by transforming ‘free water’ to chemically bound water. During this process the density of concrete increases. According to Adamson et al. (1970), the accuracy of the gamma-ray method applied to concrete is $\pm 0.5\%$ of the moisture content mass, per unit of mass. A further disadvantage of the gamma-ray method is that special safety precautions are required because of the radioactivity. Examples of the results from the use of this method and of laboratory set ups are given in Wormald et al. (1969) and Quenard et al. (1989).

2.3. Neutron Radiography

Like gamma-ray attenuation, neutron radiography is a non-destructive method using radiation. In contrast to gamma rays, neutrons interact mainly with hydrogen nuclei. The attenuation of a neutron beam, caused by scattering and absorption of the neutrons, will therefore be directly related to the total water content in the material. The intensity of a neutron beam passing through a specimen is described by an expression similar to equation (Pel, 1995)

$$I = I_0 e^{-x(\mu_{mat} + \varpi_w \kappa)}$$

where, I is the intensity of a neutron beam after passing through the material (counts s^{-1}); I_0 is the initial intensity of the neutron beam (counts s^{-1}); μ_{mat} is the macroscopic attenuation coefficient of the specific material (m^{-1}); μ_w is the macroscopic attenuation coefficient of water (m^{-1}); κ is the moisture content by volume ($\text{m}^3 \text{m}^{-3}$), x is the thickness of the material (m).

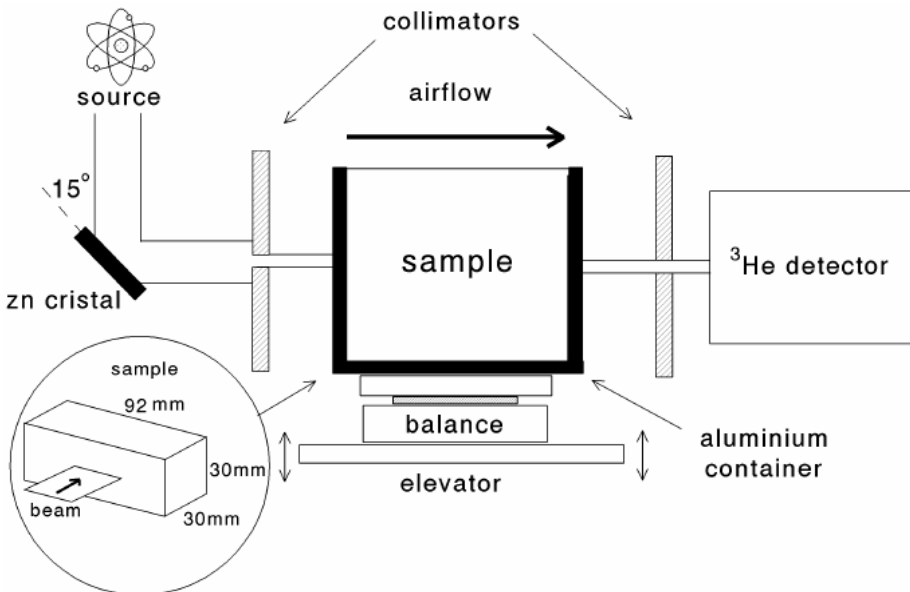


Figure 2. Simplified scheme of the neutron radiography system (Pel, 1995).

The coefficients μ_w and μ_{mat} are determined independently of each other by measuring the neutron transmission through pure water and through the dry material in question. During the test the specimen is placed between the neutron source and the detector. The neutrons can be detected by a ^3He proportional detector (Pel 1995) (see Figure 2). When conducting a neutron radiography test, safety precautions must be taken and specially trained personnel are necessary. Results from measurements with neutron radiography on different materials and experimental set ups are shown in Dawei et al. (1986), Pel (1995), and Adan (1995).

2.4. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a non-destructive method of determining water content. Its accuracy is approximately 0.5-0.1 Vol. % according to Kießel and Krus (1991). NMR has a spatial resolution of better than 1mm according Kopinga and Pel (1994), and it can also distinguish between free, physically bound, and chemically bound water. Thus NMR is quite well suited for measuring transient water movements in building materials. A primary disadvantage of NMR is that the equipment needed is rather expensive.

In an NMR measurement the number of hydrogen nuclei are “counted” by examining the interaction between the magnetic moment associated with the intrinsic spin of a material’s hydrogen nuclei and an exterior permanent magnetic field. When an electromagnetic field is applied perpendicular to the constant magnetic field, some energy is absorbed. The amount of energy absorbed is proportional to the number of hydrogen nuclei in the measured volume. It is therefore a measure of the water content in the materials tested. NMR is suitable for all fluids that, like water, contain hydrogen atoms.

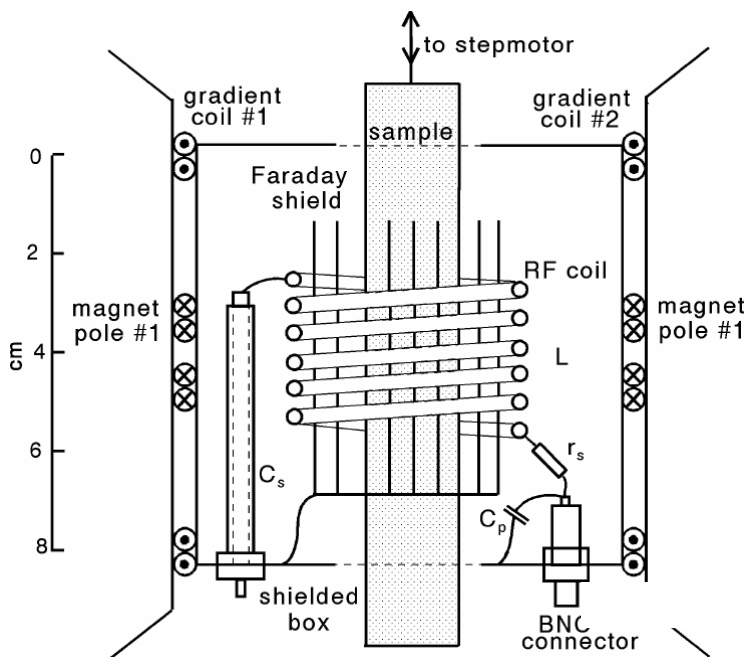


Figure 3. The Schematic diagram of the experimental set-up used by Pel, (1995).

According to Kopinga and Pel (1994), NMR offers better sensitivity than gamma-ray attenuation and neutron radiography. Unlike the results from the gamma-ray method, NMR results are directly related to the number of hydrogen nuclei. In de Freitas et al. (1995), however, a comparison between gamma-ray attenuation and NMR revealed no significant difference in accuracy. An advantage of NMR compared to gamma-ray attenuation and neutron radiography is that no radioactivity is involved during the experiment. Figure 3 shows the schematic diagram of the experimental set-up of NMR used by Pel (1995). Examples of results from NMR measurements and laboratory arrangements are shown in Pel (1995), Krus (1995), Kopinga and Pel (1994) and Kießel and Krus (1991).

2.5. Computer Tomography

The principle of Computer Tomography (CT) is to use the intensity loss of a narrow beam of the X-rays passing through the specimen to measure the density of the specific material in question. The magnitude of the loss due to absorption is measured with what is known as CT value. The scale is calibrated against distilled water. By definition, water has CT value of 0. The absorption (CT value) in air is -1000, which means that there is no absorption (100% less absorption). The absorption of X-rays in concrete is consequently 1450-1500. (Bjerkeli 1990). The difference in the CT value of air and water is an indicator for measuring the water content in the material.

However, there are many researchers, particularly in the developing countries or in some industry companies, who do not have access to such expensive methods. Therefore, it is necessary to develop some simplified but enough accurate methods (Krus et al., 1993; Kumaran, 1994) for them. In this chapter, we present two methods to evaluate the moisture transport coefficients.

3. EVALUATION OF ISOTHERMAL MOISTURE TRANSPORT COEFFICIENTS

3.1. Gravimetric Sorption-Desorption Method (LEPTAB)

Describe of the Method

The proposed method for determination of isothermal moisture transfer inside materials is based on the assumption that the moisture diffusion coefficient D_m can be considered as piecewise constant with respect to the ambient relative humidity. Given the experimental setup (Figure 4) (see Experimental section); the problem can be reduced to only one dimension. Thus, for each absorption or desorption stage, the transport equation can be written in the following form:

$$\frac{\partial w}{\partial t} = D_m \frac{\partial^2 w}{\partial x^2} \quad (1)$$

Given the experimental procedure (see experimental section), the initial condition is:

$$w|_{t=0} = w_b \quad (2)$$

and boundary conditions are:

$$-D_m \frac{\partial w}{\partial x} \Big|_{x=l} = \beta(w|_{x=l} - w_o) \quad (3)$$

$$\frac{\partial w}{\partial x} \Big|_{x=0} = 0 \quad (4)$$

where β is the convective moisture transfer coefficient.

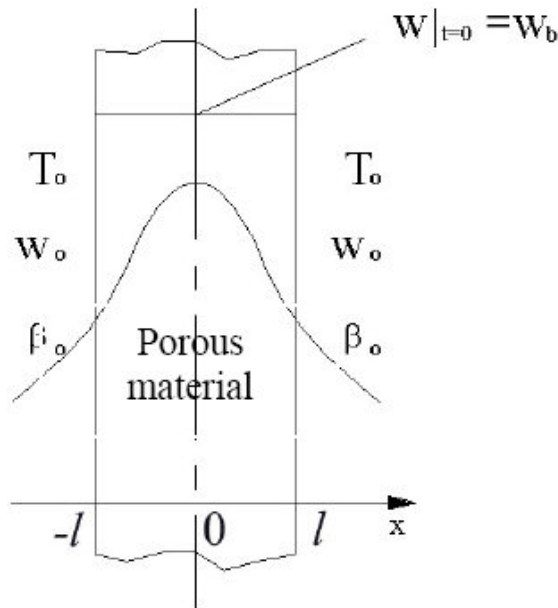


Figure 4. The schematic diagram of the test set-up.

Introducing a new variable $\psi = w - w_o$, the above model can be rewritten as:

$$\frac{\partial \psi}{\partial t} = D_m \frac{\partial^2 \psi}{\partial x^2} \quad (5)$$

The initial condition and boundary conditions become:

$$\psi|_{t=0} = \psi_b = w_b - w_o \quad (6)$$

$$-D_m \frac{\partial \psi}{\partial x} \Big|_{x=l} = \beta \cdot \psi|_{x=l} \quad (7)$$

$$\left. \frac{\partial \psi}{\partial x} \right|_{x=0} = 0 \quad (8)$$

Solution

The analytical solution of Eq. (5) is obtained by using the method of separate variable:

$$\frac{\psi(x, t)}{\psi_b} = \sum_{n=1}^{\infty} \frac{4 \sin \mu_n}{2\mu_n + \sin(2\mu_n)} \cos\left(\mu_n \frac{x}{l}\right) \exp\left(-\mu_n^2 \frac{D_m t}{l^2}\right) \quad (9)$$

where μ_n is eigenvalue, which is the solution of the following equation:

$$\mu_n \tan \mu_n = \frac{\beta l}{D_m} \quad (10)$$

The value of μ_n under different $\frac{\beta l}{D_m}$ can be found in (Dincer *et al.* 1996). Thus, we can get the expression of moisture content inside the porous material:

$$w(x, t) = \sum_{n=1}^{\infty} \frac{4 \sin \mu_n}{2\mu_n + \sin(2\mu_n)} \cos\left(\mu_n \frac{x}{l}\right) \exp\left(-\mu_n^2 \frac{D_m t}{l^2}\right) (w_b - w_o) + w_o \quad (11)$$

Eq. (11) is an infinite series. When the value of Fourier number ($Fo = \frac{D_m t}{l^2}$) is larger than 0.2, the solution can be limited to the first term, which still provide enough accurate results for most engineering applications. In most absorption and desorption processes, the duration to reach the Fourier number of 0.2 is negligibly small compared to the total time of the experiment. Thus, Eq. (11) can be simplified as:

$$w(x, t) = \frac{4 \sin \mu_1}{2\mu_1 + \sin(2\mu_1)} \cos\left(\mu_1 \frac{x}{l}\right) \exp\left(-\mu_1^2 \frac{D_m t}{l^2}\right) (w_b - w_o) + w_o \quad (12)$$

For a given stage of absorption or desorption test, the amount of water, which transported between the sample and the ambient during the time interval $[0, t]$, can be expressed by the relation:

$$M_w = \int_{-l}^l (w_b - w(x, t)) dx \quad (13)$$

The total mass of water transported during the considered stage of absorption or desorption process can be obtained by:

$$M_b - M_e = \int_{-l}^l (w_b - w_o) dx \quad (14)$$

Then, we can get the dimensionless moisture content of the material, which is expressed as follows:

$$\frac{M_w}{M_b - M_e} = 1 - \frac{4 \sin^2 \mu_1}{2\mu_1^2 + \mu_1 \sin(2\mu_1)} \cdot \exp\left(-\mu_1^2 \frac{D_m t}{l^2}\right) \quad (15)$$

or:

$$\frac{W - W_e}{W_b - W_e} = \frac{4 \sin^2 \mu_1}{2\mu_1^2 + \mu_1 \sin(2\mu_1)} \cdot \exp\left(-\mu_1^2 \frac{D_m t}{l^2}\right) \quad (16)$$

where, W is the moisture ratio of the whole specimen (kg kg^{-1}), W_e is the moisture ratio of the whole specimen at equilibrium (kg kg^{-1}), W_b is the initial moisture ratio of the whole specimen (kg kg^{-1}).

Determination of the moisture diffusion coefficient

The moisture content inside the material can be non-dimensionalized using the following equation:

$$\Phi = \frac{W - W_e}{W_b - W_e} \quad (17)$$

And the dimensionless moisture distribution can be expressed as (Dincer *et al.* 1996):

$$\Phi = G \exp(-St) \quad (18)$$

Integrating with Eq. (18), G and S can be expressed as:

$$G = \frac{4 \sin^2 \mu_1}{2\mu_1^2 + \mu_1 \sin(2\mu_1)} \quad (19)$$

$$S = \frac{\mu_1^2 D_m}{l^2} \quad (20)$$

Then D_m can be expressed as:

$$D_m = \frac{S \cdot l^2}{\mu_1^2} \quad (21)$$

where, G represents lag factor (dimensionless) and S is a coefficient related to the desorption/absorption process (s^{-1}). The dimensionless moisture content of the whole material can be obtained by gravimetric measurements. And the measured data is fitted by an exponential curve (as Eq. 18). The values of G and S can thus be determined by Eq. (18) correspondingly. Eq. (19) can be solved by some iterative methods such as Newton method. Then D_m can be calculated by Eq. (21) with μ and S obtained from Eqs. (19) and (20).

Experimental Study

Materials and Conservation

Two high strength concretes and six cement-pastes were manufactured by using three cement ratios and two types of cements: an OPC of type of CEM I–52.5 and a mixed cement-fly ash of type of CEM V–42.5A according to European Standard EN 197-1. Their chemical compositions are given in Table 1. These materials were manufactured and characterized by CEBTP (Centre d'études du bâtiment et des travaux publics) and CERIB (Centre d'études et de recherche de l'industrie du béton). They are the concrete working groups managed by ANDRA (Agence nationale de gestion des déchets radioactifs) in the frame of LEPTAB calculation on studies dealing with durability of radioactive materials (Aït-Mokhtar et al., 2005 and Qin, 2007).

Table 1. Chemical compositions of the cements used

Component (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	TiO ₂	MnO	P ₂ O ₅
CEM-I	21.25	3.47	4.23	64.95	0.93	0.27	0.11	2.71	0.17	0.10	0.44
CEM-V	29.78	11.30	3.46	46.71	2.68	1.20	0.24	2.86	0.61	0.10	0.50

Tables 2 and 3 give the composition and some properties of the concretes and the cement pastes, respectively.

Table 2. Compositions of the concretes

Material	Concrete (BI)	Concrete (BV)
Cement (kg m ⁻³)	CEM-I (400)	CEM-V (430)
Sand 0/5 (kg m ⁻³)	858	800
Grave 5/12,5 (kg m ⁻³)	945	984
Water (l m ⁻³)	168	180
Superplasticizer (kg m ⁻³)	10 (2.5 %/cement)	10.75 (2.5 % / cement)
Air content (%)	0.9	1.2
W/C	0.42	0.42
Slump (cm)	22/23/24/22	19/19.5/21.21
Volume mass (kg m ⁻³)	2460	2415
R _c * at 3 days (MPa)	42.5	36.0
R _c at 7 days (MPa)	54.0	46.5
R _c at 28 days (MPa)	72.0	69.5

* R_c is the compressive strength.

Table 3. Composition of the cement pastes

	PI			PV		
Material	PI 30	PI 42	PI 55	PV 30	PV 42	PV 55
Cement type	CEM I			CEM V		
W/C	0.30	0.42	0.55	0.30	0.42	0.55
Superplasticizer	2 %	1 %	0 %	2 %	1 %	0 %
Water retentive agent	1 %	1 %	1.33 %	1 %	1 %	1.33

After manufacture, the cylindrical samples (11×22 cm) were kept in a saturated solution of whitewash during 90 days.

Isothermal Absorption-Desorption Tests (Belarbi Et Al. 2006)

The specimens were sawed in order to obtain thin discs of 3 mm thickness and 110 mm diameter. This size of samples was chosen in the aim of reducing the experimental duration required to reach balance between the material and its ambience during absorption-desorption tests.

A climatic chamber, which allows a control of both temperature and relative humidity was used for isothermal desorption and absorption tests. These tests were carried out at a constant temperature of 25°C (± 0.1) and for four stages of relative humidity:

- Firstly a desorption process: 100 %-90 %, 90 %-75 %, 75 %-65 % and 65 %-50 %,
- Secondly a absorption process: 50 %-65 %, 65 %-75 %, 75 %-90 % and 90 %-100 %.

Given the adopted protocol, all samples were saturated in lime saturated water before the beginning of the tests.



Figure 5. the climatic box used for the tests.

For each desorption or absorption stage, the test consists in measurements of sample's mass according to time. In this way, the variation of water content of the sample is determined as a function of time.

2.1.5. Measurement Results

The relative variation of weight vs. time for concrete BI is given in Figure 6 for desorption and absorption tests.

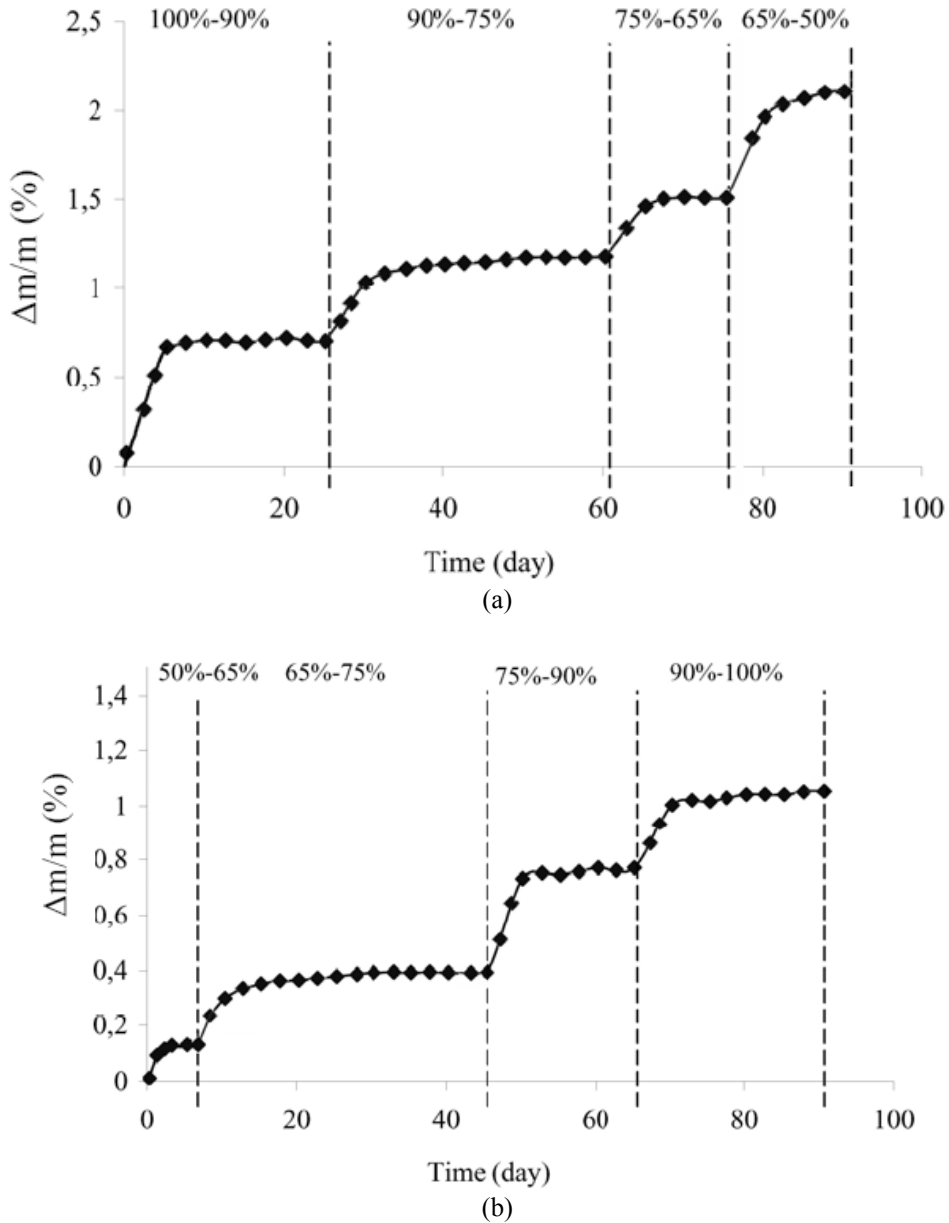


Figure 6. Relative variation of weight vs. time during desorption process (a) and absorption process (b) for concrete BI (Ait-Mokhtar et al., 2005).

The moisture diffusion coefficients obtained by Eq. (21) for concrete BI and BV vs. relative humidity are summarized in Figure 7. The value of the moisture diffusion coefficient increases with the relative humidity. A similar distribution can be found in literature (Baroghel-Bouny, 2007).

Figure 7 also shows that the moisture diffusion coefficient of absorption process calculated from Eq. (21) is larger than that of desorption process, highlighting the absorption hysteresis. As measuring results in Figure 8 show that the hysteresis between absorption and desorption isotherms is distinct. Furthermore, Figure 7 also indicates that the moisture diffusion coefficient of BV is lower than that of BI.

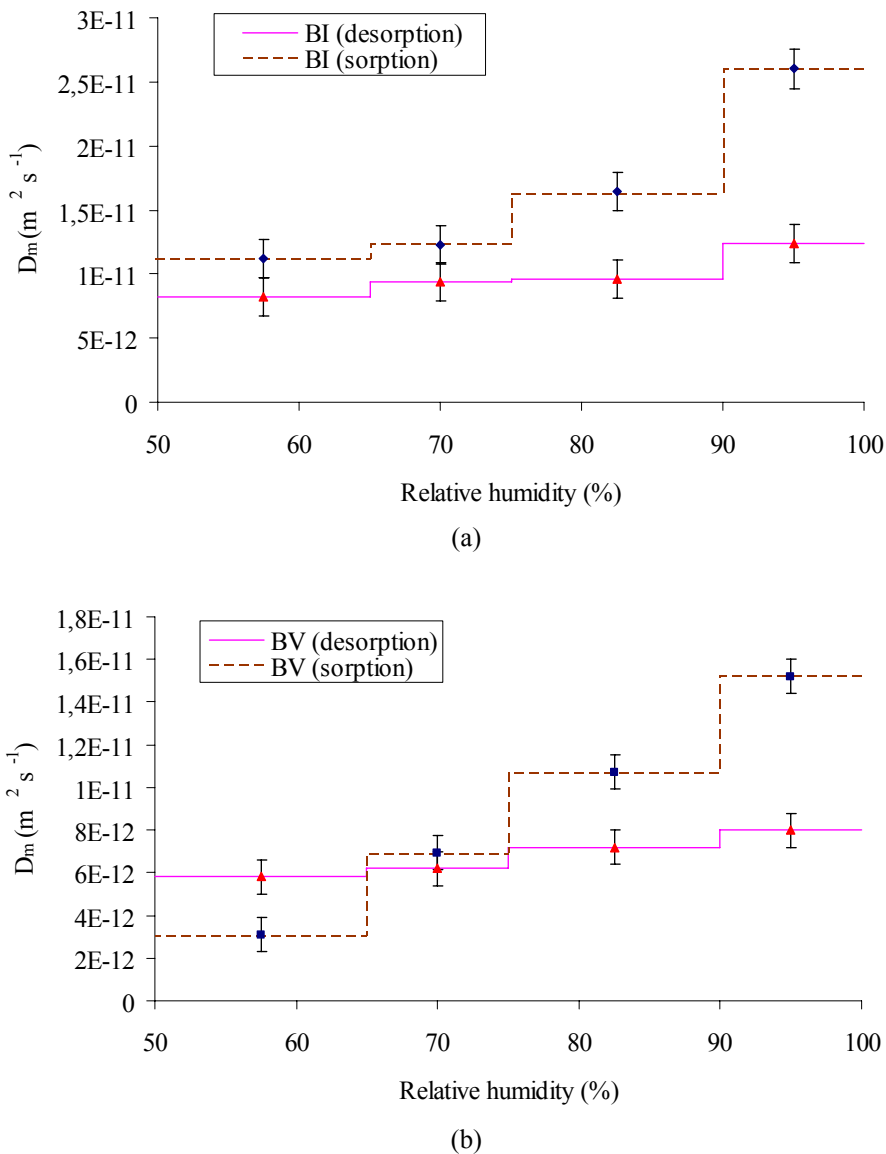


Figure 7 Moisture diffusion coefficients of BI and BV during desorption and absorption processes calculated from Eq. (21).

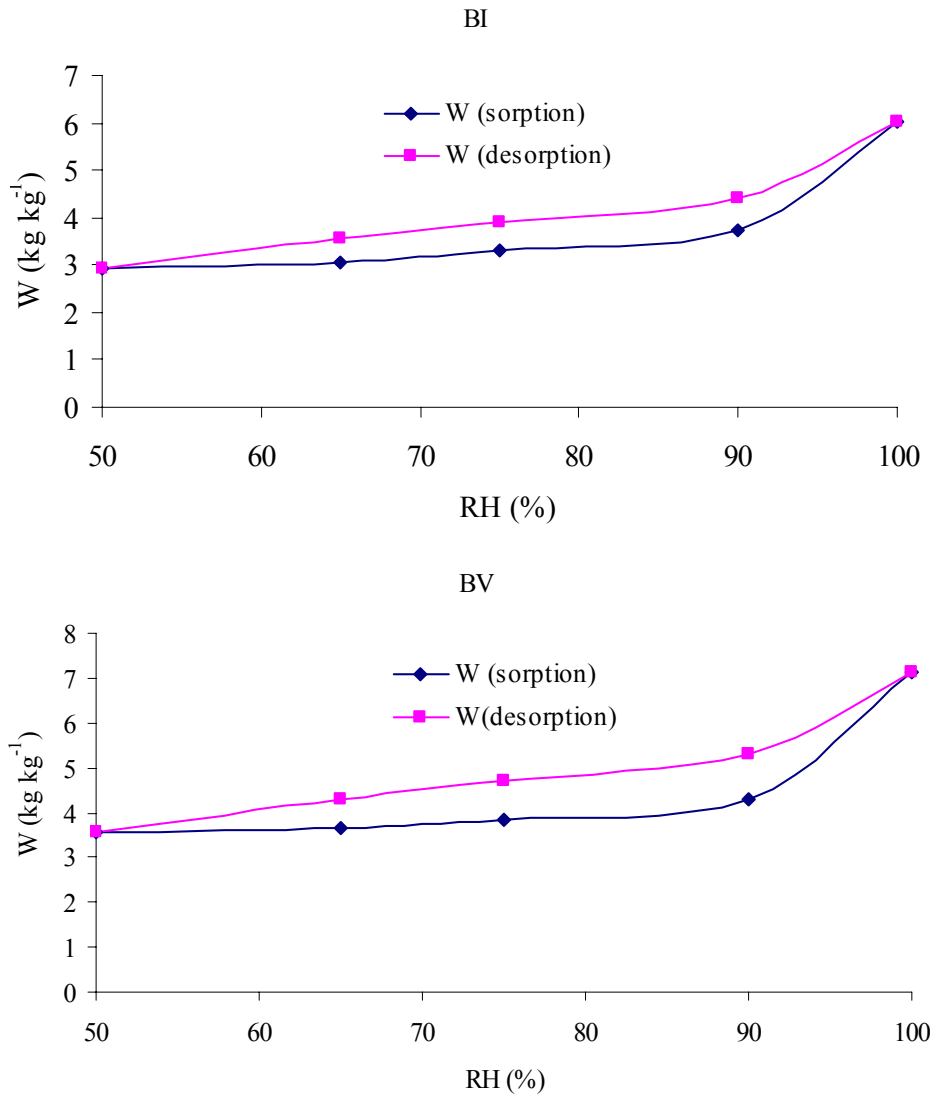


Figure 8. Scanning curves of concrete BI and BV from 50% RH.

Figure 9 shows the moisture distribution inside the two concretes BI and BV during desorption and absorption processes. All curves are calculated by the modeling presented above (Eq. 12). The change of the moisture distribution inside the material at the first few hours can be clearly observed in the figure.

Figure 10 highlights that the effect of the w/c ratio on the moisture diffusion coefficients is quite small in the range of low moistures (RH<80%), but for the high moistures, the moisture diffusion coefficients of samples with high w/c ratio are larger than that of specimens with low w/c ratio.

Namely, samples with low w/c ratio exhibit a high resistance to moisture ingress during the absorption process.

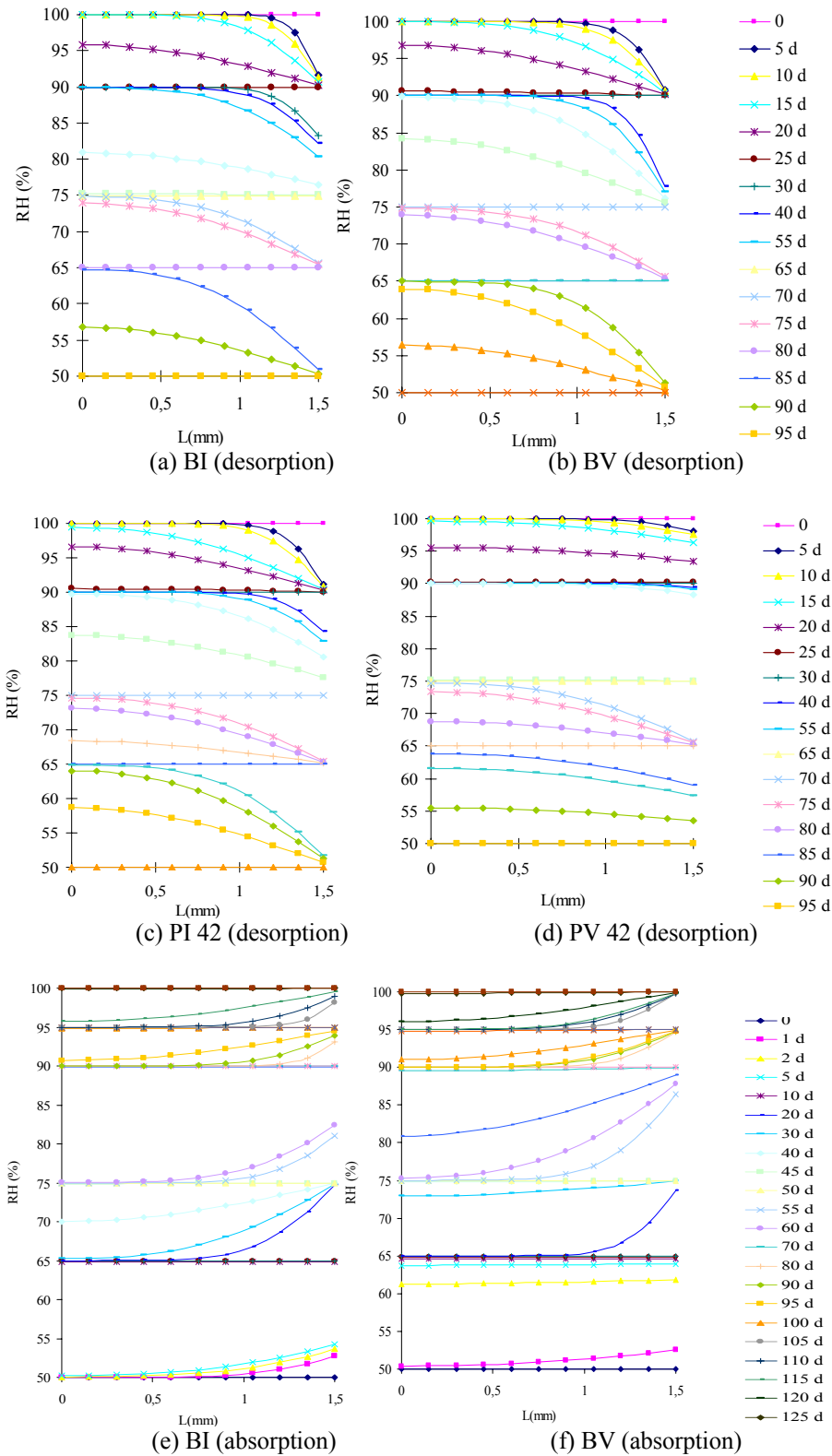


Figure 9. (Continued).

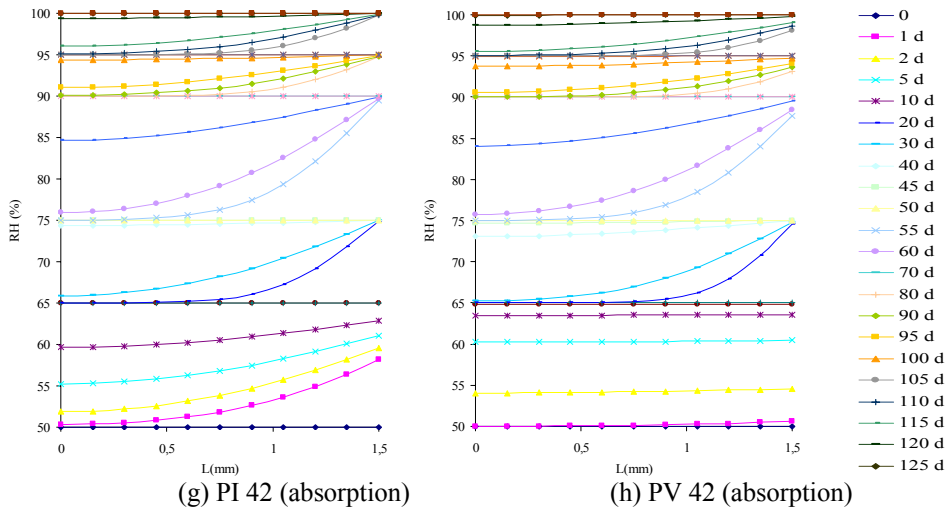


Figure 9. Profiles of the relative humidity inside the material during desorption and absorption process for concrete BI and BV and cement pastes PI 42 and PV 42/

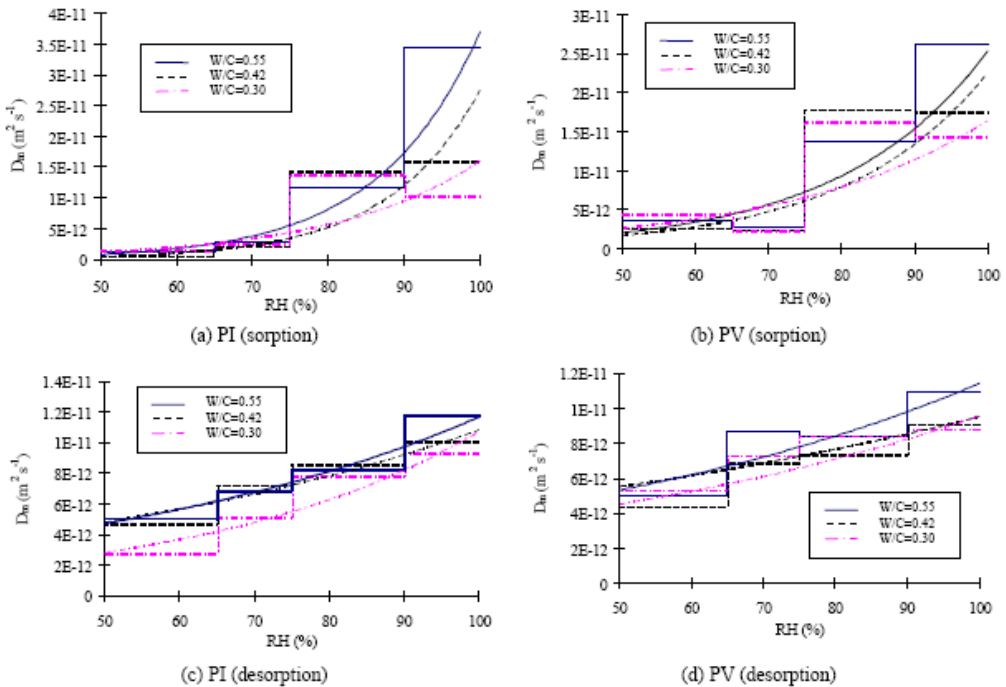


Figure 10. Influence of W/C ratio on the moisture diffusion coefficient of PI and PV.

This is mainly due to a decrease in porosity and permeability with lower w/c ratio, and thus a decrease in the number and size of pores within the cement paste. The results were also agreed with some NMR experimental data obtained by Kopinga and Pel (1994) (Figure 10). Decreasing w/c ratio normally reflects a smaller average pore size and a smaller moisture diffusion coefficient.

The present method is based on the assumption that the moisture diffusivity can be approximated by a piecewise constant function in each RH interval. This assumption could lead to certain inaccuracies that will be discussed below.

Figure 11 shows the distribution of relative humidity inside BI (100%-90%) calculated by using different moisture diffusion coefficients. The blue profiles are obtained by using the maximum D_m (100%-90%), while the red ones are calculated by using the minimum D_m (65%-50%) according to Figure 7.

The maximum RH difference due to the variation of D_m can thus be evaluated. The maximum variation due to the assumption is defined as:

$$\zeta = \frac{\Delta RH_{Max}}{RH_{ref}}$$

where, ΔRH_{max} is the maximum RH difference calculated by using maximum difference of D_m . RH_{ref} is the corresponding relative humidity calculated by using proper D_m .

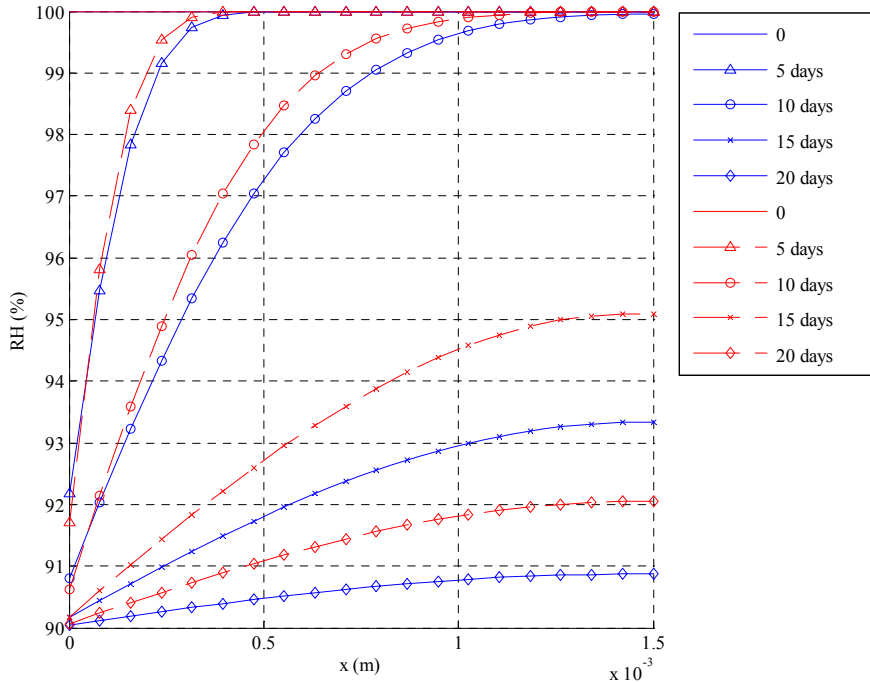


Figure 11. the distribution of relative humidity calculated by using different moisture diffusion coefficients BI (100%-90%).

The calculated results are listed in Table 4. The maximum deviation is smaller than 2.5%. It shows the assumption that the moisture diffusivity can be approximated by a piecewise constant function is reasonable and suitable for the concretes and cement pastes studied.

Table 4. The maximum variation of RH inside the material obtained from the maximum variation of the diffusion coefficient

ζ	BI	BV	PV	PV
sorption	1.93%	2.01%	2.20%	2.12%
desorption	2.12%	2.23%	2.51%	2.42%

Discussions

This section proposes a gravimetric method for the determination of moisture diffusivity by coupling with an appropriate modeling of moisture transfer within porous materials. The main advantage of the suggested method lies in the simplicity of the required device and protocol of experimental measurements. Indeed, the measurement of interior moisture distribution, which is done in some similar studies (Pel, 1995; Kopinga et al., 1994), is not required. The experimental application of the suggested method has concerned cement-based materials: concrete and hardened cement pastes. In this connection, the moisture diffusion coefficients calculated by this method fit some published experimental data (Marten, 2000). The maximum deviation obtained by using the maximum diffusion coefficient (100-90% RH) and the minimum one (65-50%) is not larger than 2.5%. Therefore the assumption for each RH interval does not affect significantly the accuracy of our approach.

Furthermore, the results highlight: (i) the hysteresis phenomena in the materials tested; (ii) that the increase of W/C ratio in the porous building materials will result in an increase of moisture diffusion coefficient; (iii) that the moisture diffusion coefficient of concrete based on cement with fly ash addition (CEMV) is lower than that based on OPC. That means the use of cement with fly ash addition in concrete could reduce kinetics of moisture transfer process.

3.2. Cup Method (DBM)

Experimental Set-Up

The cup method was adopted in our experiments. It is a well-accepted method for determination of water vapor diffusion coefficients for building materials. The method is used both for non-hygroscopic and hygroscopic materials and in both cases it is necessary to wait for a steady-state flow. In cup measurements there are isothermal conditions i.e. the temperature is uniform and constant. The process starts with an initial uniform moisture content in the material, which is placed as a cover over a cup containing a saturated salt-water solution keeping the relative humidity of the air inside the cup at a constant level (called cup climate). The cup with cover is placed in a climate chamber, where the air has a higher or lower relative humidity (called ambient climate) than inside the cup. If the ambient climate has a higher relative humidity than the cup climate it is possible to define a starting point for the time and the moisture is transported by diffusion into the cup. By weighting the cups regularly, the moisture flux can be determined. The moisture flux can be defined as the weight gain or loss of the cup in a given time interval. Based on the isothermal total moisture transport equation, the moisture diffusion coefficient can be easily calculated (Qin, 2007).

The building material used in the experimental tests was lime-cement mortar. The lime-cement mortar (Proportion by weight: Slaked lime/White cement/Aggregate = 50/50/650) was produced according to Hus AMA 98 (1998). When mixing the fresh mortars, water was added until the consistency of the mixture corresponded to that required for bricklaying. The aggregate used was Baskarp in the 0-3 mm fraction.

Eight different cups were used for conditioning the specimens (see Figure 12 and Figure 13). They were stored in a room with a temperature of 20 °C and relative humidity of 55%.

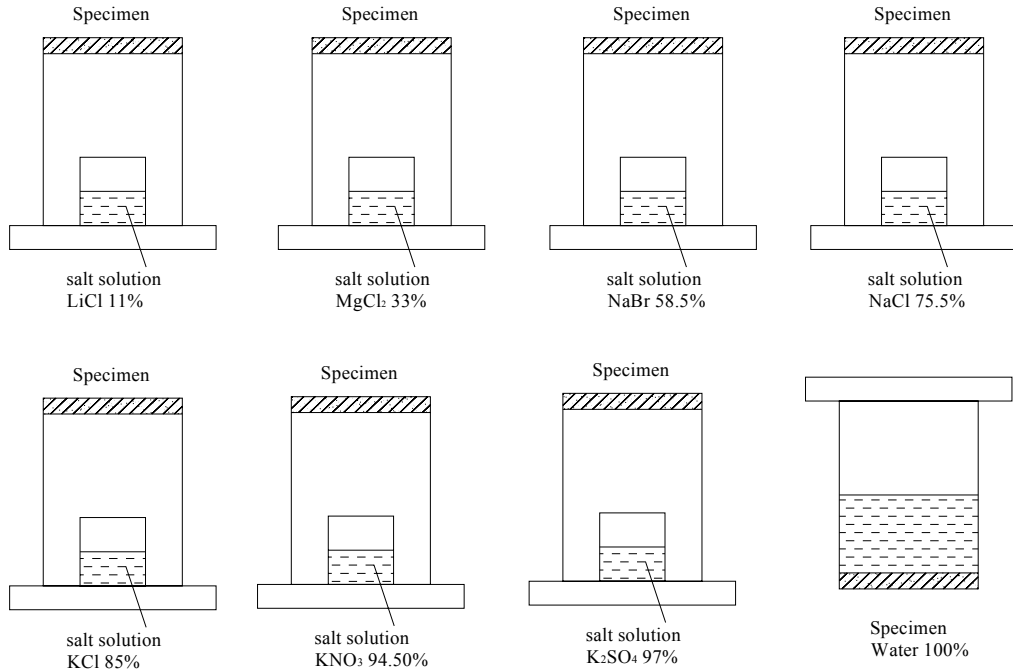


Figure 12. Schematic presentation of the cup method.



Figure 13. the photo of the cups and the balance.

The saturated salt solutions used for obtaining different relative humidities in the cups were: LiCl (11%), MgCl₂ (33%), NaBr (58.5%), NaCl (75.5%), KCl (85%), KNO₃ (94.5%), K₂SO₄ (97%) and H₂O (100%).

Measured Results

The specimens were weighted regularly until the steady-state is reached (Figure 14). Based on the measured moisture flux through the side of materials, we can calculate the moisture diffusion coefficients according to the isothermal moisture transfer equation (Eq. 1).

The moisture diffusion coefficients of the lime-cement mortar were given in Figure 15.

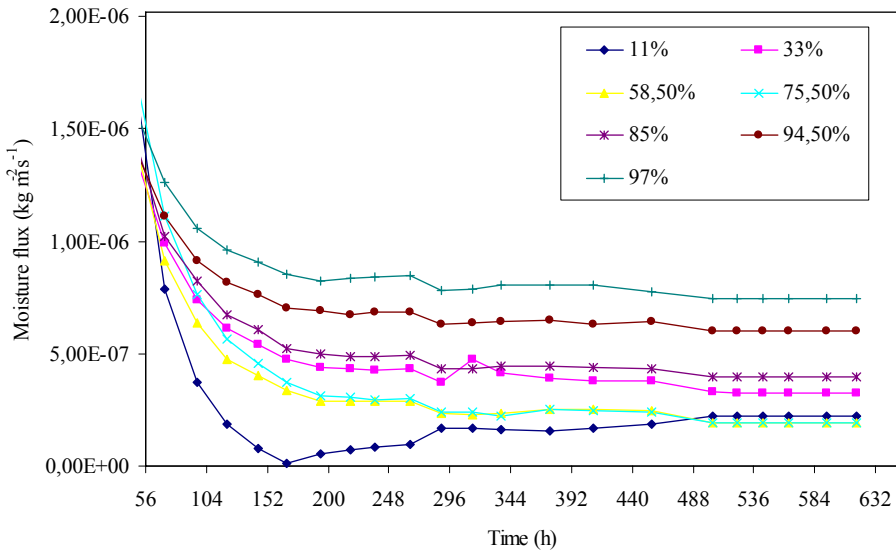


Figure 14. Moisture flux vs. time during the measurement.

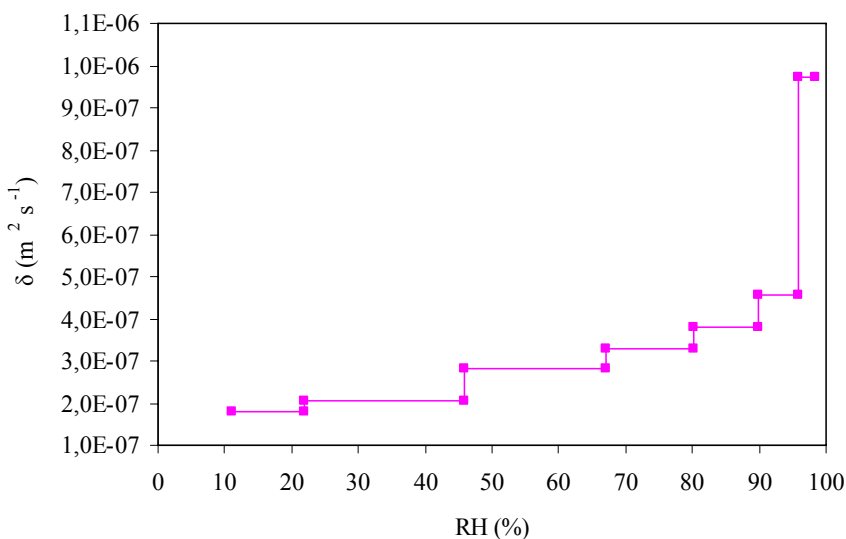


Figure 15. Average moisture diffusion coefficient as a function of RH for lime-cement mortar.

The cup method is a well-accepted and reliable approach to determine the moisture diffusivity of building materials. The similar experiments can be found in the literature (e.g. Tong, 1988 and Janz, 2000). Since the same material (lime-cement mortar) will be used for the experimental validation of our new model in Chapter 4, these experimental data is a part of the input material property database used in the simulation.

4. EVALUATION OF THE TEMPERATURE GRADIENT COEFFICIENT

4.1. Description

Normally the moisture transfer coefficients are measured under isothermal conditions. However, when both moisture and temperature conditions vary, it is difficult to find one single parameter that governs the total moisture transport alone. A logical treatment is to use the temperature directly as one of the driving potentials and let it describe the change of the moisture transport when a temperature gradient is added (Lukov, 1966, Qin et al. 2006):

$$j = -\delta \cdot \nabla v - D_T \cdot \nabla T = -\delta \cdot \nabla v - \varepsilon \cdot \delta \cdot \nabla T$$

where, j is the total moisture flux; δ is isothermal moisture diffusion coefficient; v is vapor content; T is temperature; D_T is the thermal diffusion coefficient due to the temperature gradient. The “temperature gradient coefficient” ε is the quotient between D_T and δ , and can be experimentally determined (Qin et al. 2008a). Using the general equations for isothermal and nonisothermal moisture flux, ε can be expressed as follows. In the equations below, the index i and t indicate isothermal and nonisothermal cases, respectively. Eq. (12) can be rewritten as:

$$-j_i = \delta_i \cdot \frac{dv_i}{dx} \quad (22)$$

Eq.(3) Can be rewritten as:

$$-j_t = \delta_t \cdot \frac{dv_t}{dx} + \delta_t \cdot \varepsilon \cdot \frac{dT}{dx} \quad (23)$$

Further, Eqs. (22) and (23) can be written:

$$\varepsilon \cdot \frac{dT}{dx} = -\frac{j_t}{\delta_t} - \frac{dv_t}{dx} \quad (24)$$

$$\frac{1}{\delta} = -\frac{1}{j_i} \cdot \frac{dv_i}{dx} \Big|_{v_i(x)=v}, v_i(0) \leq v \leq v_i(l) \quad (25)$$

As mentioned in Chapter 2, in the present model, the moisture diffusion coefficient δ_i in Eq. (23) is the same as the isothermal moisture coefficient δ_i used in Eq. (22). The difference between the isothermal and noisothermal cases is described by the second term on the right of the equal sign of Eq. (23), which takes into consideration that the first term is not physically correct under a temperature gradient. Insertion of Eq. (25) into Eq. (24), yields:

$$\varepsilon = \frac{1}{dT} \cdot \left[\frac{j_t}{j_i} \cdot \frac{dv_i}{dx} \Big|_{v_i(x)=v_t} - \frac{dv_t}{dx} \right] \quad (26)$$

This means that each point of $\frac{dv_i}{dx}$ is chosen at the same moisture content level as the corresponding $\frac{dv_t}{dx}$, as shown in Figure 16. The temperature gradient coefficient can thus be determined from the experimental measurements.

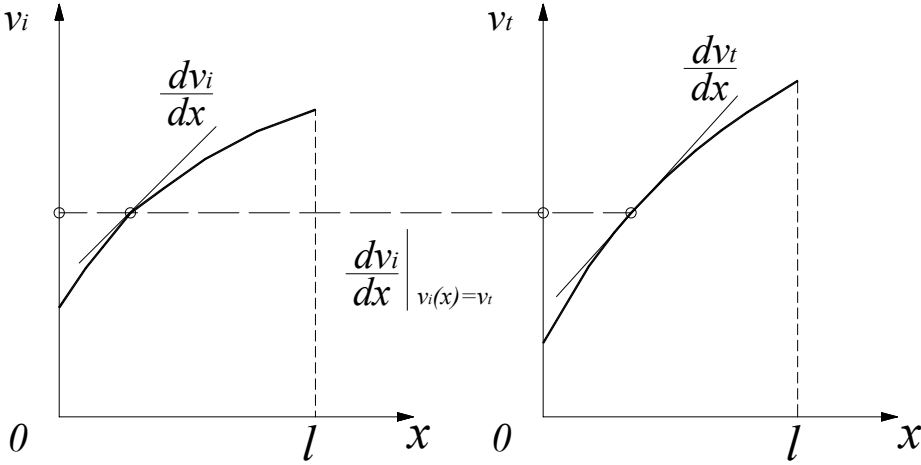


Figure 16. Evaluation of ε from measured data according to Eq. (26).

4.2. Experimental Set-Up

Materials and Preparations

Gotland sandstone (Janz, 2000) was used in this study. All specimens were drilled from the same piece of sandstone and have an overall dimension of 62 mm in diameter and 40 mm in length. In order to measure the inner moisture distribution easily, the specimen was sliced every 10 mm in length before the test. The cotton cloths were placed between interfaces of every two slices as an intermediate layer. It is proved that the cotton cloth is a perfect intermediate that can maintain continuous moisture transfer between two materials in both hygroscopic and capillary moisture ranges (Johansson, 2005). The specimens were preconditioned in two ways. Half of them were saturated by storing in water for several days.

The other half were oven-dried at 40°C for several days until equilibrium in weight was reached. Detailed data are presented in Table 5.

Table 5. Initial conditions for nonisothermal experiments

	Temperature (°C)	Relative humidity (%)
Climatic room	20 ± 1	65 ± 1.5
Specimen (initially dry)	20 ± 0.2	30 ± 1
Specimen (initially wet)	20 ± 0.2	99 ± 1
Air inside cups (at the water surface)	38 ± 0.2	82.32 ± 0.25 (Wexler et al., 1954)

Tests and Measurements

A modified cup method was used to measure the moisture flux and the moisture distribution of the porous building material during the non-isothermal process. The specimens were subjected not only to a moisture gradient but to a temperature gradient as well. A schematic view of the experimental set-up is given in Figures 17 and 18. Four cups with specimen were mounted into the expanded polystyrene, and then placed on the steel plate. Samples were fastened to cups in a traditional manner.

A heating device was used to supply a controlled temperature on the bottom side of the cups. The whole experimental set-up was placed inside a climatic room with constant temperature and RH. Meanwhile, other two cups, functioning as reference, were just put inside climatic room without temperature gradient on both sides. Initial conditions for the experiments are also listed in Table 5.

By weighing the cups regularly, the moisture loss during the experiment was measured, and then the moisture flux through the material was calculated.

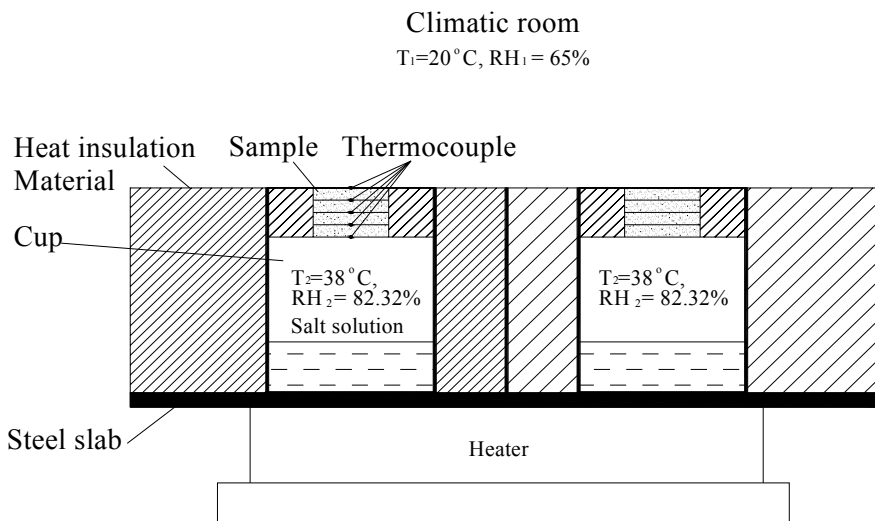


Figure 17. schematic view of the experimental set-up.



Figure 18. the photo of the experimental set-up.

During the tests, which lasted five weeks, temperature and relative humidity were logged in the climate room. The surface temperature and inner temperature distribution of specimens were measured with copper-constantan, bead thermocouples. The thermocouples were located at the interfaces of sandstone slices, as shown in Figure 17.

At the end of the tests, each slice was split into two pieces. One piece was placed in the test tube that was sealed. Later the relative humidity was determined with moisture probes (at 20°C). The other piece was weighted immediately, and then oven-dried at 105°C for 24 hours and weighted again to determine the moisture ratio. With these data, the distribution of vapor content could be obtained.

4.3. Measurement Results

The distribution of temperature, moisture ratio and relative humidity for nonisothermal and isothermal cases are shown in Figures 19—23 respectively. Using the RH distribution, the temperature distribution and the general gas law, we can determine the vapor content distributions for both cases, which are presented in Figures 24 and 25.

Figutrs 24 and 25 show the vapor content distribution of isothermal and non-isothermal cases, with the scatter expressed as one standard deviation; the regression equation and the coefficient of determination are also presented in the figures. S ince the vapor content profiles of both the nonisothermal and the isothermal cases show very small curvature, the moisture diffusion coefficient δ and temperature gradient coefficient ε can be calculated as a single average value for each case (initially dry/wet, or sorption/desorption). This will greatly simplify the resolution of the coupled system. The results are presented in Table 6.

This experimental method can be applied to evaluate the temperature gradient coefficient for most porous building materials. Theoretically, the temperature gradient coefficient is moisture dependent. However, when the isothermal and non-isothermal vapor content distributions inside the material show very small curvature, this coefficient can be regarded as a constant.

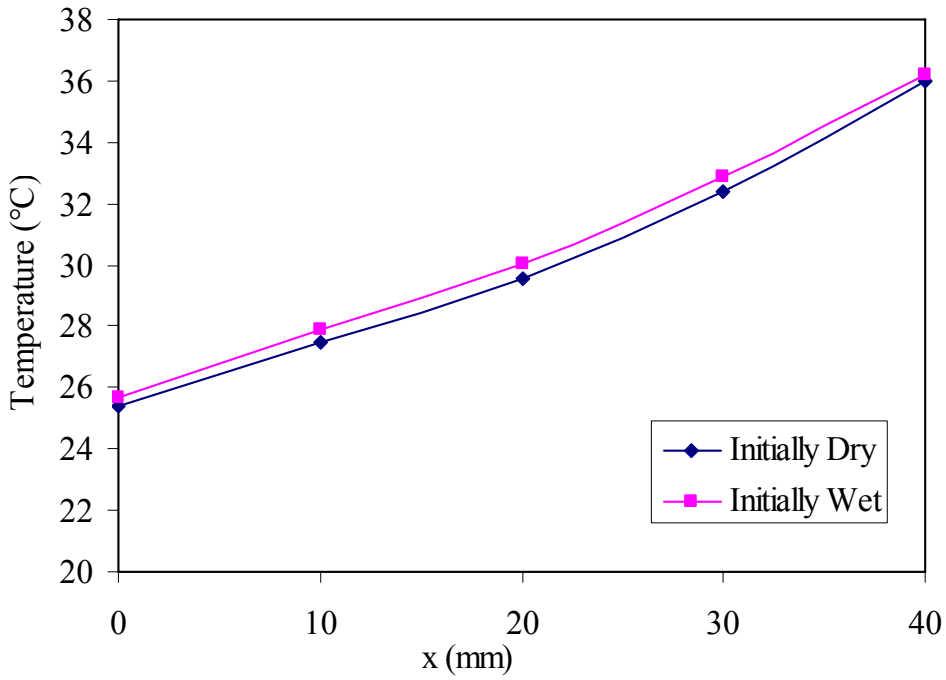


Figure 19. Temperature distribution for nonisothermal case.

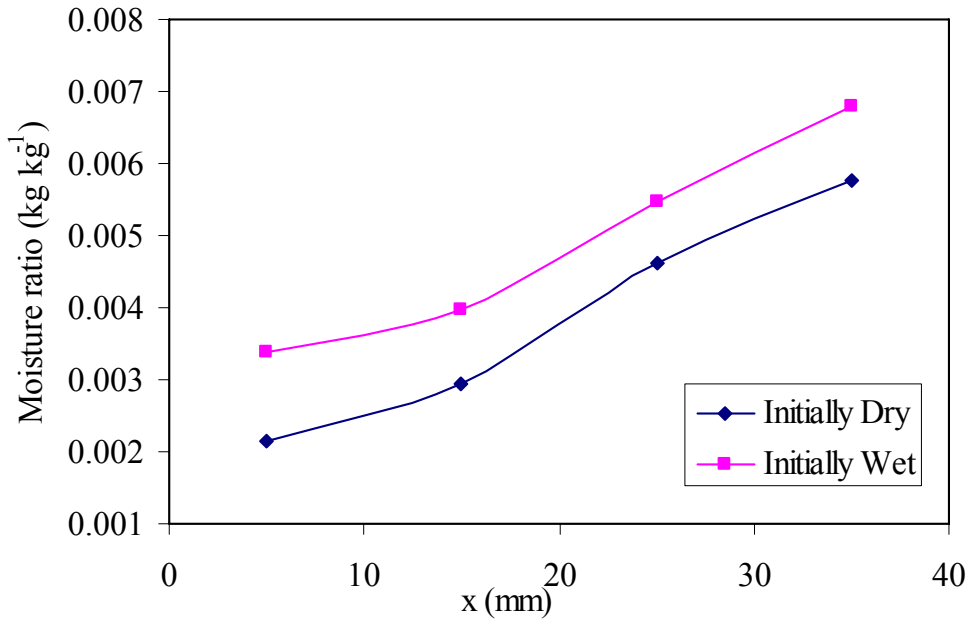


Figure 20. Moisture ratio distribution for nonisothermal case.

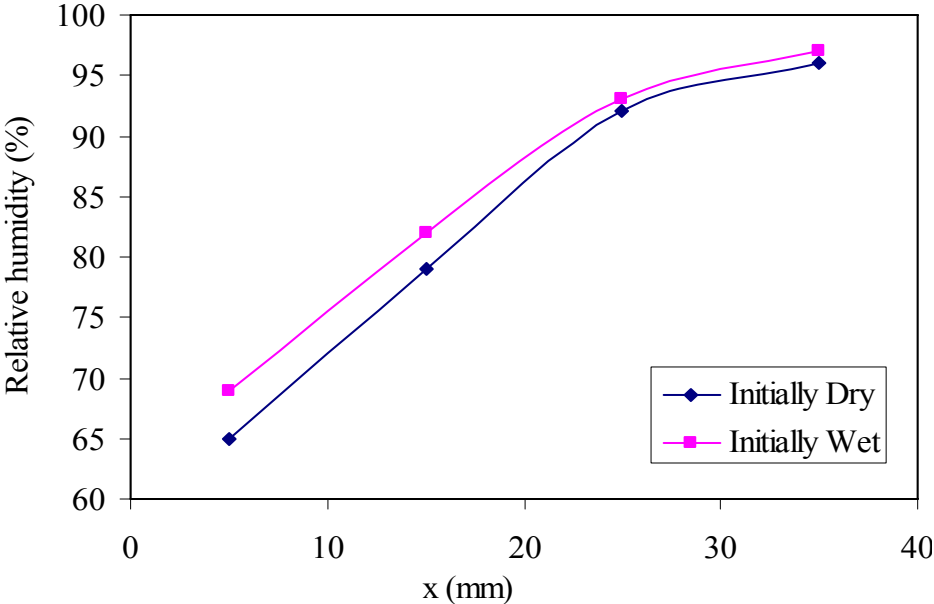


Figure 21. RH distribution for nonisothermal case.

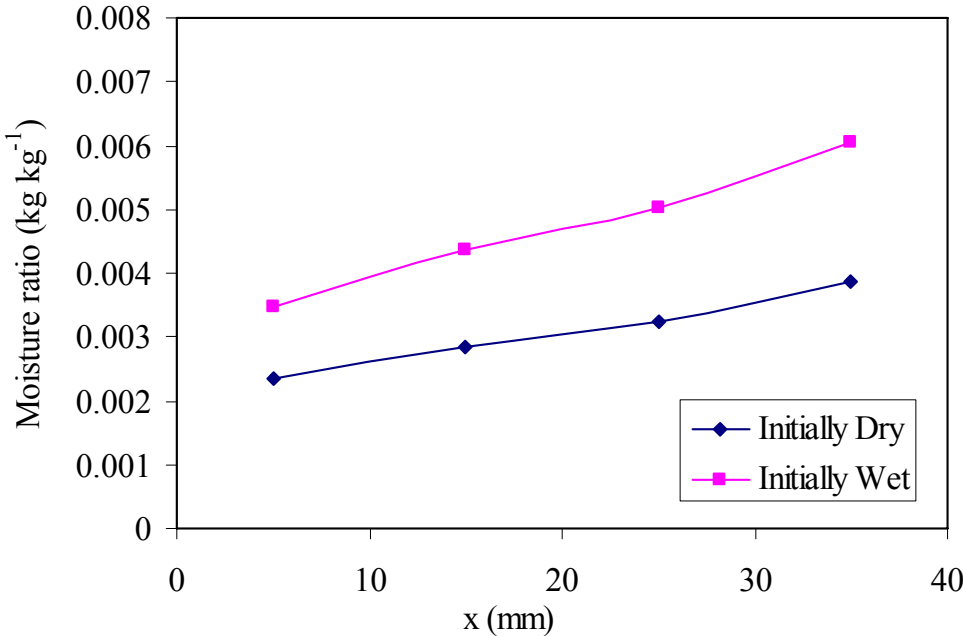


Figure 22. Moisture ratio distribution for isothermal case.

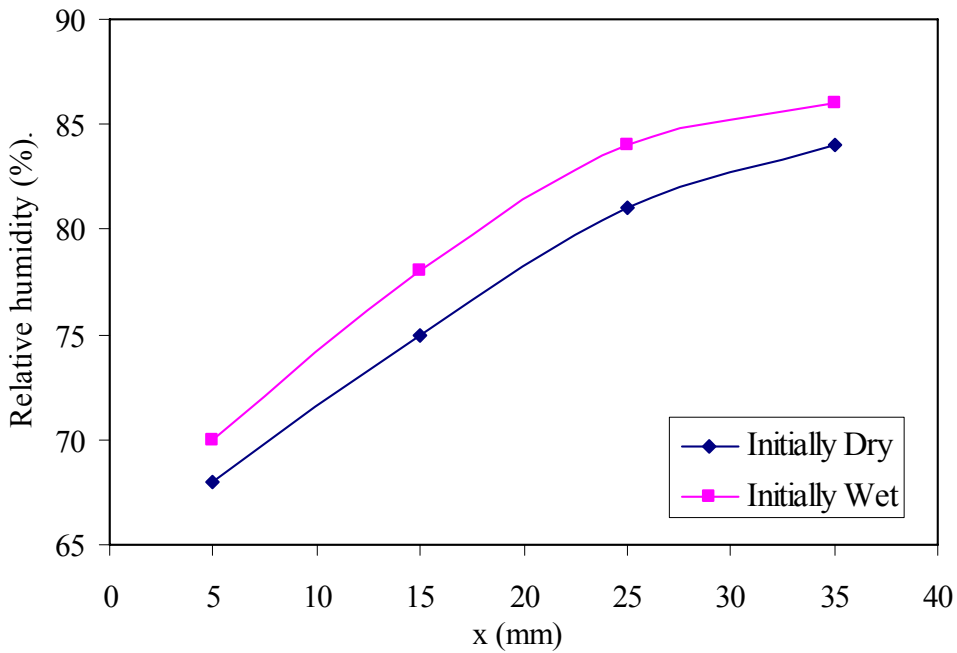


Figure 23. RH distribution for isothermal case.

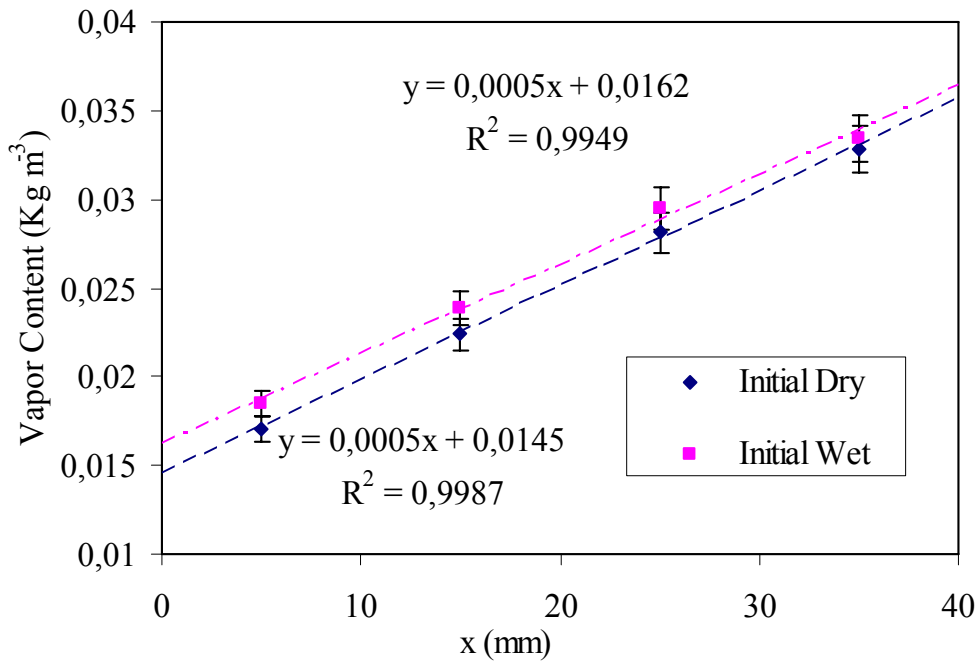


Figure 24. Vapor content distribution for nonisothermal case.

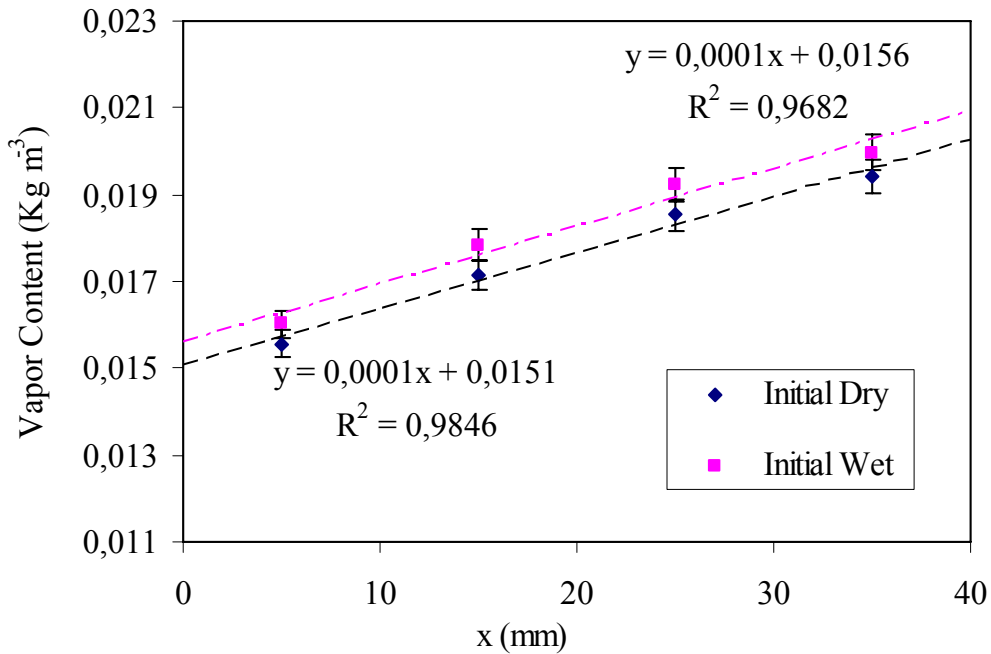


Figure 25. Vapor content distribution for isothermal case.

Table 6. Moisture diffusion coefficient and temperature gradient coefficient

	δ (m ² s ⁻¹)	ε (% K ⁻¹)
Initially Dry (Sorption process)	1.168×10^{-6}	0.03158
Initially Wet (Desorption process)	1.104×10^{-6}	0.03201

5. DETERMINATION OF THE SORPTION ISOTHERMS OF LIME-CEMENT MORTAR

5.1. Experimental Set-Up

The purpose of this experiment is to determine the absorption and desorption isotherms of cement mortar. The climate box method was used to measure the sorption isotherms. The samples to be tested were stored in tightened boxes in which a saturated salt solution is placed. A fan was installed in the box to assure that the relative humidity is the same in the whole box. The boxes in use contained saturated salt solutions that generate different relative humidity. The samples were weighted regularly, in our case, by taking the samples out of the boxes to an external balance. When the weight of samples, stored in different relative humidity, had stabilized, the equilibrium points were obtained. The boxes should be stored in a room with controlled temperature since the temperature affects the saturation pressures of the salt solution. The material used in the experimental tests was lime-cement mortar. The

lime-cement mortar CL 50/50/650 was produced according to Hus AMA 98 (1998). When mixing the fresh mortars, water was added until the consistency of the mixture corresponded to that required for bricklaying. The aggregate used was Baskarp in the 0-3 mm fraction.

Eight different boxes were used for conditioning the specimens stored in a room with a temperature of 20 °C. The saturated salt solutions used for obtaining different relative humidities in the boxes were: LiCl (11%), MgCl₂ (33%), NaBr (58.5%), NaCl (75.5%), KCl (85%), BaCl₂ (91%), KNO₃ (94.5%), K₂SO₄ (97%) and H₂O (100%). The specimens were left in the boxes until no change in weight observed over a period of 28 days. Measurements were performed both during absorption and desorption conditions. The schematic of climate box is presented in Figures 26 and 27.

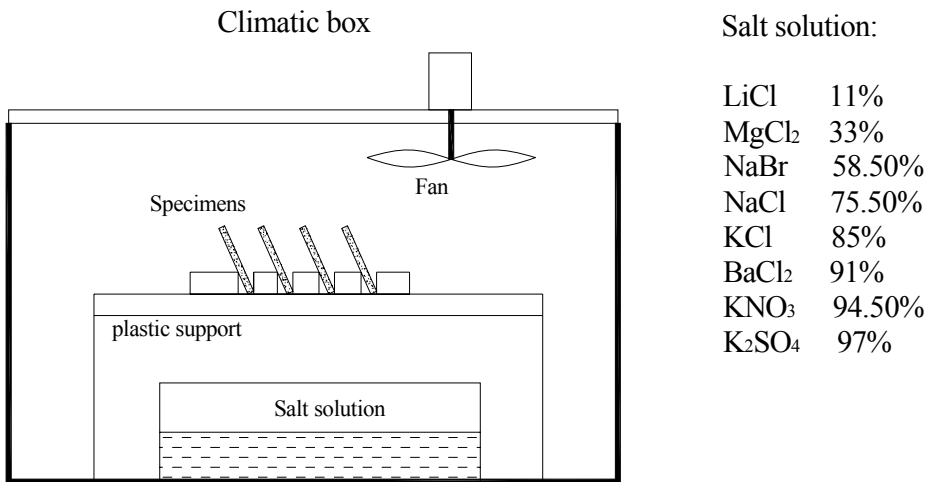


Figure 26. The schematic of the climatic box.



Figure 27. The photo of the climatic boxes.

5.2. Measurement Results

The measured sorption and desorption isotherms at the room temperature of cement mortar are presented in Figure 28. The hysteresis between the absorption and desorption isotherms can be detected with this method. However, compared with the sorption isotherms published in the reference (Janz, 2000), the hysteresis presented in Figure 28 is a little bit larger than that obtained by other more advanced methods (e.g. the sorption micro-balance method). The main reason might be a period of 28 days is not enough for the lime-cement mortar to reach the equilibrium. Nevertheless, this experiment still provides useful information about the sorption isotherms of mortar.

Although the climate box method is time-consuming for some materials, it is still the simplest and direct way of measuring the sorption isotherms, especially for the relative large samples. Another advantage of the method is that a great number of specimens can be stored in the same climate box at the same time. Therefore, this method is still widely used in the building material industry (Nilsson, 2004).

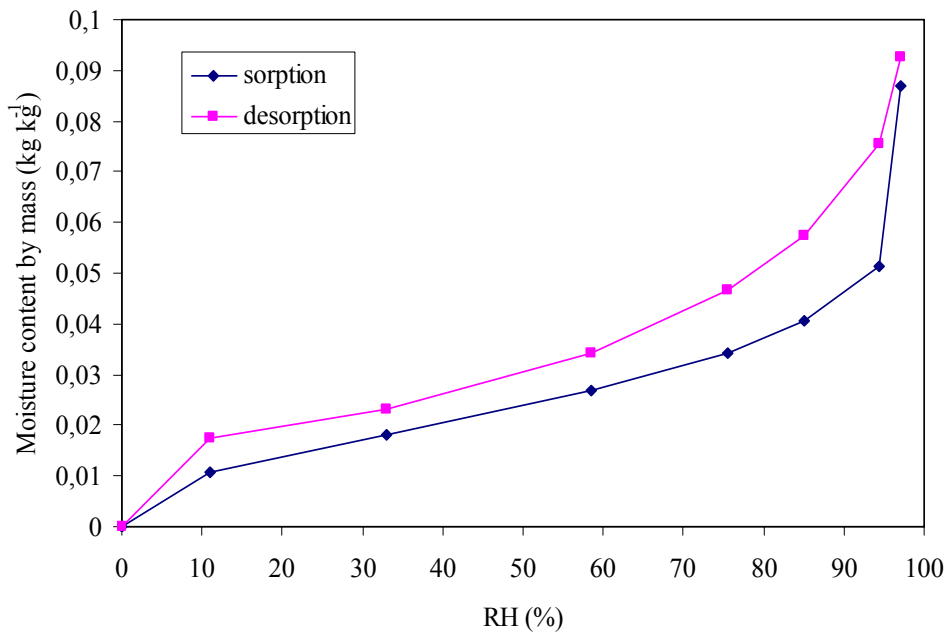


Figure 28. The sorption-desorption isotherms of lime-cement mortar.

CONCLUSIONS

In this chapter, four different experiments for evaluating the moisture transport and storage properties were presented. In section 2, a gravimetric method for the determination of moisture diffusivity and the sorption isotherms of cement-based materials was proposed. The main advantage of the method lies in the fact that the required device and protocol are relatively simple. The moisture diffusion coefficients calculated by this method fit some

published experimental data well (Marten, 2000). The classic cup method was also presented in Section 3. It was applied to evaluate the moisture diffusivity of a lime-cement mortar.

In section 4, the method for determining the temperature gradient coefficient was developed theoretically and experimentally. A modified cup method was used to measure the moisture flux and the moisture distribution of certain building material during the non-isothermal process. The specimens were subjected not only to a moisture gradient but to a temperature gradient as well. As reference, some isothermal measurements were also carried out under the same moisture gradient but no temperature gradient. The mathematical calculation is based on the model developed in Qin (2007), which assumes the moisture transfer coefficient in the non-isothermal transfer equation (Eq. 3) is the same as the moisture transfer coefficient in the isothermal case. Normally, the temperature gradient coefficient is moisture dependent, but for some materials (e.g. sandstone), if the moisture distribution inside the materials shows small curvature, the temperature gradient coefficient can be regarded as a constant. But more theoretical and experimental research is needed to verify this assumption. Nevertheless, the method can be applied to most building materials to determine the temperature gradient coefficient with a sufficient accuracy.

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Chapter 6

BUILDING MATERIALS AND ACOUSTIC COMFORT: SIMULATIONS, MEASUREMENTS AND APPLICATIONS

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ABSTRACT

Acoustic comfort is increasingly necessary in view of rising levels of noise pollution, especially in medium-sized towns and large cities. According to the WHO, noise pollution today is the type of pollution that affects the largest number of people in the world, second only to air and water pollution. Urban growth, along with the ever increasing number of circulating vehicles, greatly contributes to the higher levels of urban noise emission. Inhabitants of large cities all around the globe complain about noise, reporting irritability, rising blood pressure, headaches, sleep disorders, stress, etc. Considering that traffic and neighborhood noises (neighbors, construction work, religious buildings, commercial, cultural, and leisure activities) disturb people in their homes, it is conceivable that the sound insulation provided by façades and walls are inadequate, resulting in poor acoustic comfort. This chapter analyzes the acoustic performance of building materials with respect to their insulative properties. This performance is evaluated through *in situ* measurements of sound insulation, or alternatively, by computational simulation. This alternative is presented through real case studies in homes. The values found are compared with the limits set by International Standards for acoustic comfort. Techniques for measuring parameters that characterize building materials for acoustic comfort are presented and discussed. This chapter therefore offers an overview of building acoustics and acoustic performance of materials. The advantages and disadvantages of each of these approaches are discussed, as are technical standards in different countries.

1. INTRODUCTION

Noise and especially traffic noise are extremely annoying in urban environments. Traffic noise interferes with the quality of life (sleep, leisure and in the workplace). Noise in large

cities is now seen as a factor that impairs quality of life (Lebiedowska, 2005). The World Health Organization reports that, after air and water pollution, noise is the type of pollution that affects the largest number of people.

Urban traffic noise is an environmental source of pollution worldwide. Noise pollution in urban settings is increasingly significant as urban environments are becoming more crowded and dynamic (Raimbault and Dubois, 2005). Many field surveys have been conducted to evaluate urban noise pollution (Langdon, 1976; Burgess, 1977; Lam and Brown, 1977; Griffiths and Langdon, 1986; Arana and Garcia, 1998; Morillas et.al., 2002; Zannin et.al., 2002; Zannin et.al. 2003; Diniz and Zannin, 2004; Alves et.al. 2004; Diniz and Zannin, 2005; Paz et.al., 2005; Coensel et.al., 2005; Gündogdu et.al., 2005; Tansatcha et.al., 2005).

The growth of cities, and in consequence, rising numbers of noise sources from busses, cars, motorcycles, trains, planes, industry, people, etc. have contributed to further enhance the emissions and the immission noise levels in urban environments. Several researchers have attempted to characterize the noise pollution (Garcia et al., 1992; Yoshida et al., 1997; Osada et al., 1997; Kageyama et al.; Saadu et al., 1996; Maschke, 1999; Zannin et al., 2001; Zannin et al., 2002).

A survey conducted in a large Brazilian city, Curitiba (~1,7 million inhabitants), by (Zannin et al., 2001, 2002) showed that noise generated by vehicle traffic is the most annoying type of noise, followed by noise from neighbors. Of the 860 participants of the survey, 73% considered road traffic the main source of noise.

Since both traffic and neighborhood noises disturb people in their homes, it is reasonable to assume that the latter perform poorly in terms of acoustic insulation and are therefore not fulfilling one of their purposes, which is to provide comfort to their occupants. This fact is even more critical in countries like Brazil, which, unlike countries such as France, Germany, the US, UK and Spain, do not have standards specifying minimum values of performance with respect to noise insulation of homes.

In view of the above, the purpose of this work was to measure the sound insulation indices of façades. To this end, we used the international standard ISO 140-5:1998–Acoustics – Measurement of sound insulation in buildings and of building elements – Part 5: Field measurements of airborne sound insulation of façade elements and façades. The results are presented in the form of single-number quantities of airborne sound insulation in buildings, according to the method described in the international standard ISO 717-1:1996 – Acoustics – Rating of sound insulation in buildings and of building elements – Part 1: Airborne sound insulation (ISO 717-1:1996). The sound insulation indices between rooms in a building can be measured based on the international standard ISO 140-4:1998 – Acoustics – Measurement of sound insulation in buildings and of building elements – Part 4: Field measurement of airborne sound insulation between rooms. However, this chapter presents only measurements of the sound insulation indices of façades.

The importance of *in situ* measurements lies in the fact that data on physical properties of acoustic materials found in classical works such as those of Cremer and Müller (1978), Cremer and Hubert (1990), Beranek and Vér (1992), Heckl and Müller (1994), Harris (1998), Fasold and Veres (2003) and Kuttruff (2006), among others, generally refer to acoustic data obtained in the laboratory. These data, e.g., sound insulation indices, are usually higher than those obtained *in situ*, since laboratory environments ensure that sound energy is transmitted preferentially through the material being tested, while *in situ* measurements are subject to the effect of sound energy transmission through the flanks.

The international standard, ISO 140-3: 1995 – Acoustics – Measurement of sound insulation in buildings and of building elements – Part 3: Laboratory measurements of airborne sound insulation of building elements, gives all the necessary details to carry out measurements of sound insulation indices in the laboratory.

The present work also includes a simulation of sound insulation using the software program Bastian 2.3 (Bastian, 2003). The Bastian program is based on the calculation procedure of the European standards EN 123454-1:2000 and EN 12354-3:2000, which consider sound transmission through the flanks (European Norm, 2000).

The computational prediction of sound insulation indices has proved an important auxiliary tool in building design. Even before the actual construction, it allows for viability tests and a choice of the most suitable solutions.

Moreover, properly adjusted predictions can be used to estimate the performance of existing structures and, in this case, the costs of computational models are considerably lower when compared with *in situ* measuring systems. The digital models require less logistic effort, fewer teams to collect data, and are independent of meteorological conditions (i.e., *in situ* measurements cannot be taken on rainy days or in high winds).

2. SOUND INSULATION – SOUND INSULATION INDEX – ACOUSTICS DEFINITIONS

According to Beranek (1960 apud Harris 1998), acoustic insulation is the ability of a structure to reduce the sound that is transmitted from an emitting space to a receiving space. Acoustic insulation deals with the quantity of sound emitted, which is transmitted from one environment to another. Heckl (1980) affirms that good sound insulation is achieved by using construction materials with high surface density. The higher the mass of the constructive element and the greater the frequency of the incident sound the greater the difficulty to make the material vibrate, thus ensuring more efficient insulation.

When sound waves hit a constructive element, part of the energy is reflected and part of it is stored inside the element, causing it to vibrate and converting into a source of noise (Meisser, 1973 apud Ferreira, 2004 and Fasfold and Veres, 2003).

Figure 1 shows the paths travelled by sound energy. Part of this energy is transmitted directly through the element of separation between the rooms. This portion is called direct transmission. Another part is transmitted through the flanks (ceiling and floor slabs) and is called indirect transmission. The portions of direct and indirect sound transmission make up the total energy transmitted between the sound emitting environment and the receiving one.

Every building has many possibilities for sound transmission trajectories. In most cases, part of the sound produced in a room is transmitted indirectly to adjacent rooms through flanking elements such as lateral walls, ceilings and floors (Elmallawany, 1983). The loss of sound transmission between two rooms depends on the material used in the construction of the dividing wall between them, as well as on the trajectory of the sound that propagates through the flanks (Elmallawany, 1983).

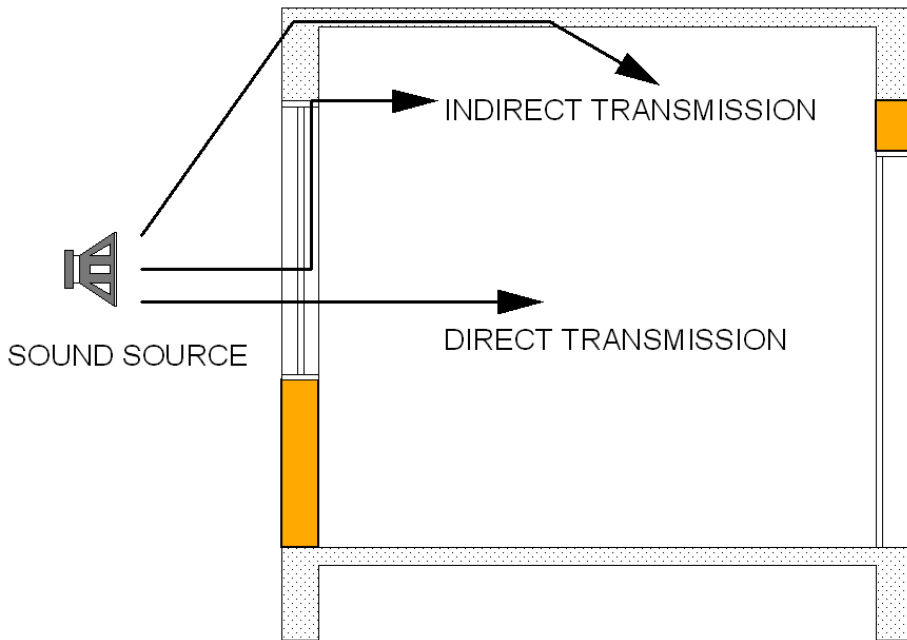


Figure 1. Sound transmission paths: direct and indirect transmission (through the flanks).

Airborne sound insulation between two rooms is determined by the difference between the sound pressure levels measured in the room where the sound is generated and those in the room where the sound is received. The procedure for measuring the sound insulation index of constructive elements such as doors, walls, windowpanes and windows in the laboratory is specified by the ISO 140-3:1995 standard.

According to the ISO 140-3:1978 standard, the Sound Reduction Index R is given by the relation:

$$R = L_1 - L_2 + 10 \log \frac{S}{A} \text{ (dB)} \quad (1)$$

where: L_1 = sound pressure level at the acoustic emission site (dB); L_2 = sound pressure level in the receiving room (dB); S = area of common wall between emitting and receiving the rooms (m^2); A = equivalent sound absorption of the sound receiving room (m^2).

For *in situ* measurements of existing buildings, the ISO 140-4:1998 standard presents the following definitions of sound insulation indices:

- 1) Standardized Level Difference D_{nT} in which the reverberation time of the environment where the sound is received is related to the reverberation time of reference.

$$D_{nT} = L_1 - L_2 + 10 \log \frac{T}{T_0} \text{ (dB)} \quad (2)$$

where: L_1 = sound pressure level at the acoustic emission site (dB); L_2 = sound pressure level in the receiving room (dB); T = reverberation time of the sound receiving room (s); T_0 = reverberation time of reference (0.5 s).

- 2) The Apparent Sound Reduction Index R' considers the wall area, the reverberation time and the volume of the rooms where the sounds are received, presupposing the existence of diffuse sound fields in the two rooms.

$$R' = L_1 - L_2 + 10 \log \frac{S}{A} \text{ (dB)} \quad (3)$$

where: L_1 = sound pressure level at the acoustic emission site (dB); L_2 = sound pressure level in the receiving room (dB); S = area of the common surface between the emitting and receiving rooms (m^2); A = equivalent sound absorption area in the receiving room in m^2 .

The Apparent Sound Reduction Index R' and the Standardized Level Difference $D_{n,T}$ are sound insulation values given for each frequency of the measure spectrum. The ISO 717-1:1996 standard presents a single index for the sound insulation related to the ISO 140-4:1998 standard, providing a weighted value for insulation indices. These weighted indices are called Weighted apparent sound reduction index R'_w and Weighted standardized level difference $D_{nT,w}$.

The sound insulation indices obtained by means of these expressions allow one to evaluate the acoustic protection the building affords its occupants, and to verify if the constructive elements meet the design specifications, as well as to check if failures occurred during the construction process.

According to the ISO 140-5:1998 standard, the sound insulation index of external constructive elements (doors, windows) can be determined by two methods: 1) the loudspeaker method, which uses a sound box as the external noise source, and 2) the road traffic method, which uses the vehicle traffic passing in front of the building as the sound source in evaluations.

The ISO 140-5:1998 standard also presents other methods, not discussed here, which use airborne noise – the air traffic method, or railway noise – the railway traffic method – as the external noise source.

The sound insulation of constructive elements of the façade can be determined using the flow of vehicles passing in front of the building under evaluation as the sound source. However, because of the inevitable fluctuation of sound levels from the source of emission, they should be measured simultaneously with the sound levels inside the house.

For both the loudspeaker method and the road traffic method, the ISO 140-5:1998 standard lists the indices below for evaluation of the sound insulation of façades:

- 1) Apparent Sound Reduction Index $R'_{w,s}$: sound insulation of the building's façade when the sound source is vehicle traffic, considering the free-field situation:

$$R'_{tr,s} = L_{eq,1,s} - L_{eq,2} + 10 \log \frac{S}{A} - 3 \text{ (dB)} \quad (4)$$

where: $L_{eq,1,s}$ = equivalent sound pressure level measured outside the building, in dB; $L_{eq,2}$ = equivalent sound pressure level at the receiving room (dB); S = area of the test specimen in m^2 , determined according to ISO 140-5:1998 annex A; A = equivalent sound absorption area in the receiving room in m^2 .

- 2) Standardized Level Difference $D_{tr,2m,nT}$: a method for measuring the global acoustic insulation of the façade when the sound source is vehicle traffic and the external microphone is positioned 2 meters from the measured surface.

$$D_{tr,2m,nT} = L_{1,2m} - L_2 + 10 \log \frac{T}{T_0} \text{ (dB)} \quad (5)$$

where: $L_{1,2m}$ = sound pressure level measured outside the building with the microphone placed 2 meters from the measured surface (dB); L_2 = sound pressure level in the receiving room (dB); T = reverberation time in the sound receiving room (s); T_0 = reverberation time of reference (0.5 s).

- 3) Apparent sound reduction index R'_{45° : used to measure the acoustic insulation of the external elements of the building when the sound source is a sound box and when the sound incidence angle is 45° . The sound incidence angle is the angle between the center of the sound box normal to the center of the surface of the façade. R'_{45° is calculated by:

$$R'_{45^\circ} = L_{1,s} - L_2 + 10 \log(S/A) - 1.5 \text{ (dB)} \quad (6)$$

where: $L_{1,s}$ = Mean sound pressure level at the surface of the façade (dB); L_2 = Mean sound pressure level in the receiving room (dB); S = Area of the façade under analysis (m^2); A = equivalent sound absorption area in the receiving room in m^2 .

The Apparent Sound Reduction Index $R'_{tr,s}$, the Apparent Sound Reduction Index R'_{45° , and the Standardized Level Difference $D_{tr,2m,nT}$, are sound insulation values given for each frequency of the measure spectrum. The ISO 717-1:1996 standard presents a single index for sound insulation related to the ISO 140-5:1998 standard, providing a weighted value for the insulation indices.

3. FIELD MEASUREMENTS AND SIMULATION OF THE SOUND INSULATION INDEX

The results of this work were obtained from *in situ* measurements of the sound insulation indices of façades. Simulations were also made of these indices, using the Bastian 2.3 software program, which uses the calculation method of the European standards EN 12354-1, which prescribes a method to predict the sound insulation index between rooms of a home, and EN 12354-3, which presents a method to simulate the sound insulation of façades.

Using the road traffic method, measurements were taken of the sound insulation index $R'_{w,s,w}$ Weighted Apparent Sound Reduction Index, in eleven homes. Taking measurements is a task that requires considerable logistic effort and planning due to the need to transport equipment, its distribution in the rooms, and the noise generated during the measuring process.

The number of measured points evaluated in each room was determined according to its dimensions, and was never less than 3. A minimum distance of 0.5 m between the wall and the microphone was also established.

The external, L_1 (traffic noise) and internal, L_2 (receiving room) sound levels were measured at the same time, i.e., in real time, as indicated by the ISO 140-5:1998 standard for the determination of the insulation index of façades.

An important item of the measuring system is the use of a flat cable. Figure 2 illustrates the use of the Brüel and Kjaer AR 0014 flat cable, which allows the cable connecting the external microphone to the BK2260 acoustic analyzer, located in the receiving room, to pass through the window without requiring the window to remain ajar. The use of the flat cable helps reduce errors in field measurements due to sound transmission through cracks.



Figure 2. Use of a flat cable in measurements of the sound insulation of façades.

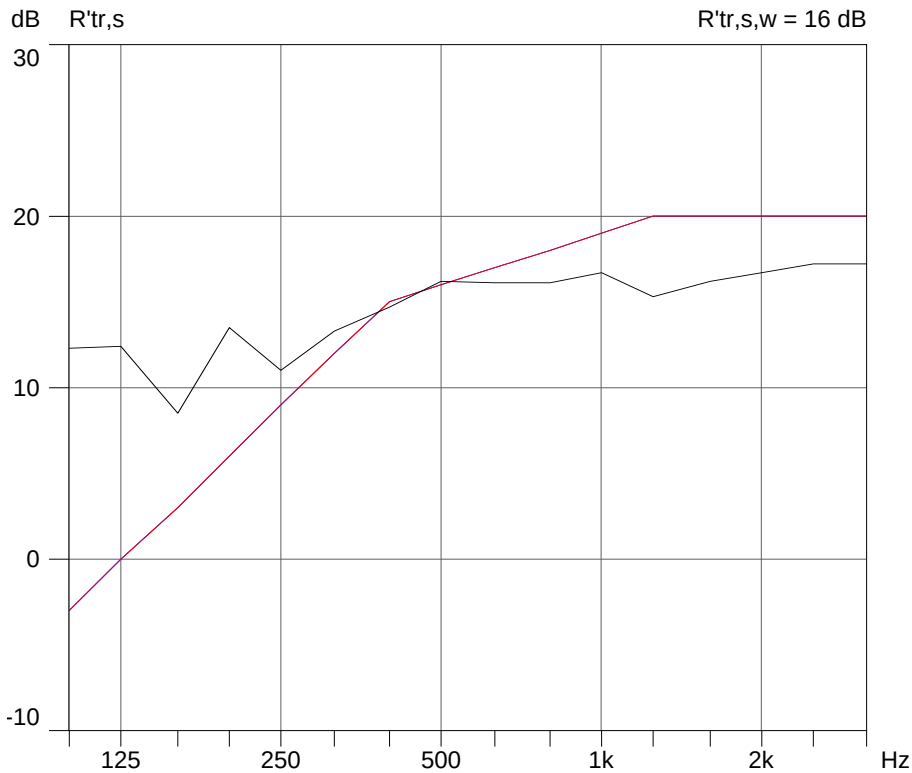


Figure 3. Graph generated by the BK 7830 software from façade sound insulation indices as a function of frequency $R'_{tr,s}$ and weighted sound insulation number $R'_{tr,s,w}=16\text{ dB}$, obtained according to the procedure of the ISO 717-1:1996 standard.

The field measurements were processed using the BK 7830 Qualifier software, which supplies as output data the graphs that present the sound insulation indices in one-third octave frequency bands, and the single number of sound insulation, as depicted in Figure 2. The single number of sound insulation, the weighted apparent sound reduction index $R'_{tr,s,w}=16\text{ dB}$, which is shown in the upper right-hand corner of Figure 3, is calculated according to the graphic procedure established by the ISO 717-1:1996 standard.

The equipment and software used here were as follows: 1) Brüel and Kjaer 2260 Investigator acoustic analyzer; 2) Brüel and Kjaer BZ 7204 Building Acoustics Software; 3) Brüel and Kjaer 7830 Software Qualifier; 4) Brüel and Kjaer 2716 power amplifier; 5) Brüel and Kjaer 4296 dodecahedron loudspeaker; 6) a set of Brüel and Kjaer 4190 free field $\frac{1}{2}$ " microphones; 7) a set of Brüel and Kjaer cables and preamplifiers; and 8) Brüel and Kjaer 4231 sound calibrator.

The Figures 4 and 5 below illustrates the some equipment used in the measurements.

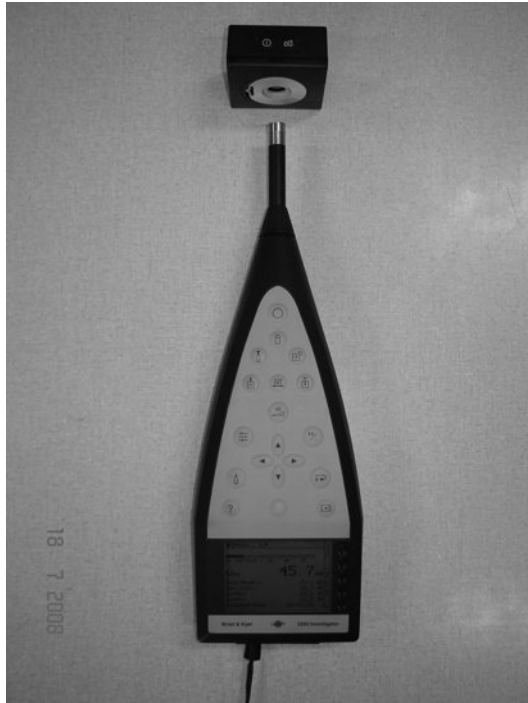


Figure 4. Brüel and Kjaer 2260 acoustic analyzer and Brüel and Kjaer BK 4231 calibrator.



Figure 5. Omnidirectional Sound Source.

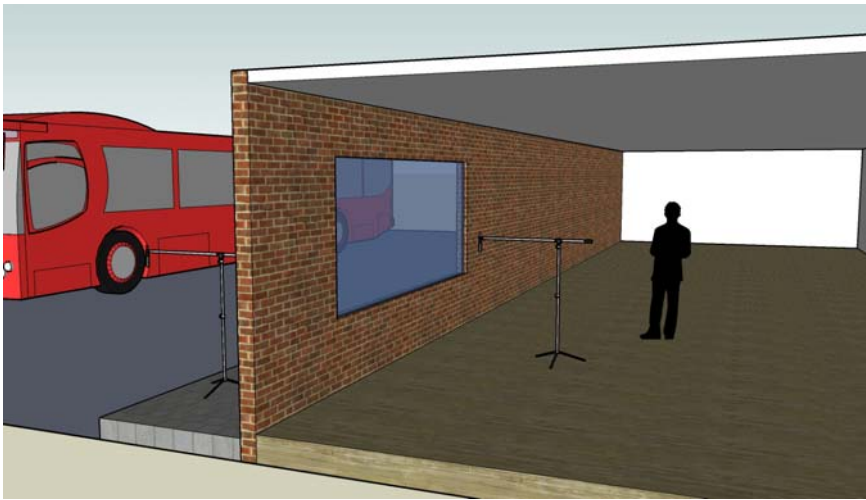


Figure 6. Measurement of façade sound insulation by the road traffic method following the ISO 140-5:1998 standard. Dual channel real-time measurements.

Figure 6 shows the façade insulation measured by the road traffic method, according to the ISO 140-5:1998 standard. In this figure, the sound source is characterized by traffic noise. The figure also depicts the microphone used for measuring external noise levels and the microphone for measuring internal noise levels. Measurements are taken in real time using the BK 2260 analyzer (see Figure 4). This type of measurement uses the flat cable illustrated in Figure 2. The Bastian 2.3 software program was used for the computational simulation of the sound insulation index of façades $R'_{tr,s,w}$.

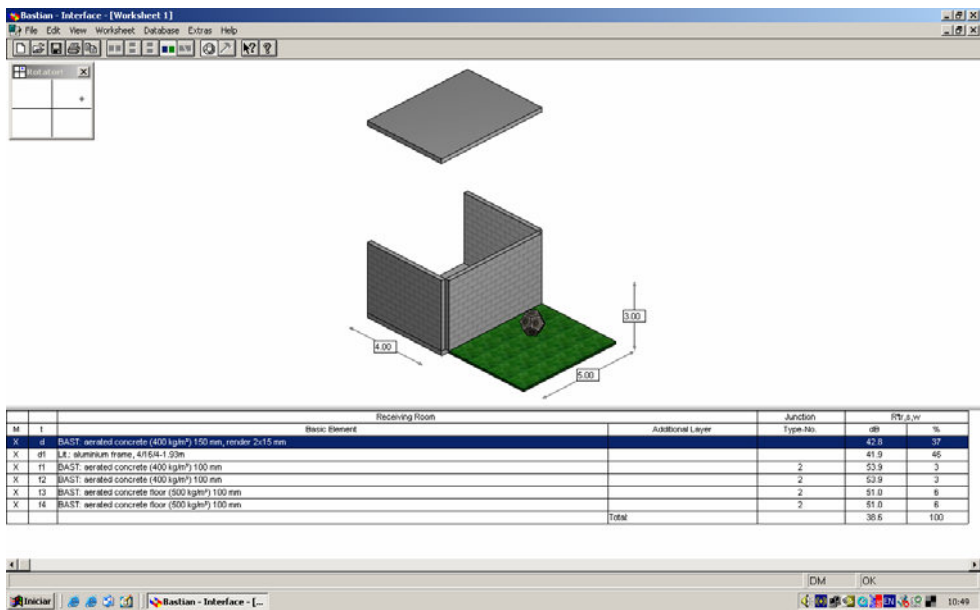


Figure 7. Work screen of the Bastian software 2.3, and different configurations of the software for determining the Weighted Apparent Sound Reduction Index $R'_{tr,s,w}$.

To predict the sound insulation of façades, this program uses the calculation procedure described by the European standard EN 12354-3:2000 (Simmons, 2001; Simmons, 2002; Craik, 2002; Saarinen, 2002).

The Bastian software has a large database composed of a variety of constructive elements: simple walls, double walls, ceiling slabs, windows, doors, etc. This database contains acoustic parameters of constructive elements measured in the laboratory, such as the sound reduction index R and the critical f_c partition frequency.

Figure 7 illustrates the work screen of the Bastian 2.3 software for determining the Weighted Apparent Sound Reduction Index $R'_{tr,s,w}$. The dodecahedron in this figure represents the external sound source, in this case traffic noise at the façade under analysis, measured by the road traffic method (ISO 140-5:1998).

4. MEASUREMENTS AND APPLICATIONS

A description is given below of the residences (homes) evaluated and of the results of the measurements of façade sound insulation indices. These indices are presented as single numbers, following the ISO 717-1:1996 standard and expressed as the weighted apparent sound reduction index $R'_{tr,s,w}$.

Home 1

An apartment located on the 9th floor of a residential building (Figure 8).



Figure 8. Façade of the evaluated building.

The external walls are made of bricks with 6 horizontal holes, mortared on both sides, with a total thickness of approximately 200 mm. The windows have aluminum frames and single glass panes. The dimensions of the window in the façade are 1.45 x 1.45 m.

Figure 9 shows the floor plan of the evaluated apartment, indicating the façade used for the measurement.

Para a medição do índice de isolamento sonoro da fachada utilizou-se o ruído de tráfego como fonte sonora externa e o espectro desta fonte é apresentado na Figura 10.

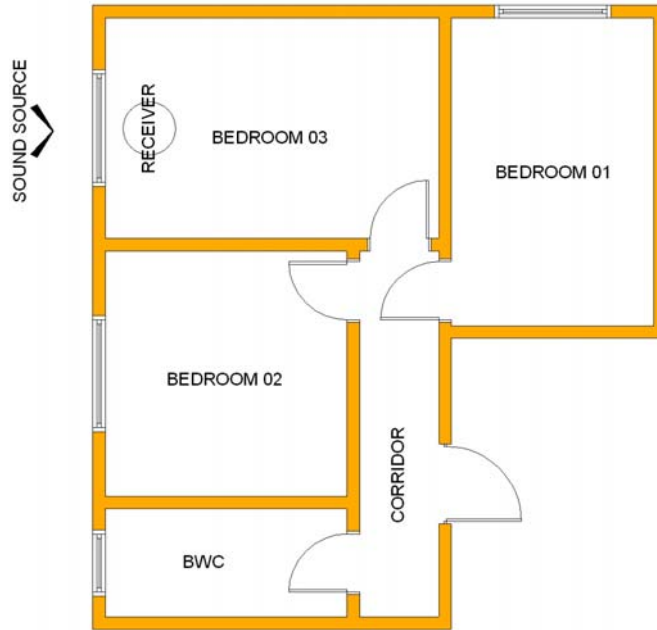


Figure 9. Measurement of Façade Insulation – Home 1.

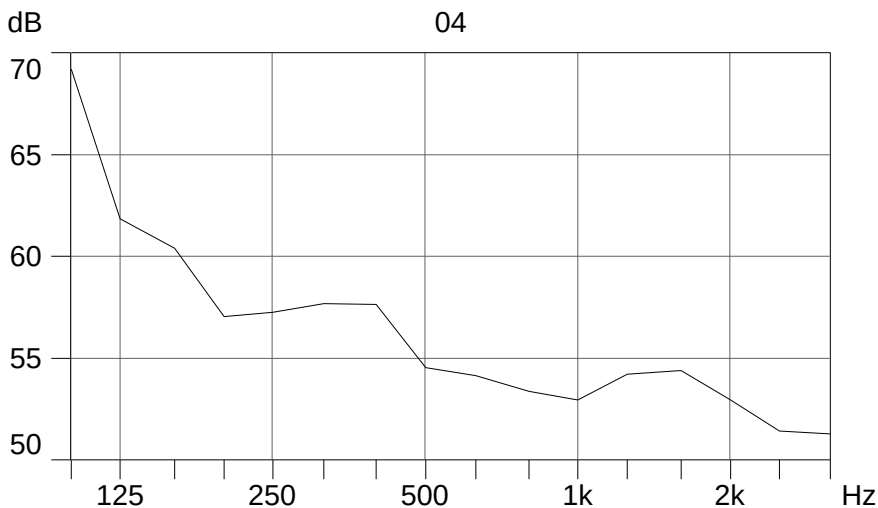


Figure 10. Spectrum of traffic noise frequencies – Home 1.

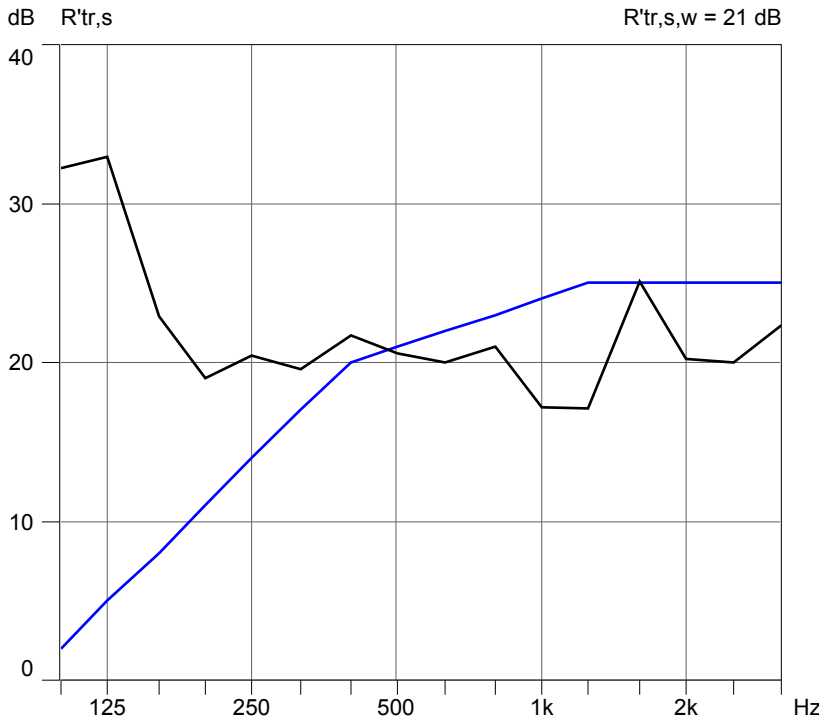


Figure 11. Sound insulation index measured at the façade of Home 1 – $R'_{tr,s,w} = 21$ dB.

The graph in Figure 11 represents the measurement of the façade sound insulation index of Home 1 as a function of frequency, as well as the single-number of airborne sound insulation, $R'_{tr,s,w} = 21$ dB.

The measured sound index was unacceptable when compared with the façade insulation values recommended by international standards such as DIN 4109 (DIN, 1989). The DIN 4109 standard presents values for the façade sound insulation index for rooms for different purposes (see Table 3).

Table 3. Façade sound insulation index $R'_{w,res}$ as a function of the external noise level (adapted from DIN 4109, 1989)

External Noise Level	Types of Rooms: Living Rooms, Bedrooms, Classrooms and Similar rooms
L_{eq} dB(A)	Façade Sound Insulation $R'_{w,res}$ dB
Up to 55	30
56 to 60	30
61 to 65	35
66 to 70	40
71 to 75	45
76 to 80	50
Higher than 80	Special noise control measures are required

The façade sound insulation values are recommended according to the level of external noise. In this case, the measured sound insulation index, 21 dB, is clearly well below the minimum level required even for quiet regions, which is 30 dB. When this value of 21 dB is compared with the level recommended by the standard as a function of external noise, which, for the location of Home 1, presented a level of 71.8 dB(A), it proves to be even more deficient since, in this case, the standard recommends a sound insulation index of 45 dB.

Home 2

An apartment located on the 17th floor of a residential building. The external walls are made of bricks with 6 horizontal holes, mortared on both sides, with a total thickness of approximately 200 mm. The windows have aluminum frames and single 4mm thick glass panes.

Figure 12 shows the floor plan of the evaluated apartment, indicating the façade used for the measurement.

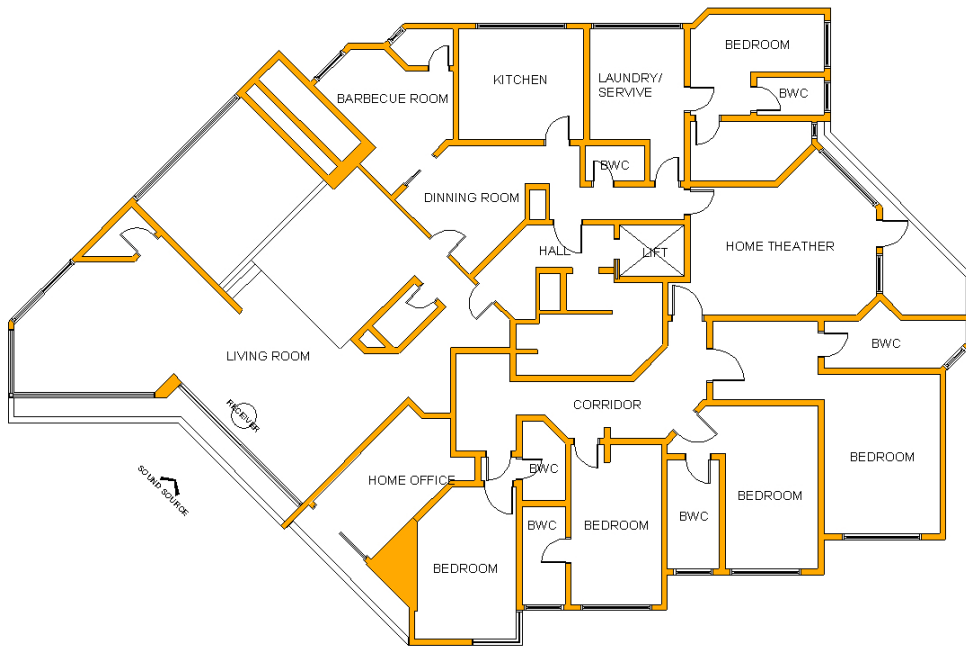


Figure 12. Location of the façades – Home 2.

The façade sound insulation index of this home was measured using traffic noise as the external sound source, whose spectrum is depicted in Figure 13.

The graph in Figure 14 represents the measurement of the façade sound insulation index of Home 2 as a function of frequency, as well as the single-number of airborne sound insulation, $R'_{tr,s,w} = 22$ dB.

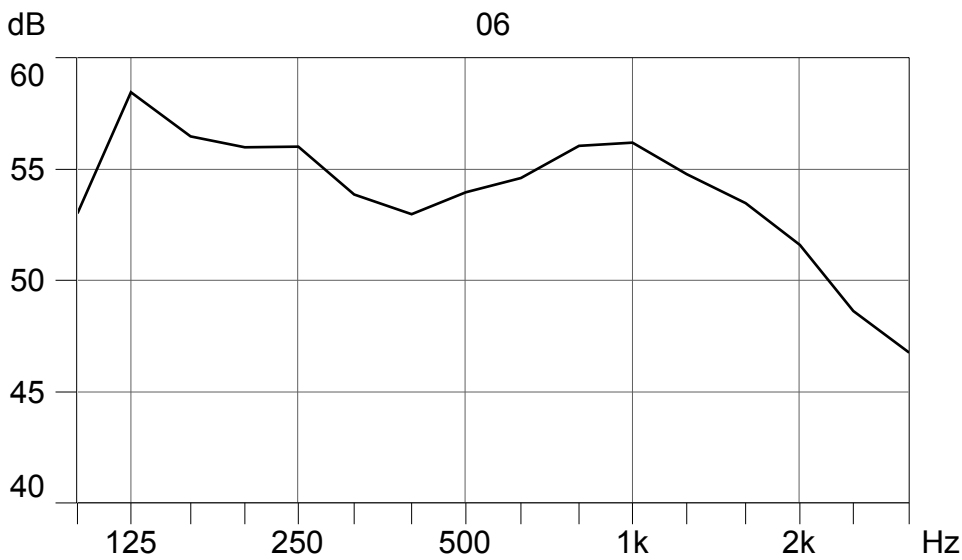


Figure 13. Spectrum of traffic noise frequencies – Home 2.

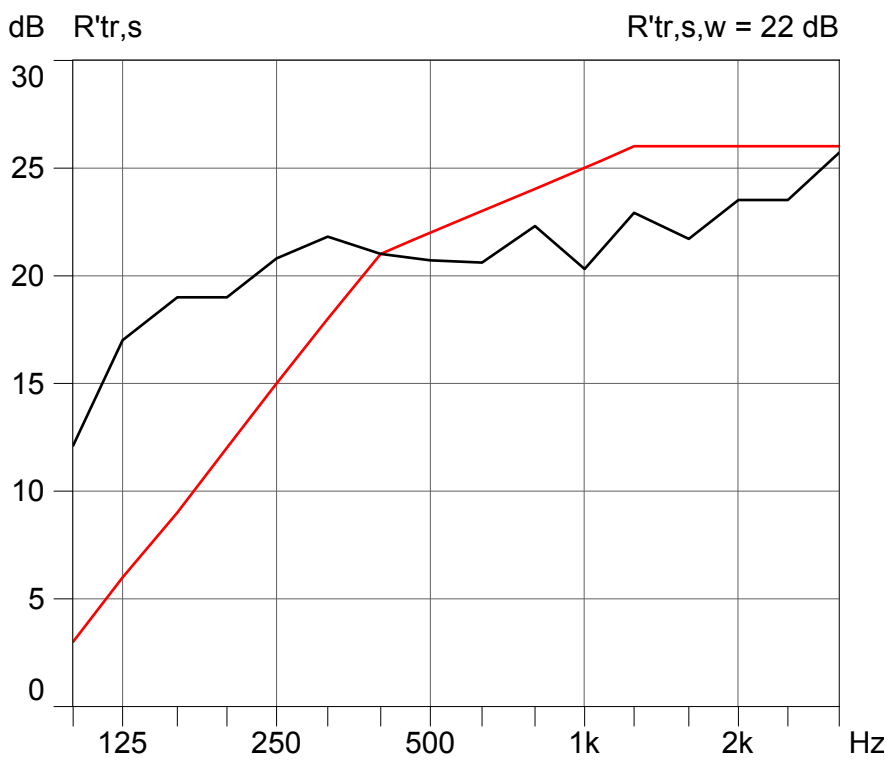


Figure 14. Sound insulation index measured at façade 4 of Home 2 – $R'_{tr,s,w} = 22$ dB.

The measured sound insulation index was well below the levels recommended by the DIN 4109 standard, as indicated in Table 3. In this case, the measured value was below the minimum level required even for quiet regions, which is 30 dB. When this value is compared

with the level recommended by the standard as a function of external noise, which, for the location of Home 2 is 66.7 dB(A), the façade insulation is even more deficient since, in this case, the standard recommends a sound insulation index of 40 dB.

Home 3

An apartment located on the 8th floor of a residential building. The external walls are made of bricks with 6 horizontal holes, mortared on both sides, with a total thickness of approximately 200 mm. The windows have aluminum frames and single 4mm thick glass panes.

Figure 15 shows the floor plan of the evaluated apartment, indicating the position of the façade used for the measurements.

Traffic noise was used to measure the façade insulation coefficient, and the spectrum of this noise is presented in Figure 16.

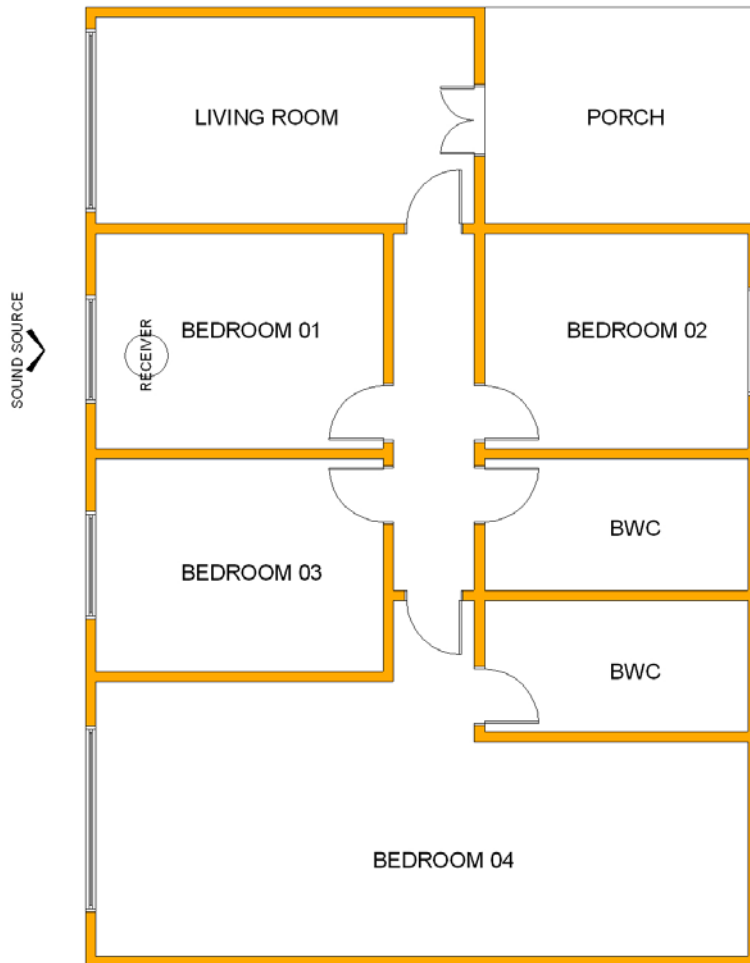


Figure 15. Location of the measurements – Home 3.

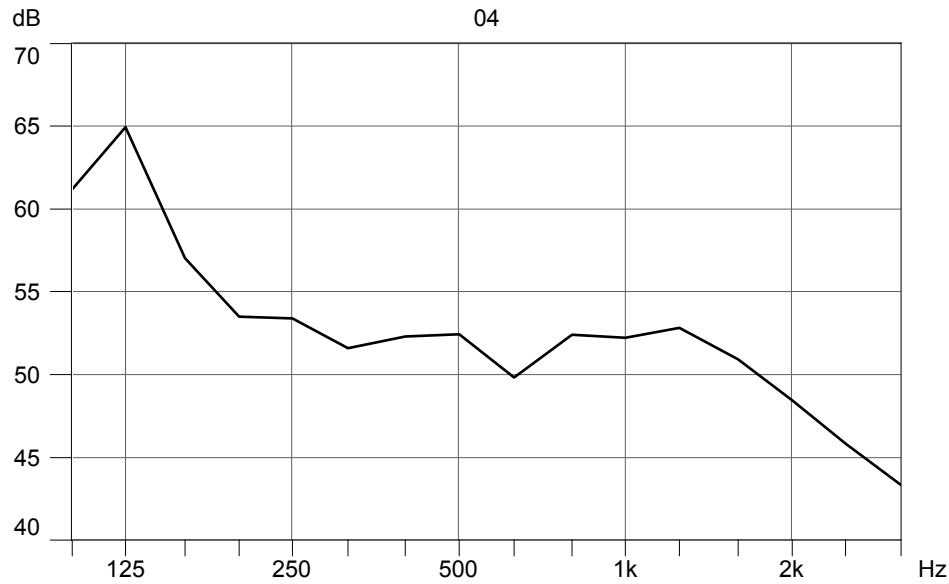


Figure 16. Traffic noise frequency spectrum – Home 3.

A Figure 17 mostra o gráfico da medição do índice de isolamento sonoro da fachada da residência 3, em função da frequência, assim como o single-number of airborne sound insulation $R'_{tr,s,w} = 19$ dB.

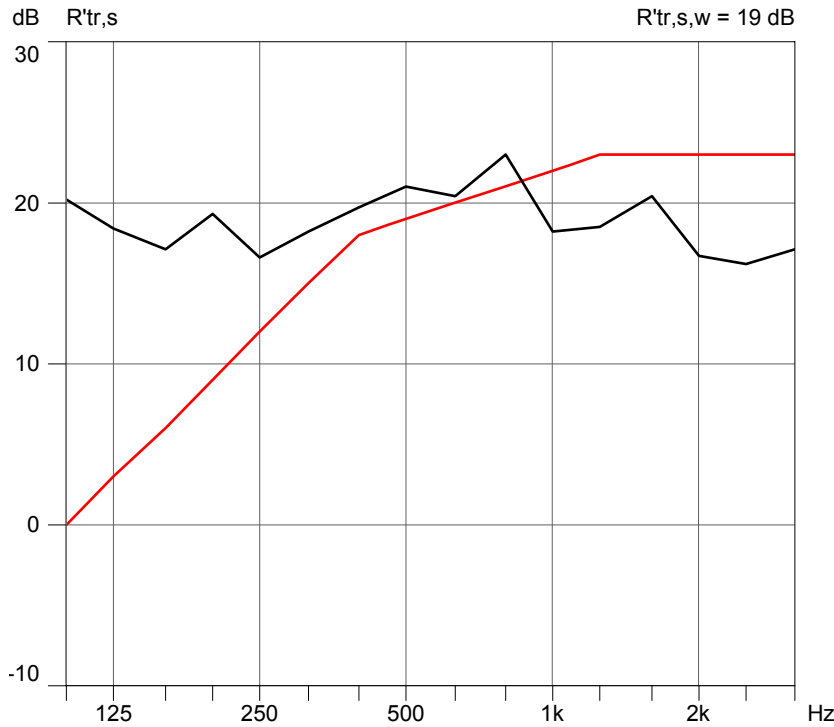


Figure 17. Sound insulation index measured at the façade of Home 3 – $R'_{tr,s,w} = 19$ dB.

The measured insulation index was well below the levels recommended by the DIN 4109 standard, as indicated in Table 3. Note that, in this case, the measured values were lower than the minimum recommended value even for quiet regions, which is 30 dB. A comparison of this value with that recommended by the standard as a function of external noise, which, for the location of Home 3 is 68.2 dB(A), the façade insulation proved even more deficient, since the standard recommends a minimum insulation index of 40 dB in this case.

Home 4

A home located in a strictly residential area (figure 18). The external walls are built of bricks with 6 vertical holes, mortared on both sides, with a total thickness of approximately 160 mm. The windows have aluminum frames and single 4mm thick glass panes. Figure 18 shows the façade of home 4.

The sound insulation index of the façade was measured using traffic noise as the external source. Figure 20 presents the spectrum of this noise.

Figure 21 shows a graph of the measurement of the sound insulation index of the façade of Home 4 as a function of frequency, and the single-number of airborne sound insulation, $R'_{tr,s,w} = 23$ dB.



Figure 18. Façade of Home 4.

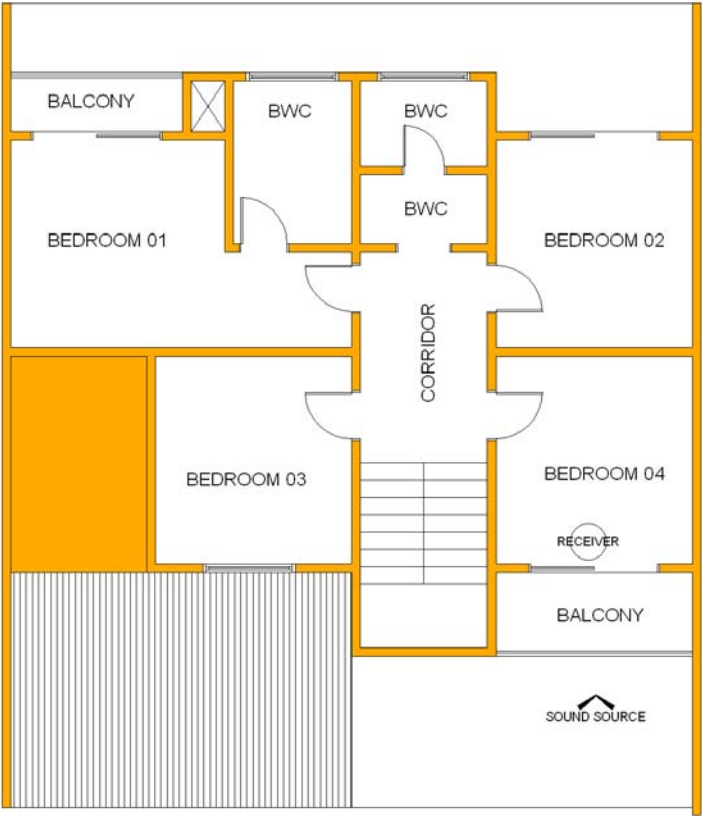


Figure 19. Location of the façade of Home 4.

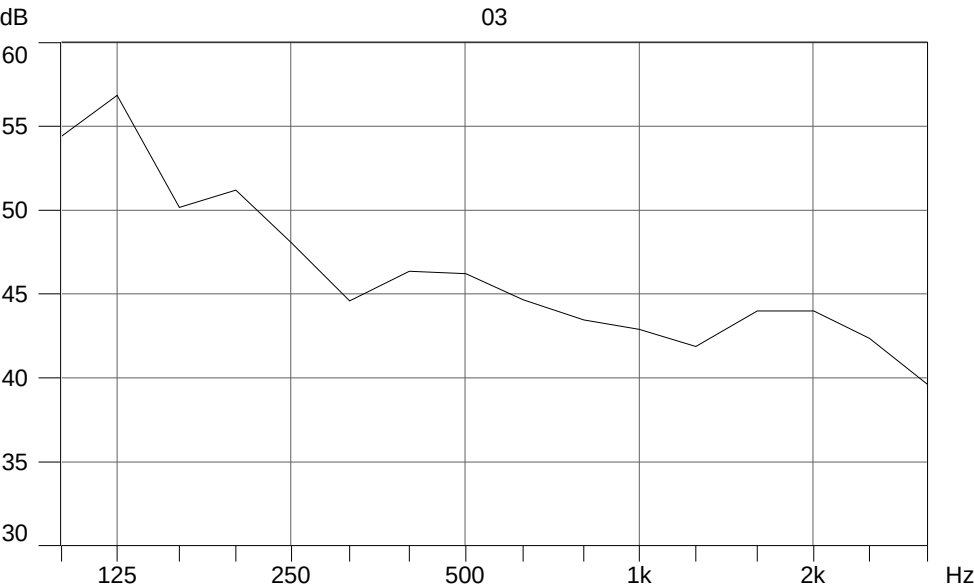


Figure 20. Traffic noise frequency spectrum – Home 4.

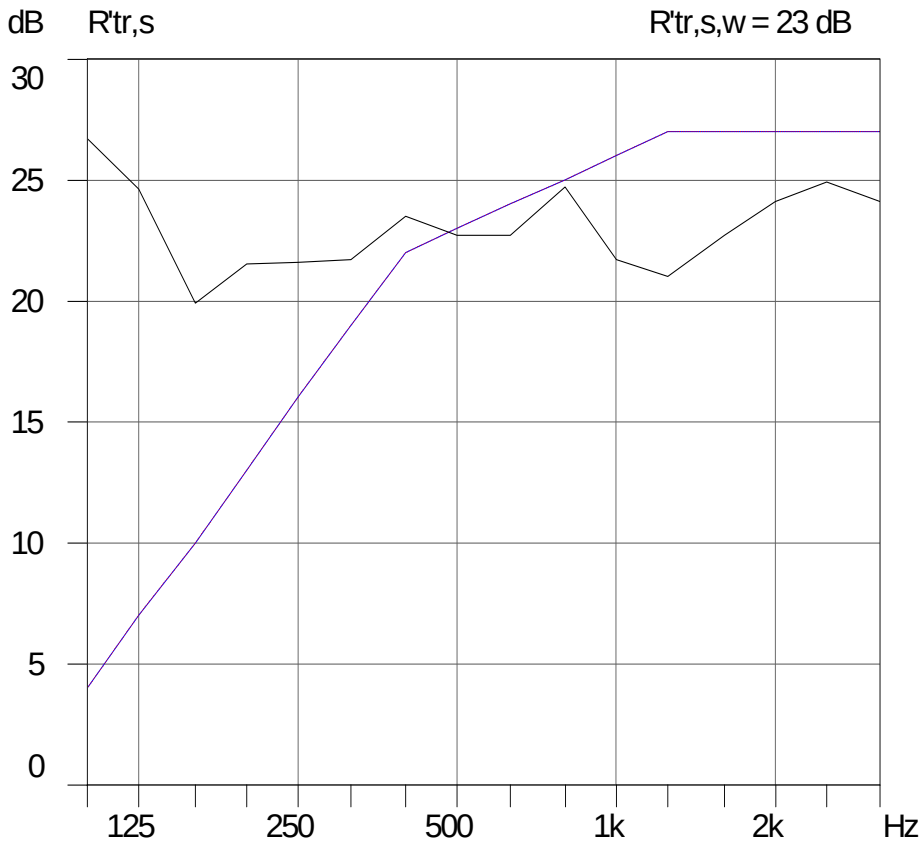


Figure 21. Sound insulation index measured at the façade of Home 4 – $R'_{tr,s,w} = 23$ dB.

Again, the measured insulation index was well below that recommended by the DIN 4109 standard listed in Table 3. In this case, note that the measured values fell below the minimum recommended value even for quiet regions, which is 30 dB. Comparing this value with that recommended as a function of external noise, which, for the location of Home 4 is 61.2 dB(A), the façade insulation is poor since, in this case, the standard recommends a minimum insulation index of 35 dB.

Home 5

A apartment located on the 4th floor of a residential building. The external walls are built of bricks with 6 horizontal holes, mortared on both sides, with a total thickness of approximately 200 mm. The windows have aluminum frames and single 4mm thick glass panes. Figure 22 shows the floor plan of home 5.

The sound insulation coefficient of the façade was measured using traffic noise as the external source. Figure 23 presents the spectrum of this noise.



Figure 22. Location of the façade of Home 5.

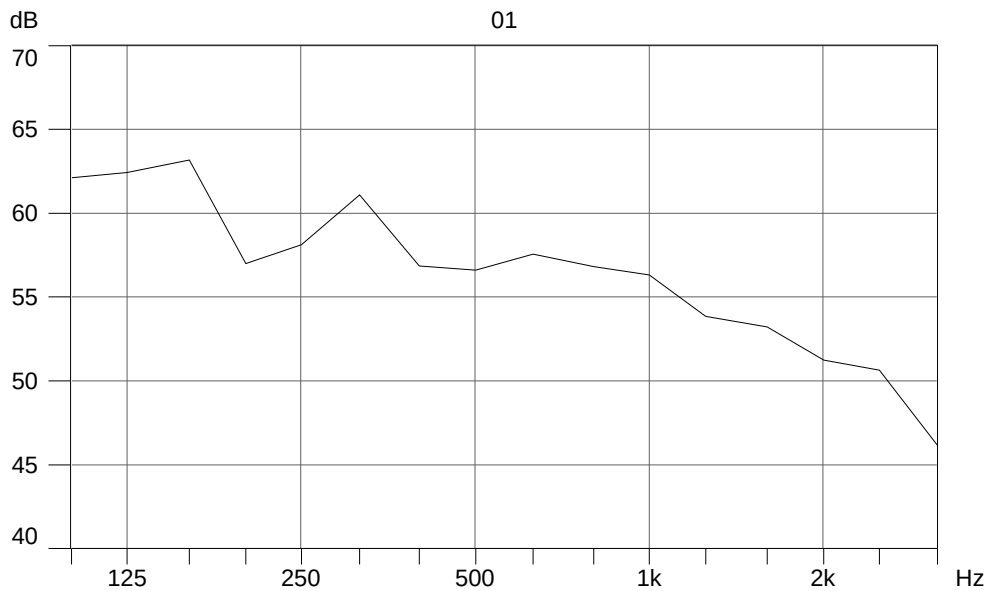


Figure 23. Traffic noise frequency spectrum – Home 5.

Figure 24 depicts the graph of the sound insulation index measured at the façade of Home 5 as a function of frequency, as well as the single-number of airborne sound insulation $R'_{tr,s,w}$ = 23 dB.

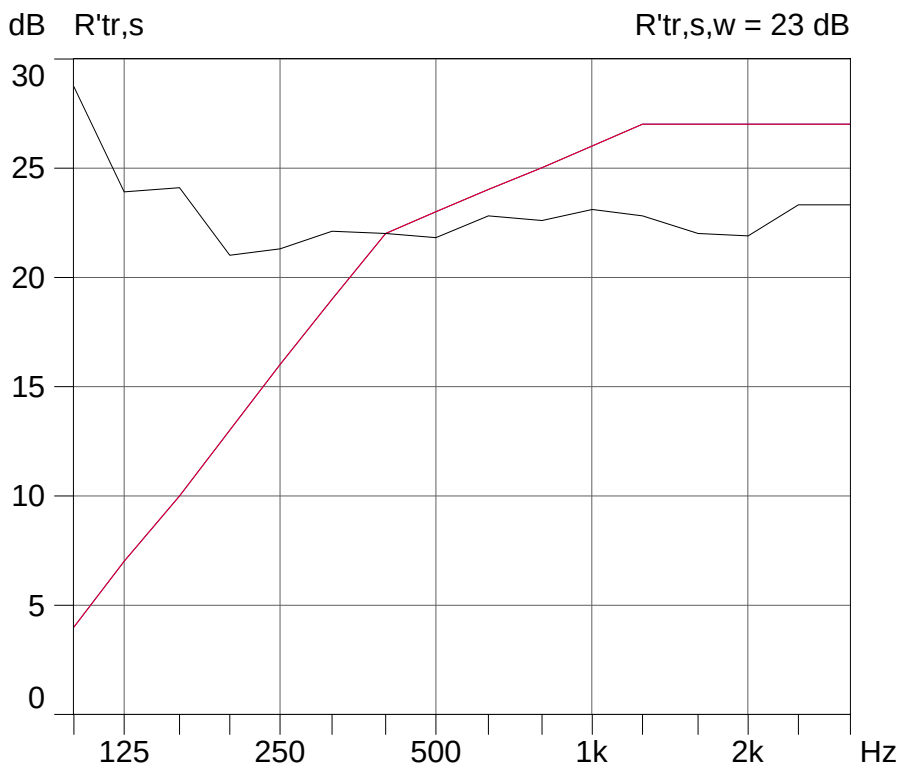


Figure 24. Sound insulation index measured for the façade of Home 5 – $R'_{tr,s,w} = 23$ dB.

In this case as well, the measured insulation index fell below the values recommended by the DIN 4109 standard given in Table 3. Note that the measured value was lower than the recommended minimum even for quiet regions, i.e., 30 dB. Comparing this value against the one recommended by the standard for this level of external noise, which was 70.4 dB(A) at the location of this home, indicates that the façade insulation was deficient, since the standard recommends a minimum insulation index of 40 dB in this case.

Home 6

A semi-detached townhouse (Figure 25), with external and internal walls made of bricks with 6 vertical holes, mortared on both sides, with a thickness of approximately 160 mm. The windows have aluminum frames and single glass panes. Figure 26 shows a floor plan of Home 6.

The insulation coefficient of the façade was measured using traffic noise as the external sound source. Figure 27 presents the spectrum of this noise.

The graph in Figure 28 illustrates the sound insulation index measured at the façade of Home 6 as a function of frequency, as well as the single-number of airborne sound insulation $R'_{tr,s,w} = 19$ dB.



Figure 25.Façade of the semi-detached townhouse.



Figure 26. Floor plan of Home 6.

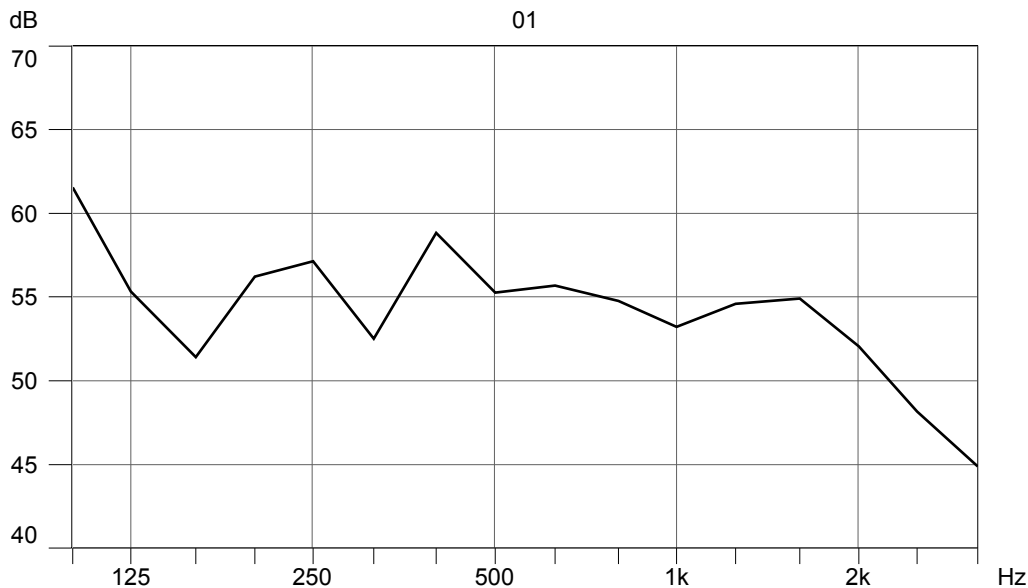


Figure 27. Traffic noise frequency spectrum – Home 6.

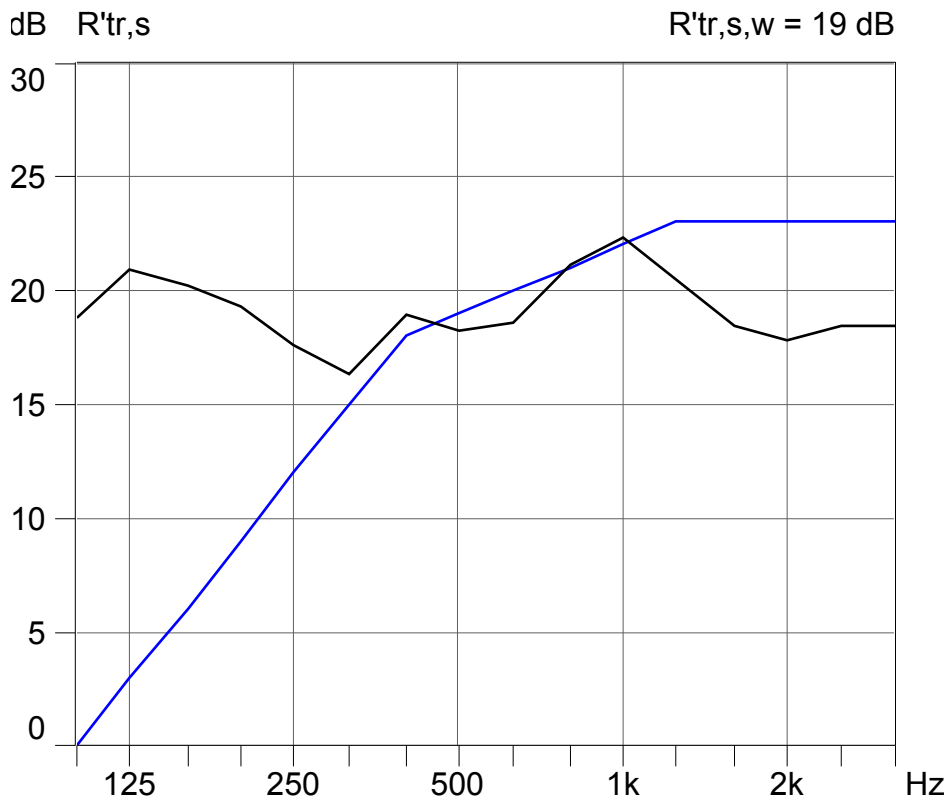


Figure 28. Sound insulation index measured at the façade of Home 6 – $R'_{tr,s,w} = 19$ dB.

The measured sound insulation index was well below the minimum values recommended by the DIN 4109 standard (Table 3) even for quiet regions, which is 30 dB. Comparing this index to the values recommended by the standard for this level of external noise, which is 67.6 dB(A) at the location of Home 6, indicates that the façade insulation is very poor, since the standard recommends a minimum insulation index of 40 dB for such locations.

Home 7

A low income family home, this building is depicted in figure 29. The internal and external walls are made of 14x19x39 cm load-bearing concrete blocks for a specific weight of 2010 kg/m³. All the walls are mortared on both sides. The ceiling is composed of wooden laths and the roofing is of concrete tiles. Figure 30 shows a floor plan of home 7.

The insulation coefficient of the façade was measured using traffic noise as the external sound source. Figure 31 presents the spectrum of this noise.

The graph in Figure 32 shows the sound insulation index measured at the façade of Home 7 as a function of frequency, as well as the single-number of airborne sound insulation $R'_{tr,s,w} = 20$ dB.

The measured sound insulation index in this case was also well below the minimum values recommended by the DIN 4109 standard (Table 3). These measurements fell below the minimum recommended level even for quiet regions, which is 30 dB.



Figure 29. Façade of the home for low income families.

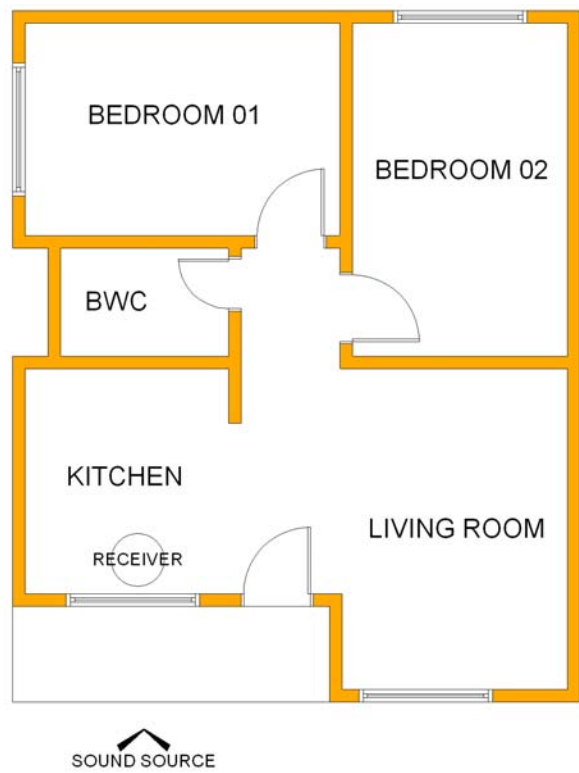


Figure 30. Location of the façade of Home 7.

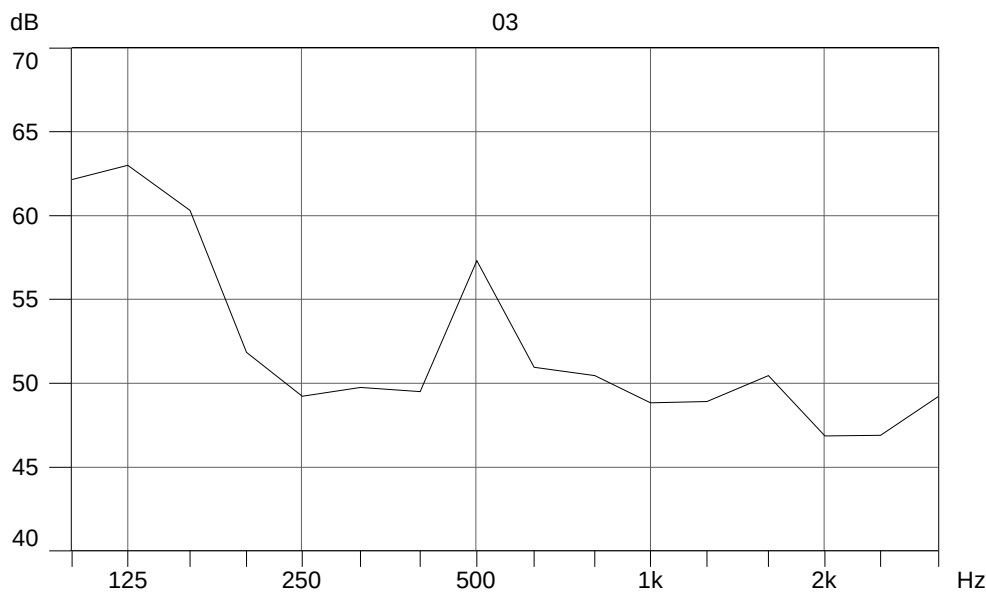


Figure 31. Traffic noise frequency spectrum – Home 7.

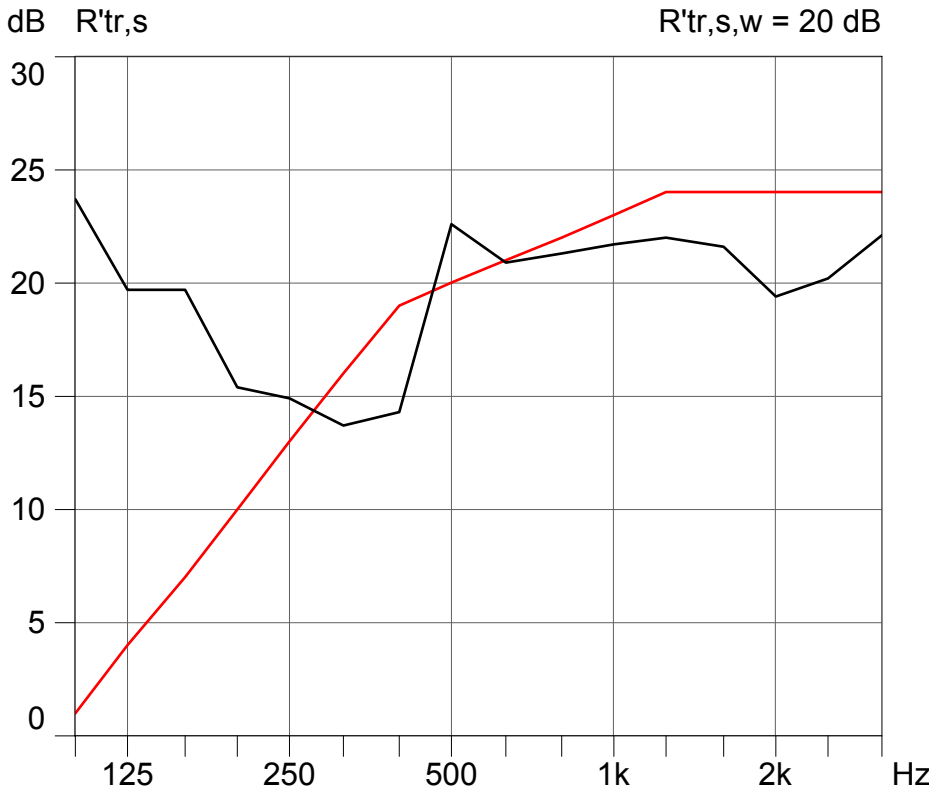


Figure 32. Sound insulation index measured at the façade of Home 7 – $R'_{tr,s,w} = 20$ dB.

Comparing this index to the values recommended by the standard as a function of external noise, which is 68 dB(A) for the location of Home 7, the façade insulation was found to be even more deficient since, in this case, the standard recommends a minimum insulation index of 40 dB.

Home 8

An experimental home for low income families, as depicted in figure 33. The walls are made of an expanded polystyrene core wrapped in steel mesh and mortared, while the ceiling is composed of pine match boarding and the doors are wooden. The windows are of the sliding type, with iron frames and single glass panes.

The insulation coefficient of the façade was measured based on traffic noise as the external sound source. The spectrum of this noise is shown in Figure 34.

The graph in Figure 35 shows the sound insulation index measured at the façade of Home 8 as a function of frequency, and the single-number of airborne sound insulation $R'_{tr,s,w} = 18$ dB.



Figure 33. Location of the façade in Home 8.

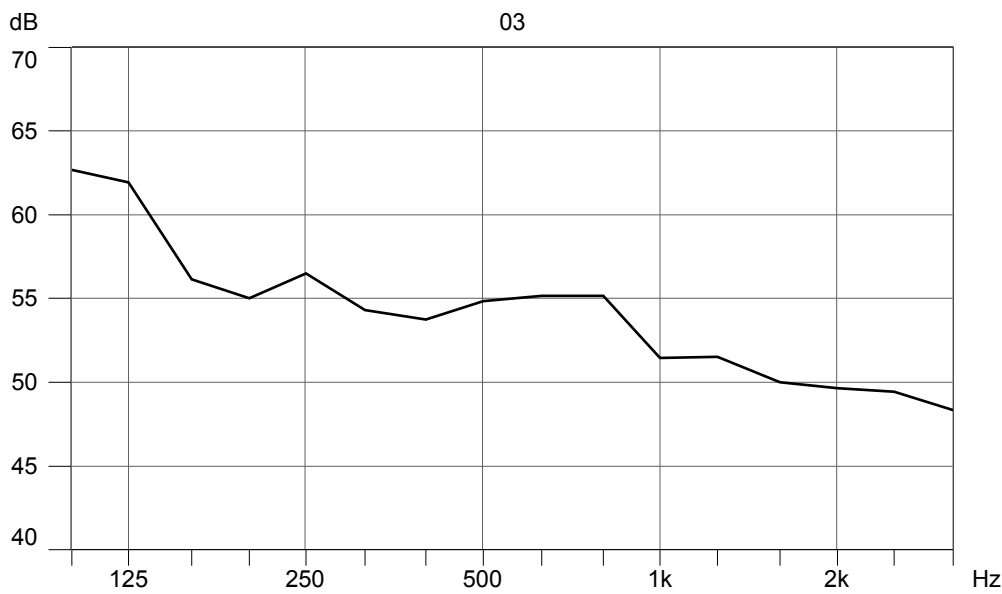


Figure 34. Traffic noise frequency spectrum – Home 8.

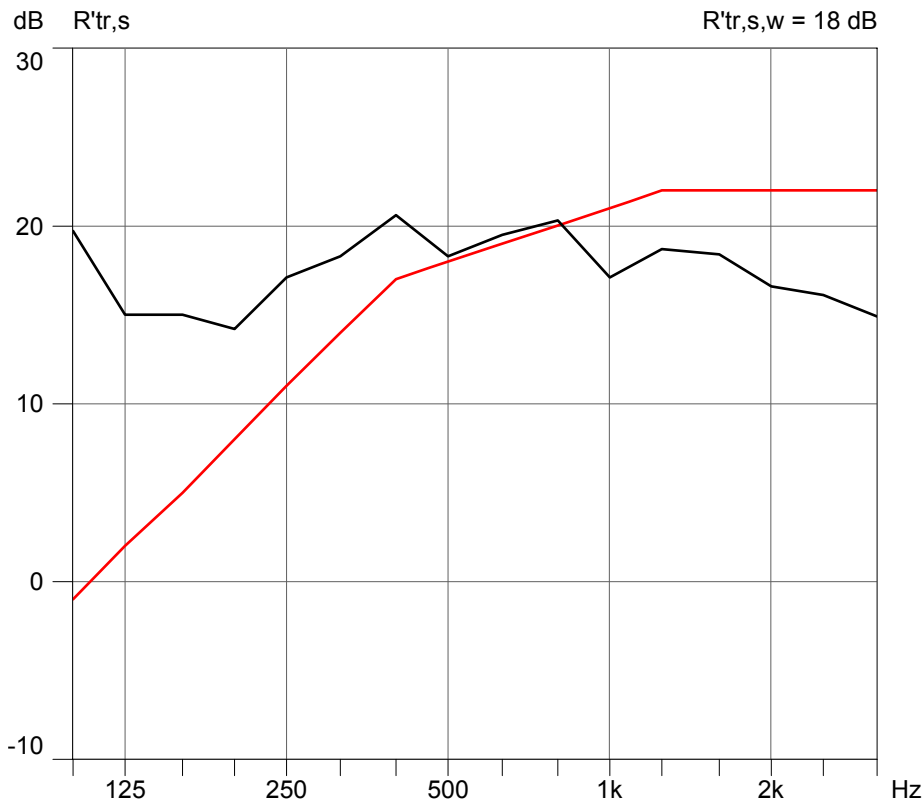


Figure 35. Sound insulation index measured at the façade of Home 8 – $R'_{tr,s,w} = 18$ dB.

The measured sound insulation index was well below the values prescribed by the DIN 4109 standard (see Table 3). In this case, the measured value fell below the minimum required even for quiet regions, i.e., 30 dB.

The results of the measurements of the façade insulation index for the eight homes evaluated here revealed the very poor performance of these façades in terms of sound insulation.

Based on the diagnosis of the current situation, computational simulations were made using the Bastian 2.3 software program in search of solutions for the façades evaluated here.

The window frames of the façades of all the buildings are made of aluminum, of the two pane sliding type, with single glass panes approximately 4 mm thick. Therefore, simulations were made in which the windows of the façades were replaced by aluminum window frames with 4 mm thick double panes separated by a 10 mm air layer. This type of double glazing is widely available in Brazil's civil construction market. However, it should be noted that these panes are not part of the average construction standard in the country.

Table 4, below, presents the results of *in situ* measurements and the simulated façade sound insulation indices:

Table 4. Results of *in situ* measurements and the simulated façade sound insulation indices

	Sound level measured outside the homes L_{eq} dB(A)	Façade sound insulation index recommended by the DIN 4109 standard (see Table 3) $R'_{tr,s,w}$ dB	Measured façade sound insulation index $R'_{tr,s,w}$ dB	Simulated façade sound insulation index $R'_{tr,s,w}$ dB
Home				
1	71.8	45	21	38
2	66.7	40	22	37
3	68.2	40	19	34
4	61.2	35	23	36
5	70.4	40	23	37
6	67.6	40	19	37
7	68	40	20	32
8	64.8	35	18	31

The simulations clearly indicate an improvement in the façade sound insulation as a result of replacing single paned windows with double paned windows, considerably augmenting the acoustic comfort inside the homes. However, as can be seen in Table 4, despite this improvement, the final result of sound insulation provided by double glazing still falls below the minimum level recommended by the DIN 4109 standard due to the external noise levels (see Table 3). Strictly speaking, only Home 3 meets the DIN 4109 standard after the single panes are exchanged for double panes.

The Bastian software program was calibrated prior to using it for these simulations. All the *in situ* measurements were also simulated. The measured and simulated data were subjected to an inferential statistical analysis using Hotelling's *t*-test. This test was considered the most appropriate due to the following premises tested: 1) sampling size equal to or lower than 30; 2) normal distribution; 3) independent variables; and 4) equal real covariances. An initial " H_0 " hypothesis was then formulated, which assumed that $\mu_1 = \mu_2$, in other words, the average of the measured parameters (μ_1) is equal to the average of the simulated parameters (μ_2), at a 5% level of significant (a strict criterion), i.e., a 95% possibility of the test being correct. The initial hypothesis was confirmed, since the condition for its acceptance – the statistics of the test should present a value lower than that of *F-Normal* – was met, yielding a statistical result of 4.1182, which is lower than the *F-Normal* value of 4.2252. Therefore, the hypothesis of the equal means was confirmed, indicating that the samples were equal or similar within a confidence interval of 95%.

CONCLUSIONS

Based on *in situ* measurements, this work evaluated the sound insulation indices of residential façades, composed of constructive elements widely employed in Brazilian civil construction.

The field measurements were based on the recommendations of the ISO 140-5:1998 standard – International Organization for Standardization ISO 140-5: Acoustic – Measurement of sound insulation in buildings and of building elements – Part 5: Field measurements of airborne sound of façade elements and façades. The determination of the weighted indices of sound insulation was based on the recommendations of the ISO 717-1:1996 standard – International Organization for Standardization ISO 717-1: Acoustic – Rating of sound insulation in buildings and of building elements – Part 1: Airborne sound insulation.

This work also included the prediction of sound insulation indices of façades by means of computational simulations with the Bastian 2.3 software, which works based on the calculation models of the European Standard EN 12354-1: Building Acoustics – Estimation of acoustic performance of buildings from the performance of elements, Part 1: Airborne sound insulation between rooms and European Standard EN 12354-3: Building Acoustics – Estimation of acoustic performance of buildings from the performance of elements, Part 3: Airborne sound insulation against outdoor sound.

The sound insulation indices of the façades analyzed in all the 8 residences evaluated here presented values below acceptable levels when compared with those prescribed by international standards such as DIN 4109. In the residences evaluated, the measured values of the sound insulation index for façades were found to be lower than the minimum value required by the DIN 4109 standard, as indicated in Table 3, even for quiet regions, which is 30 dB.

The simulations indicated that replacing simple glass windows with double glass windows substantially improved the sound insulation of façades. On the other hand, only residence 4 reached the minimum value suggested by the DIN 4109 standard for façade sound insulation from external traffic noise. Around the world, the growth of cities, their populations and the number of vehicles in circulation has led to rising noise levels in urban environments. This situation requires homes to present a sound performance that adequately offsets environmental noise, although there is also an urgent need to reduce and control this type of urban pollution.

It was also found that there was no significant difference between the sound insulation indices in the high standard residences (see for reference Figures 8 and 18) and those measured in the popular standard ones (see for reference Figures 25 and 29). This finding led to the conclusion that home builders are not taking acoustic comfort into account when designing and building homes, since people who purchase high standard homes can afford constructive elements that provide greater comfort, and if they do not do so it is for lack of knowledge or lack of choice.

With regard to the use of the Bastian software, whose method of calculation is based on the set of European standards EN 12354, the conclusion drawn was that it performed well, in the simulation of the coefficients of façade insulation and between the rooms of the residences evaluated. This statement was confirmed by the *T-Hotelling* statistical test of equality of means, which was carried out with a 95% confidence interval for the sample evaluated.

The use of the Bastian software requires care in modeling the rooms to be evaluated, since the graphic module of the program only allows the inclusion of simple geometries, and approximations have to be made for more complex geometries. However, one should: 1) keep the same volume of the room evaluated, 2) the same area of the partition exposed directly to

noise, and 3) the same proportion between the area of wall and the area of the elements. Although this method of adjustment of the room's geometry presented good results when this work was carried out, it is advisable to use it with great care.

It should also be noted that the software was developed for use in the prediction of the coefficients of acoustic insulation in the design phase, or where it is not possible to take measurements, and not for the purpose of substituting the process of *in situ* measurements. Whenever possible, the latter should be the preferred method for obtaining sound insulation indices, because although these measurements involve a logistically complicated and costly procedure, expensive and sophisticated equipment, specialized people to take the measurements, and discomfort for the residents of the sites that are being evaluated, if the building is occupied, it is the method that produces the most reliable and accurate results.

As for the standards used and cited in this chapter, the reader should note that there are other standards for acoustic measurements, such as the German standards of the Deutsches Institut für Normung – DIN, and the standards of the American National Standards Institute – ANSI. Our choice for using as reference the standards of the International Organization for Standardization ISO was based on the fact that they are international standards and that many national standards follow the guidelines of the ISO standards. Another reason for this choice is that the equipment used for the measurements follows the procedures recommended by the ISO standards.

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Chapter 7

RADON EXHALATION RATES OF BUILDING MATERIALS: EXPERIMENTAL, ANALYTICAL PROTOCOL AND CLASSIFICATION CRITERIA

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ABSTRACT

The strict correlation between indoor radon exposure and potential health hazard to occupants is well known. The indoor radon concentrations mainly depend on radon exhalation from surrounding soil, but also on exhalation from building materials and radon in domestic water supply. The radon emanating from building materials achieves a larger relevance in some areas of the world, where rocks enriched in radon precursors, are used in construction industry, either as cut-stone or in a granular form to prepare cements. The parameter that better expresses the indoor accumulation of radon released by geological materials is the radon exhalation rate. With a view to this, it is very important to study factors that influence the phenomenon and to standardise the experimental procedure to measure radon exhalation rates. An experimental set-up to measure simultaneously ^{222}Rn and ^{220}Rn release from building material is presented. The method makes use of a continuous monitor equipped with a solid-state alpha detector, in-line connected to a small accumulation chamber. Parameters controlling exhalation rates are discussed: temperature, air mixing, humidity and particle size. Guidelines for a standard experimental protocol are advanced and a tentative classification of building materials is proposed on the basis of radon exhalation rates required to reach legal indoor radon action levels.

INTRODUCTION

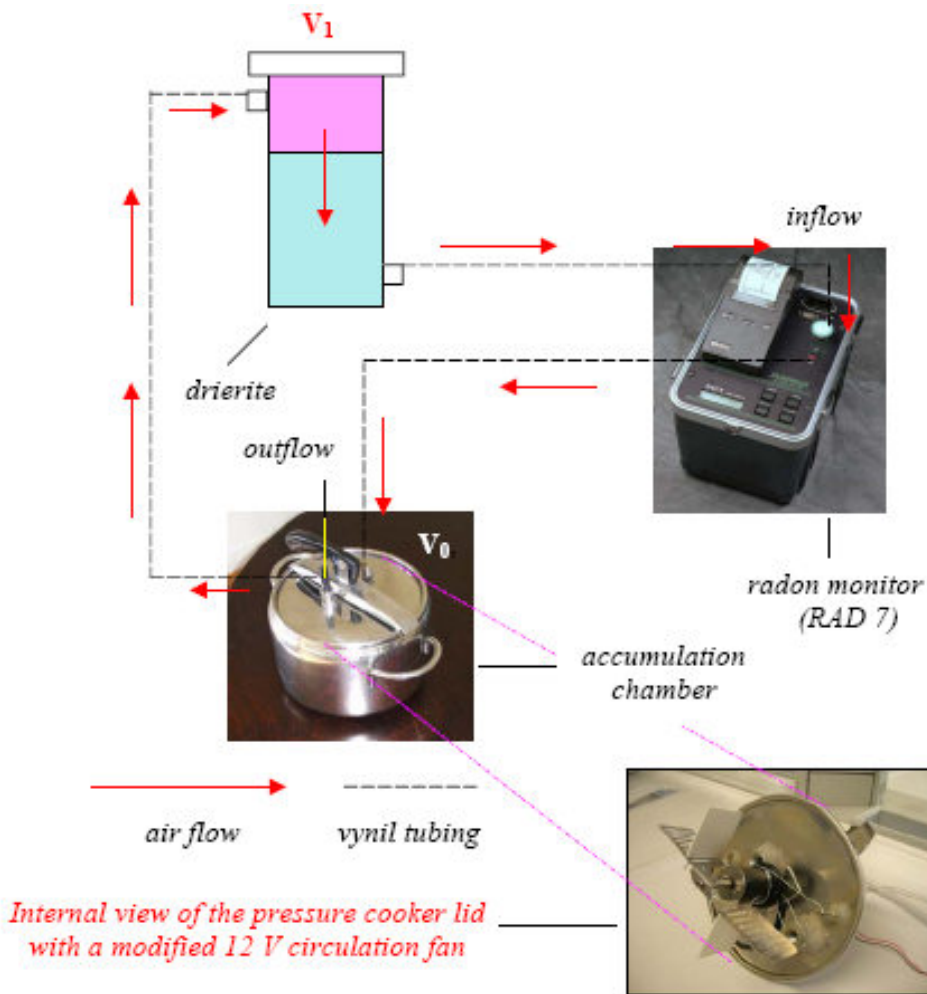
European Commission has examined the issue of regulatory control of building materials with regard to their content of naturally occurring radionuclides (EC-Radiation Protection, 1999). The purpose of setting regulatory controls on the radioactivity of building materials is to limit the radiation exposure due to materials with enhanced or elevated levels of natural radionuclides. Nonetheless, human exposure to radioactivity is at a large extent (55 %) due to radon (UNSCEAR, 2000) and the activity of naturally occurring radionuclides, expressed as activity concentration index (I) or radium equivalent activity (Ra-eq, Kovler et al., 2005), is not able to predict satisfactorily radon indoor concentrations due to the exhalation of radon from surrounding soil or from building materials. A parameter that better expresses the indoor accumulation of radon released by geological materials is the radon exhalation rate (Carrera et al., 1997). With a view to this, it is very important to study the parameters that influence the phenomenon and to standardise the experimental procedure to measure radon exhalation rates (Quindos et al., 1994; Chao et al., 1997; De Martino et al., 1998; Keller et al., 2001; Petropoulos et al., 2001; Ferry et al., 2002; Gutiérrez et al., 2004; Kovler et al., 2005; Tuccimei et al., 2006).

This chapter reports on the simultaneous measurements of ^{222}Rn and ^{220}Rn (also known as thoron) exhalation rates from building materials using a small stainless steel accumulation chamber, in line connected to a radon monitor. Validation tests of the experimental set-up are presented in order to support the method; mixing and temperature-control facilities are also illustrated. The influence of temperature, particle size and humidity on radon exhalation rates is discussed. On this basis, a standard analytical protocol is proposed and data of radon exhalation rates of volcanic cut-stone and cements commercialised in central Italy are listed. Finally the basic of classification criteria to apply to building materials is advanced.

EXPERIMENTAL SET-UP

The experimental set-up reported in this section is the development of a previous apparatus described in Tuccimei et al. (2006). The old system, consisting of a small PVC accumulation chamber, sealed with silicon, was affected by gas leakage out of the container and radon back-diffusion to the material due to radon building up in the chamber. These phenomena produced a reduction of the accumulated radon and lead to the determination of exhalation rates about 30 % lower than true values. Proper corrections to evaluate free exhalation rates were however proposed. On the basis of the gained experience, the previous experimental set-up was modified and the PVC accumulation chamber was replaced with a modified pressure cooker to remove leakage and back-diffusion.

The new method makes use of a continuous monitor equipped with a solid state alpha detector, in line connected to an accumulation chamber, consisting of a 5.1 L modified stainless steel pressure cooker with a mechanical tightness system, supplied with a 12 V circulation fan (17-cm diameter) for mixing purposes (Figure 1). The chamber is connected via vinyl tubing to a gas-drying unit filled with a desiccant (CaSO_4 , 3% CoCl_2 , as indicator) and to the RAD7 radon monitor (Durrige Company Inc). The instrument draws air from the chamber, through the desiccant and an inlet filter, into the monitor.



V_0 = free volume of accumulation chamber
 V_1 = volume between outflow of accumulation chamber and inflow of the radon monitor
 V = total volume of the analytical system

Figure 1. Experimental set-up to measure ^{222}Rn and ^{220}Rn exhalation rates.

The air is then returned to the enclosure from the RAD7 outlet. The filtered air decays inside the monitor chamber, producing detectable alpha emitting progeny, particularly the polonium isotopes. A high voltage of 2500 V is applied to the chamber walls. The solid state silicon detector converts alpha radiation directly to an electrical signal discriminating the electrical pulses generated by α -particles from the polonium isotopes (^{218}Po , ^{216}Po , ^{214}Po , ^{212}Po) with energies of 6.0, 6.7, 7.7 and 8.8 MeV, respectively. Using this approach, it is possible to use only the ^{218}Po peak for ^{222}Rn and ^{216}Po for ^{220}Rn , obtaining a rapid equilibrium between polonium and radon nuclides, because the equilibrium between ^{218}Po and ^{222}Rn is achieved in about 15 min (about five times the half-life of ^{218}Po), and between ^{216}Po and ^{220}Rn in a few seconds. The ^{222}Rn growth curve is monitored with cycle times from 15 minutes up to 2 hours for a day in order to calculate the exhalation rate that is proportional to the slope of the growth curve. The measurement allows the simultaneous determination of

^{222}Rn and ^{220}Rn exhalation rates that can be referred to the mass or the surface of the material. The detection limit of the experimental apparatus is equal to 0.01 Bq h^{-1} for ^{222}Rn and to 6 Bq h^{-1} for ^{220}Rn .

VALIDATION TEST

In order to test the experimental set-up and samples preparation procedures, validation tests have been carried out using “Tufo Rosso a Scorie Nere” (TRSN) pyroclastic flow as standard material. This tuff, emitted from Vico volcanic apparatus (50 km north-east of Roma, Italy), is commonly used in cut-stone and concrete masonry because of its lightness, tenacity and machinability. TRSN standard, crushed and sieved between 2 and 1 mm, has been always dried at 110°C for 24 hours and weighed (800 g), before the beginning of experiments. Validation tests have been performed with air mixing and temperature has been kept constant at 20°C , unless indicated otherwise.

The first test was aimed at demonstrating that the new apparatus was not affected by leakage and back diffusion phenomena so that ^{222}Rn concentration increase in the closed loop configuration is effectively described by ^{222}Rn decay constant. A 24-hour experiment was performed and ^{222}Rn activity concentration was measured with cycles of 15 minutes in order to have enough data to process and fit according to the following conventional equation (Petropoulos et al., 2001):

$$C = C_0 \cdot e^{(-\lambda \cdot t)} + \frac{E \cdot (1 - e^{-\lambda \cdot t})}{\lambda \cdot V} \quad (1)$$

where C is ^{222}Rn activity concentration [Bq m^{-3}], C_0 is the initial concentration [Bq m^{-3}], λ is the decay constant [h^{-1}], t is time [h], E is ^{222}Rn exhalation rate [Bq h^{-1}] and V is the free total volume of the analytical system [m^3]. The first term of the equation takes into account the decrease of radon initially present in the measuring apparatus, whereas the second represents radon exponential increase in the closed circuit up to equilibrium conditions. The purpose of this procedure is to estimate the values of C_0 , λ and E that better describe the data, choosing the parameters that would minimise the deviations of the theoretical curve from the experimental points.

This experiment (test 1-1) was compared with a second test (test 1-2) performed under the same conditions, but using the PVC accumulation chamber (Figure 2) in order to prove that present set-up is better in terms of radon loss. Best-fitting parameters of experimental data are: $C_0 = 20 \text{ Bq m}^{-3}$ in both cases; $\lambda = 0.0076$ and 0.018 h^{-1} for stainless steel and PVC test, respectively and $E = 0.07$ and 0.04 Bq h^{-1} , correspondingly for test 1-1 and 1-2. Curve fitting provided a value of C_0 , which is actually the average indoor radon value in the laboratory and an estimation of λ in test 1-1 which is equal to ^{222}Rn decay constant, significantly lower than that from test 1-2. The goodness of the fit (R^2) is about 0.98. Test 1-1 was repeated several times in order to verify the outcomes, demonstrating the repeatability of the measurements with the new experimental design.

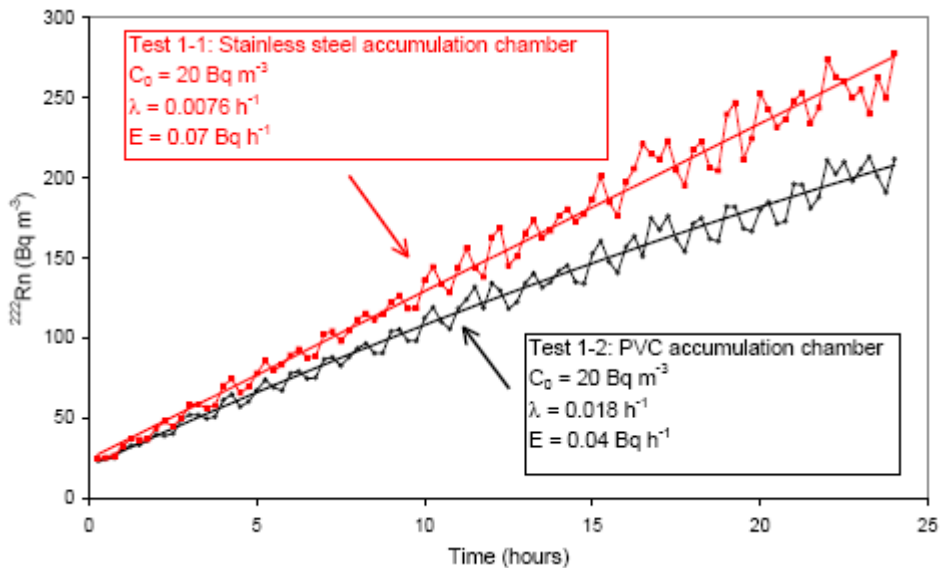


Figure 2. Experimental ^{222}Rn concentration growth of TRSN standard over a 24-hour experiment using the stainless steel (test 1-1, red squares) and the PVC (test 1-2, black circles) accumulation chambers. Least-squares fitting curves described by equation 1 provided values of C_0 , λ and E for both experiments. Errors are around 5 %.

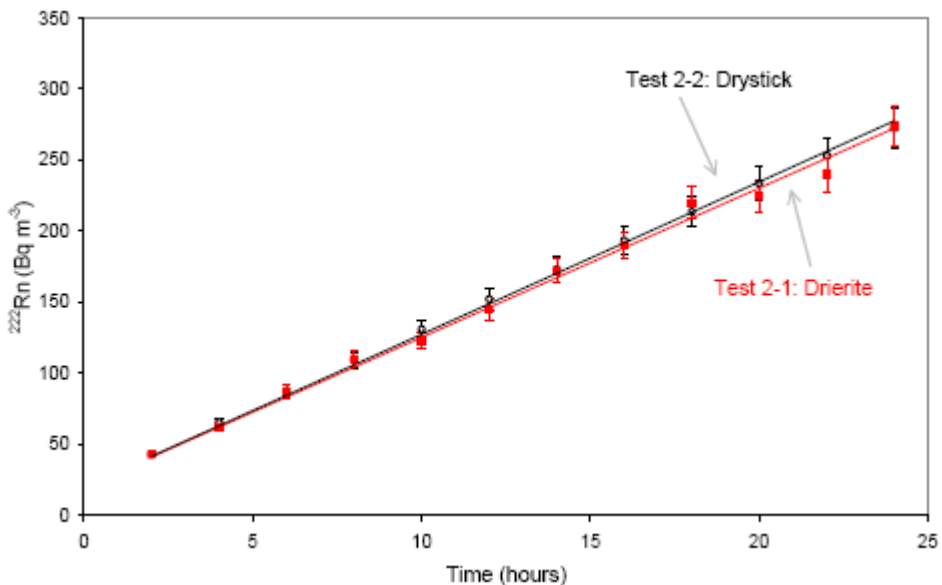


Figure 3. Experimental ^{222}Rn growth curves of TRSN standard over a 24-hour experiment using the stainless steel accumulation chamber equipped with the drierite (test 2-1, red squares) or the drystick (test 2-2, black circles) device.

A second set of experiments was performed to demonstrate that CaSO_4 grains, used as desiccant, did not absorb radon, reducing exhalation rate. In order to prove that, two tests were conducted using TRSN standard under the same experimental conditions described for

previous experiments, with the exception of the device used to capture moisture: CaSO₄ (drierite, test 2-1) and a large drystick (test 2-2). Drystick is commercialised by DurrIDGE Company Inc. (www.durrIDGE.com) and consists of a set of tubes made of NAFION, a Teflon based material that allows removing water molecule, without absorbing radon. Before starting test 2-2, the system was run using the drierite to reduce humidity down to 1-2 %. Drierite was then removed and replaced with a large drystick, capable to maintain constant the moisture content during the 24-hour test and dried TRSN standard was put in the chamber. Results of tests 2-1 and 2-2 are reported in Figure 3 and show that data overlap within the error range, showing a negligible effect of gas sorption by CaSO₄ grains.

EXHALATION RATES CALCULATION

Radon Exhalation Calculation

Conventionally, ²²²Rn exhalation rate, E_{222} , [Bq h⁻¹] is calculated according to the following equation, which is equation 1 solved with respect to E:

$$E_{222} = \frac{(C - C_0 e^{-\lambda_{222} \cdot t})}{1 - e^{-\lambda_{222} \cdot t}} \cdot \lambda_{222} \cdot V \quad (2)$$

where C is the equilibrium concentration [Bq m⁻³], C_0 is the initial radon concentration [Bq m⁻³], λ_{222} is ²²²Rn decay constant [h⁻¹], V is the free total volume of the analytical system [m³] and t is time [h].

However, a simplified formula is routinely used and provides comparable results when applied to 24-hour experiments:

$$E_{222} = (m + \lambda_{222} \cdot C_0) \cdot V \quad (3)$$

where m [Bq m⁻³ h⁻¹], is the initial slope of the radon growth curve. The equivalence of equation 2 and 3 is here demonstrated (Table 1) by comparing ²²²Rn exhalation rate of TRSN standard obtained from a 19-day experiment (test 3) according to equation 2 with that determined from data collected during the first 24 hours of the test and calculated using equation 3. Duration of 19 days was chosen because ²²²Rn reaches equilibrium conditions between exhaled and decayed radon just after that time (Figure 4). In conclusion, it is worth noting that exhalation rates can be referred to the unity of surface [Bq m⁻² h⁻¹] or that of mass [Bq kg⁻¹ h⁻¹].

The latter is probably more suitable for granular materials where a precise calculation of the exhaling surface is difficult and strongly depends on grain size. Surface or mass exhalation rates are simply obtained by equation 3 (or 2) dividing the value of E_{222} [Bq h⁻¹] by the surface [m²] or the mass [kg] of the sample.

Table 1. ^{222}Rn and ^{220}Rn exhalation rates of a TRSN standard (2-1 mm) and a selection of volcanic rocks and cements used in cut-stone and concrete masonry in Italy

Material	Description	E_{222} (a) $\text{Bq m}^{-2} \text{h}^{-1}$	E_{222} (b) $\text{Bq m}^{-2} \text{h}^{-1}$	E_{222} (c) $\text{Bq kg}^{-1} \text{h}^{-1}$	E_{220} (d) $\text{Bq m}^{-2} \text{h}^{-1}$	E_{220} (e) $\text{Bq kg}^{-1} \text{h}^{-1}$	Classification on the basis of E
TRSN standard	Pyroclastic flow - granular	1.58 ± 0.06	1.57 ± 0.07	0.047 ± 0.002	5282 ± 264	158 ± 8	C2
TRSN standard	Pyroclastic flow - granular	-	2.68 ± 0.13 (f)	0.080 ± 0.004 (f)	8979 ± 449 (f)	269 ± 13 (f)	D3 (f)
Tufo Lionato	Pyroclastic flow - slab	-	0.86 ± 0.04	0.026 ± 0.001	972 ± 49	29 ± 1	B1
Peperino from Marino	Pyroclastic flow - slab	-	1.33 ± 0.06	0.040 ± 0.002	896 ± 49	27 ± 1	C1
Peperino from Albano	Pyroclastic flow - slab	-	1.55 ± 0.07	0.046 ± 0.002	389 ± 19	12 ± 1	C1
Peperino from Via Flaminia	Pyroclastic flow - slab	-	0.83 ± 0.04	0.026 ± 0.001	1537 ± 77	46 ± 2	B1
Tufo Giallo Napoletano	Pyroclastic flow - slab	-	2.66 ± 0.13	0.080 ± 0.004	583 ± 29	17 ± 1	D1
Lava from Nemi	Pyroclastic flow - slab	-	2.23 ± 0.11	0.067 ± 0.003	292 ± 15	9 ± 1	D1
Black Pozzolan	Siliceous volcanic ash - granular	-	37.08 ± 1.32	1.112 ± 0.056	22644 ± 1132	670 ± 34	D4
Lapilli	Fragments of Pyroclastic flow - granular	-	2.41 ± 0.12	0.072 ± 0.004	3150 ± 157	94 ± 5	D2
Cement (Cementerie A. Barbetti)	I 52,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Cementerie A. Barbetti)	II/A-LL 42,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Buzzi Unicem)	II/B-LL 32,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Micron Mineral)	III/A 32,5 R	-	bdl	bdl	bdl	bdl	A1
Cement (Cementerie A. Barbetti)	IV/B (P) 32,5 R	-	0.49 ± 0.12	0.015 ± 0.001	1175 ± 22	35 ± 2	B1
Cement (Colacem)	IV/B (P) 32,5 R	-	0.72 ± 0.12	0.022 ± 0.001	2190 ± 17	66 ± 3	B1
Cement (Italcementi)	IV/B (P) 32,5 R	-	0.75 ± 0.13	0.022 ± 0.001	2014 ± 20	60 ± 3	B1
Cement (Italcementi)	V/A (S-P) 32,5 R	-	bdl	bdl	bdl	bdl	A1

(a) calculated according to equation 2 (19-day long experiment) and divided by sample surface.

(b) calculated according to equation 3 (24-hour long experiment) and divided by sample exhaling surface.

(c) calculated according to equation 3 (24-hour long experiment) and divided by sample mass.

(d) calculated according to equation 5 (24-hour long experiment) and divided by sample exhaling surface.

(e) calculated according to equation 5 (24-hour long experiment), divided by sample mass.

(f) experiment at 30°C .

bdl stands for below detection limit.

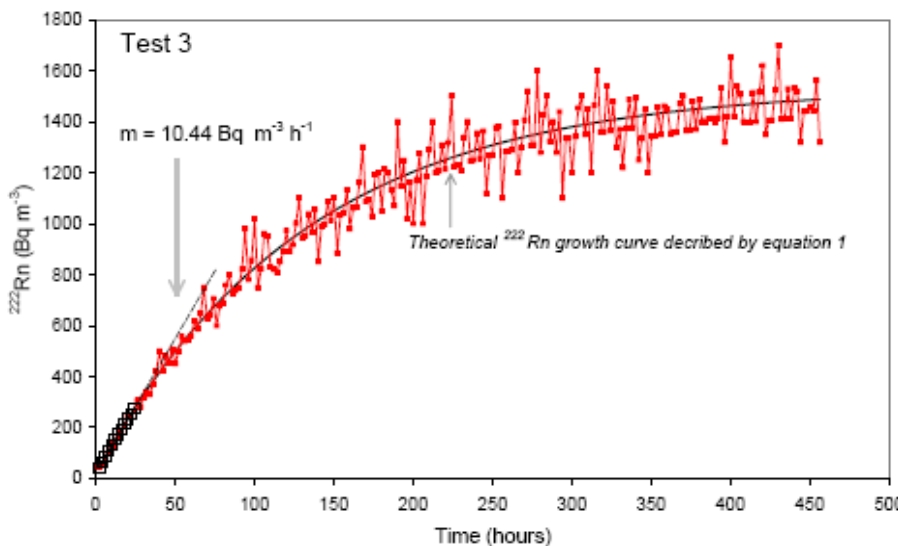


Figure 4. Experimental ^{222}Rn growth curve of TRSN standard (red squares) over a 19-day experiment (test 3) compared with a theoretical curve described by equation 1. The angular coefficient (m) of linear fitting performed on data from first 24 hours is reported. Errors are around 5 %.

Thoron Exhalation Calculations

As demonstrated by validation tests based on non-linear fitting of experimental data, ^{222}Rn growth curve in the closed loop set-up is actually described by ^{222}Rn decay constant and is not affected by leakage, back-diffusion and absorption at the desiccant. The same approach is not applicable to ^{220}Rn because of its short half-life and consequently it is necessary to hypothesise that no thoron loss other than decay occurs within the measuring apparatus, by analogy with ^{222}Rn .

The ^{220}Rn exhalation rate, E_{220} [Bq h^{-1}], can be calculated according to the following equation:

$$E_{220} = (\lambda_{220} \cdot V_0) \cdot \frac{C_m}{e^{-\lambda_{220} \cdot (V_1 / Q)}} \quad (4)$$

where λ_{220} is ^{220}Rn decay constant (h^{-1}), V_0 is the volume of the accumulation chamber (m^3), C_m is the measured ^{220}Rn concentration [Bq m^{-3}], V_1 is the volume between the outflow of the accumulation chamber and the inflow of the radon monitor (see also Figure 1) and Q is the flow rate in the system. The second term of the equation corrects for the decay of ^{220}Rn during the transport in the closed system, because thoron half-life (55.61 s) is comparable with time required to complete a whole loop, causing the underestimation of thoron activity concentration.

An alternative approach to determine thoron exhalation rate with the present set-up is to use a calibrated thoron source, measure its activity concentration and calculate a correction factor (f_c) from the ratio between certified and measured value. This factor is then used to correct values of thoron concentration activities (C_m), obtained with the same experimental configuration and conditions, and to calculate E_{220} according to the following simplified equation:

$$E_{220} = \lambda_{220} \cdot V_0 \cdot C_m \cdot f_c \quad (5)$$

This second approach is preferable because the calibration factor summarises different points, like detector efficiency and effective duration of gas transport from exhalation to detection. The latter is extremely variable and difficult to determine because it strongly depends on experimental conditions, like for example air mixing. In order to show the influence of air circulation on detected ^{220}Rn concentration activity, two different 24-hour tests (Figure 5), have been performed on TRSN standard using the same analytical conditions and configuration except for circulation fan on (test 4-1) or off (4-2). Thoron equilibrium value is significantly reduced without air circulation because of easier stratification at the bottom of the accumulation chamber and presumably longer transport to the radon monitor. Conversely, ^{222}Rn data from the two experiments overlap within the error range because radon half-life (3.82 days) is about two orders of magnitude higher than duration of transport within the measuring apparatus, showing that air mixing is not discriminative for ^{222}Rn exhalation rate.

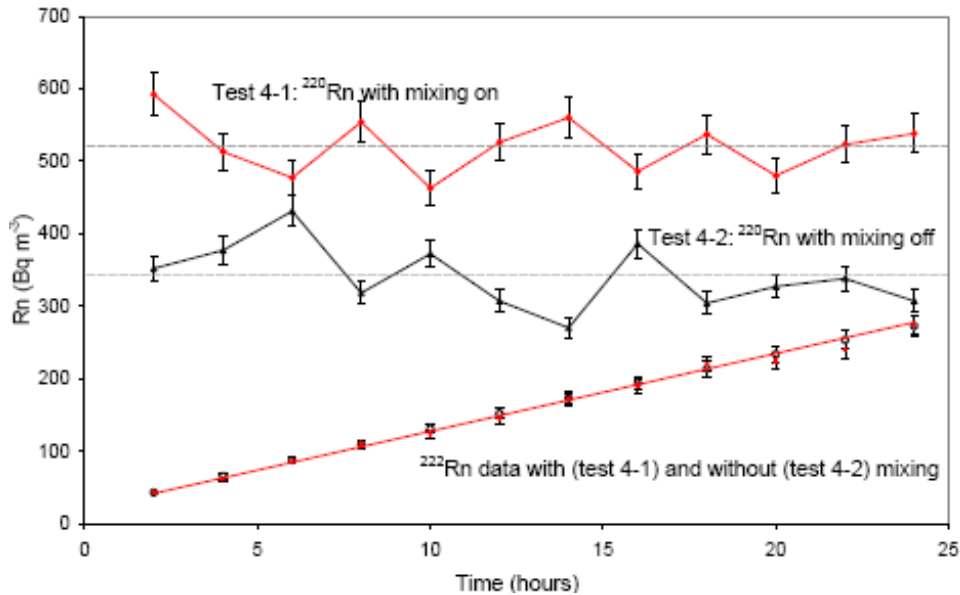


Figure 5. Experimental ^{222}Rn growth curves and ^{220}Rn activity concentration data of TRSN standard over a 24-hour experiment using the stainless steel accumulation chamber with mixing device on (test 4-1) or off (test 4-2). Closed squares and open circles refer to ^{222}Rn data collected respectively with or without mixing; red diamonds and black triangles stand for ^{220}Rn activity concentrations measured under both experimental configuration. Average thoron concentrations are indicated with dashed horizontal lines.

^{220}Rn exhalation rate can be referred to the unit of surface [$\text{Bq m}^{-2} \text{h}^{-1}$] or that of mass [$\text{Bq kg}^{-1} \text{h}^{-1}$], as stated for ^{222}Rn , dividing the value of E_{220} [Bq h^{-1}] from equation 5 by the surface [m^2] or the mass [kg] of the sample.

THE INFLUENCE OF TEMPERATURE ON RADON EXHALATION RATES

Among parameters affecting radon exhalation rate, temperature is undoubtedly relevant and deserves special attention. Its influence can be visualized from a 19-day experiment (test 5) performed on TRSN standard (Figure 6), allowed to undergo ambient temperature fluctuations. ^{222}Rn growth curve from test 5 is compared with the theoretical curve that well describes experimental data from test 3 (Figure 4), where temperature was set and kept at 20°C .

It is evident that during the first segment of test 5 (about 250-hour long), when temperature changes were not relevant (less than 2°C), ^{222}Rn experimental data approached the theoretical curve described by equation 1 (Figure 6). Successively, and up to 370 hours after the beginning of the test (segment 2), significant and rapid temperature fluctuations were recorded along with corresponding changes of radon concentration. In general, this segment of the experiment is characterised by a general temperature decrease up to 360 hours from the start, with radon data falling below the theoretical curve, but during the last 10-12 hours of the segment, an abrupt temperature increase of 12°C makes radon concentration rise up to the curve. Throughout the last section of the experiment (segment 3), temperature fluctuations are

accompanied by parallel oscillations of radon data in the frame of a general decrease of both variables, with radon concentrations always below the curve.

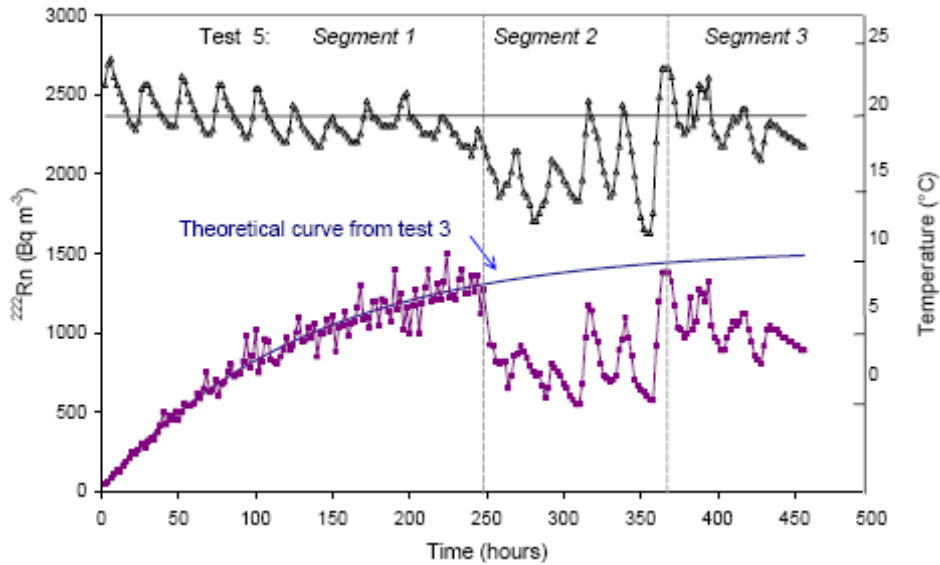


Figure 6. Experimental ^{222}Rn growth curve of TRSN standard (purple squares) over a 19-day experiment (test 5) performed at ambient conditions (variable temperature) compared with theoretical radon curve from test 3 conducted at a constant temperature of 20°C . Temperature data are indicated with black triangles. The reference temperature of 20°C is indicated with a full horizontal line. Errors are around 5 %.

Test 5 clearly shows a direct correlation between large temperature changes and variations of radon concentration within the experimental set-up, the latter being realistically due to a change of radon release from the standard. This is simply demonstrated by two 24-hour experiments carried out on TRSN standard under the same experimental condition, except for temperature, kept constant at 20 and 30°C . Results show that radon exhalation rates are different within the error range (see first and second lines of Table 1).

A similar finding on the effect of rapid temperature increases on radon exhalation rate (as in the last 10 hours of segment 2 – test 5) was reported in Kovler (2006a, b) where peaks of radon exhalation rates coincide with those of temperature measured on the surface of cement pastes, due to hydration heat development during the shrinkage phase. The author states that heating of the material weakens physical adsorption of radon gas atoms on the newly formed solid surfaces, enhancing radon release. Slighter temperature changes during longer periods (as in segment 1 of test 5) do not seem to affect significantly ^{222}Rn exhalation rates.

GUIDELINES TO SET A STANDARD PROTOCOL TO MEASURE RADON EXHALATION RATES

On the basis of validation experiments reported above, guidelines for an experimental protocol to measure simultaneously ^{222}Rn and ^{220}Rn exhalation rates are proposed. A special attention is devoted to minimise factors influencing values of exhalation rates: temperature,

air mixing, humidity and grain size. The development of a specific protocol to certify building materials, evaluating their attitude to release radon gas, meets the statements of EC directive 89/106/EEC concerning construction products. This regulation reports the requirements applicable to building materials for their use in construction, among which that they should not emit dangerous radiations nor develop toxic gases. The protocol can be used alone or in conjunction with the activity concentration index (EC-Radiation Protection, 1999) to better determine the exhalation rates of building materials.

The protocol can be applied to cut-stone or granular material, grounded and sieved according to specific use, taking into account that grain size strongly influences exhalation rates, the smaller the grain size, the larger the exhaling surface (De Martino et al., 1998; Kovler et al., 2005; Tuccimei et al., 2006). In addition, when analysing a cut-stone, it should be considered that its exhalation rate increases considerably if the block is grounded. A reference grain size (if a granular material is analysed) and sample weight and volume should be introduced.

Samples have to be weighed (from 0.5 to 1 Kg) and dried at 110°C for 24 hours. The last operation is essential because of the lower recoil distance of radon in water-filled pores than in air-filled pores, resulting in a higher probability of the recoiled radon atoms to stay into the water-filled pores and not be reabsorbed by other grains and, in turn, determining larger exhalation rates from humid samples (Carrera et al., 1997; Wiegand, 2001; Tuccimei et al., 2006).

The analysis is to be performed for 24 hours and the activity concentration of radon isotopes is recorded hourly or every two hours, along with the humidity content and the temperature in the radon monitor inner chamber. The circulation fan should be on, to reach higher equilibrium concentration of thoron and thus determine the relative exhalation rate with better precision. ^{222}Rn and ^{220}Rn exhalation rates are calculated according to equation 3 and 5, respectively. It is advisable to perform experiments at constant temperature because rapid and strong variations of this parameter affect the ^{222}Rn exhalation rate, as demonstrated previously. A reference temperature could be 20 °C, because it corresponds to average temperature in air-conditioned environments. Good operation of the experimental apparatus should be checked periodically by measuring a standard and certified material. This is particularly useful in order to control if the circulation fan works properly and air mixing in the accumulation chamber is guaranteed. A slowing down of the ventilator rotation is likely to occur over time if it is powered to a voltage lower than the proper functioning value. This circumstance could occur if the operator had to reduce the speed of the fan during the analyses of very fine samples that could spread out and being pumped up along the tubing. With a view to this, it is advisable to choose a light and two-blade ventilator (see Figure 1) to have a correct rotation speed, powered at the correct operating voltage. Finally, filters and tubing should be cleaned regularly to keep airflow constant within the experimental apparatus and drierite (tending to release a fine powder) should be sieved and periodically replaced.

Exhalation Rates of Building Materials and Proposal of a Classification Scheme

This section reports on the results of some analyses carried out on six blocks of pyroclastic flows used as cut-stone, two loose volcanic products and eight different

unhydrated cements traded in Italy, according to the previously described standard protocol (Table 1). Results are discussed and a proposal of a classification scheme to apply to building materials is advanced.

The blocks of tuff are quarried in Colli Albani and Sabatini districts near Roma (central Italy) and in the area of Napoli (southern Italy). Black pozzolan (a siliceous volcanic ash) and lapilli tuffs (fragments of pyroclastic rocks measuring between 2 and 64 mm), both from Colli Albani area, are used to produce grout, mortar and hydraulic cement. A selection of cements is presented, choosing at least one sample from each of the types that the European Committee for Standardization (CEN, 2000) has established in EN 197-1: 2000. Briefly, type I is Portland cement, consisting of at least 95 % of clinker (hydraulic material consisting of calcium silicates, aluminium- and iron-containing oxides); type II is Portland cement (at least 79 %) mixed with other components (e.g. granulated blast furnace slag, limestone or pozzolan); type III is slag cement with variable contents of clinker; type IV is pozzolan cement with different percentage of clinker; type V is composite cement with a reduced proportion of clinker added with a mixture of slag, pozzolan, coal fly ash and silica fume.

^{222}Rn exhalation rates of pyroclastic rocks resulted generally relevant, whereas ^{220}Rn release becomes significant only for granular samples, like pozzolan or lapilli tuffs, characterised by a larger exhaling surface. Cements belonging to classes I and II (see details in Table 1), being a mixture of clinker and limestone, provided exhalation rates lower than detection limits of the experimental apparatus. Also cements of classes III and V, essentially a mixture of clinker and slag, gave the same results, whereas pozzolan cements (type IV) presented higher ^{222}Rn and ^{220}Rn exhalation rate. These results are consistent with the high abundance of radium and thorium (radon precursors) in volcanic products from Italian districts.

On this basis, a classification scheme of building materials, applicable to rocks and cements, is proposed (Table 2). An alphanumeric codex that labels the exhalation rate classes (with letters from A to D for ^{222}Rn and numbers from 1 to 4 for ^{220}Rn) supports the classification. From A to D (codex 222 in Table 2) and from 1 to 4 (codex 220 in Table 2), radon exhalation rates progressively increase. The limits between classes are chosen as a function of radon exhalation rates required to reach predetermined equilibrium activity concentrations in a standard confined environment (the model room of 56 m³, reported in EC-Radiation Protection, 1999), completely covered with the investigated material. The preset values of radon equilibrium concentrations are 200 and 400 Bq m⁻³, suggested by the EC recommendation 90/143/Euratom, as action levels in the new and old houses, respectively. These activity concentrations correspond to reference levels of 10 and 20 mSv per year effective dose equivalent, respectively. The choice of setting a class between 100 and 200 Bq m⁻³ is due to significant ^{220}Rn exhalation rates from some building materials, whose contribution adds to indoor ^{222}Rn gas. This additional input is generally neglected, but needs to be accounted for, otherwise its potential risk is underestimated. This view is clearly expressed in Steinhauser et al. (1994) who underlined that the existing database on ^{220}Rn in the environment, the experimental validation of dosimetric models and potential health effects are scarce, but identifies circumstances where the ^{220}Rn dose becomes relevant, as in the indoor environment if building materials with high concentrations of ^{220}Rn precursor are present.

Table 2. Proposal of a classification scheme for building materials. Codex 222 and codex 220 are attributed to samples on the basis of their ^{222}Rn and ^{220}Rn exhalation rates, respectively. The combination of Codex 222 and Codex 220 (in this order) identifies the class of material (see text for explanation)

Codex 222	Equilibrium ^{222}Rn Bq m^{-3}	E_{222} $\text{Bq m}^{-2} \text{h}^{-1}$	E_{222} $\text{Bq kg}^{-1} \text{h}^{-1}$	Codex 220	Equilibrium ^{220}Rn Bq m^{-3}	E_{220} $\text{Bq m}^{-2} \text{h}^{-1}$	E_{220} $\text{Bq kg}^{-1} \text{h}^{-1}$
A	< 100	< 0.49	< 0.015	1	< 100	< 2849	< 85
B	100-200	0.49 - 0.97	0.015 - 0.029	2	100-200	2849 - 5697	85 - 171
C	200 - 400	0.97 - 1.94	0.029 - 0.058	3	200 - 400	5697 - 11394	171 - 342
D	> 400	> 1.94	> 0.058	4	> 400	> 11394	> 342

According to this classification, blocks of pyroclastic rocks are to be referred to subclass B to D, but mainly to the latter ($> 400 \text{ Bq m}^{-3}$ due to ^{222}Rn), whereas granular volcanics are classified as D, with the additional contribution of ^{220}Rn (subclass 2 to 4). TRSN standard, which is a pyroclastic rock grounded and sieved between 2 and 1 mm, is coherently referred to class C2 when measured at 20°C and to class D3 if the test is conducted at 30°C (Table 1). This difference shows how important the introduction of a reference temperature is, in terms of building materials classification. Generally speaking, it is evident that pyroclastic rocks deserve special attention when used in construction, because they can produce indoor radon concentration beyond the action limits recommended by the European legislation.

As far as unhydrated cements of class I, II, III and V are concerned, our analyses show that most of them are classified as A1 material and are not a potential source of risk. However, cements of type IV (pozzolan cement), belonging to class B1, show an higher radon exhalation rate, even if lower than action levels reported by EC recommendation 90/143/Euratom. Finally, it is worth noting that our analyses and classification are referred to unhydrated cements, without taking into consideration the possible effect of cement hydration on the increase of radon exhalation rate (Kovler, 2006a, b).

CONCLUSION

The main conclusion of this chapter can be summarised as follows:

- 1) The experimental apparatus permits the determination of radon free exhalation rates, as shown by validation tests based on non-linear fitting of experimental data. This is clearly shown by the obtained time constant that minimise the deviations from the theoretical curve. Phenomena like sorption of radon by CaSO_4 grains used as desiccant are negligible.
- 2) The experimental set-up makes possible to measure simultaneously ^{222}Rn and ^{220}Rn exhalation rates, taking into account the decay of ^{220}Rn during the transport within the measurement closed-loop from the accumulation chamber to the radon monitor.

- 3) Air circulation during the test affects considerably thoron activity concentration and the use of a certified thoron source is chosen to calibrate the set-up either with air mixing or without it, providing specific thoron calibration factors for both experimental procedures.
- 4) Major and rapid temperature fluctuations are positively correlated with ^{222}Rn activity concentration detected during the measurement. This is probably due to changed exhalation rates as a function of temperature, as shown by the results of two experiments carried out at 20 and 30 °C. Such outcome implies the need to keep the temperature constant during the experiment.
- 5) A standard protocol to measure radon and thoron exhalation rate is proposed and basic maintenance procedures are advanced with the aim of keeping constant airflow within the experimental apparatus.
- 6) Samples of cut-stones and cements used in central Italy as building materials have been analysed and classified according to a tentative scheme on the basis of exhalation rates required to reach the indoor radon action levels recommend by European Community in a model room completely covered with the investigated material.
- 7) Pyroclastic rocks, mainly in granular form, can produce indoor radon concentration beyond the action limits recommended by the European legislation. When added to clinker to prepare pozzolan cement, they contribute to increase radon exhalation rate.
- 8) The role of ^{220}Rn , generally underestimated, is to be considered when evaluating indoor radon risk due to building materials because its contribution can supply a significant amount of radon in a confined environment, as in the case of pozzolan and lapilli tuffs used to prepare grouts, mortar and cements.

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Chapter 8

HIGH TEMPERATURES BEHAVIOR OF MASONRY STRUCTURES: MODELIZATION AND PARAMETRIC STUDY

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ABSTRACT

The behavior of building materials submitted to fire points out the important role of water content. The experimental results show in some cases that a significant plateau appears at a given temperature (around 100 °C). The specificity of this study is to presents a coupled hydro-thermal model based on the mechanics of partially saturated porous media. Such a model is used to simulate a thermal loading up to 1100 °C applied on a thin wall. The effect of phase-change phenomenon is taken into account. The model can also takes into account the effect of vapor pressure on the position of plateau. A parametric study is achieved illustrating the influence of: initial water content, intrinsic permeability and the form of isotherm sorption curve on the hydro-thermal response of thin wall. Compared to the experimental curves obtained in Scientific Center and Technical of Building (CSTB France), the predicted results for the phase-change phenomenon by the hydro-thermal model are in accordance with the experimental observations.

Keywords: Hydro-thermal coupling, Phase-change phenomenon, Fire resistance masonry, Testing fire walls, Modeling.

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NOMENCLATURE

- b_i = Biot's coefficient of each (i) phase; L = latent heat of water vaporization;
 $c_{p\ell}$ = mass heat capacity of the liquid at constant pressure;
 c_{pv} = mass heat capacity of the vapor at constant pressure;
 C_i = specific heat of phase (i) ($i = \ell, v, s$); D_{va} = diffusivity coefficient;
 C_ε^d = heat capacity at constant deformation under non drained conditions;
 H_r = relative humidity in the porous media; K_s = Bulk modulus of the skeleton;
 K_d = incompressibility modulus of porous media in drained conditions;
 K_l = Bulk modulus of the liquid phase; K_v = Bulk modulus of the vapor phase;
 $k_{r\ell}$ = relative permeability to liquid; k_{rg} = relative permeability to gas;
 m_i = variation in mass content of fluid (i) ($i = \ell, v, a$) per unit of the initial skeleton;
 $m_{\ell \rightarrow v}^\circ$ = the rate of fluid mass change from liquid (ℓ) to vapor (v);
 M_i = molar mass of each phase (i) ($i = \ell, v, a, g$);
 N_{ij} = tangent capillary modulus (inverse of Biot's modulus);
 p_i = interstitial pressure of (i) phase ($i = \ell, v, a, g$);
 p_{v_sat} = water vapor saturation pressure; p_{atm} = atmospheric pressure
 p_g = gas pressure; q = heat flow vector; R = universal gas constant;
 s_i^m = mass entropy of fluid (i) ($i = \ell, v, a$); T = temperature; w = water content;
 $\vec{w}_i$ = relative flow vector of fluid mass of each fluid phase (i);
 α_α = coefficient of thermal expansion of vapor or dry air;
 α_ℓ^p = thermal-hygro expansion coefficient for the liquid phase;
 α_g^p = thermal-hygro expansion coefficient for the gaseous phase;
 ρ_d = mass density of the porous media at dry state; ρ_ℓ = liquid water density;
 ρ_v = vapor water density; ρ_a = dry air density; ϕ_0 = material's porosity;
 λ = apparent thermal conductivity of the porous media; τ = tortuosity coefficient;
 λ_i = thermal conductivity of each (i) phase ($i = s, \ell, g$);

1. INTRODUCTION

The structural materials are usually made from mixtures of cement mortar containing certain water content. The phase-change phenomenon, which occurs in these materials, plays

an important role in their resistance to fire. To investigate these aspects, a number of studies have been published without taking into account the hydrous effect on the resistance to fire of porous building materials [1-7]. The last ones are only limited to predict the thermal response of walls subjected to fire. The resistance to fire of masonry wall [8-12] includes not only the capacity of constitutive blocks alone, but also the one of its constituent materials (aggregate, cement and water) [13]. Although there is much research concerning the effect of cement and aggregate on the resistance to fire of masonry walls, there is a need to pay attention to the role of water content [14] and humidity [15]. Therefore, a theoretical model is needed allowing to analyze and to forecast the combined heat and mass transfer in wet porous media subjected to high temperatures (up to 1100 °C). The present work reveals the complexity of these phenomena and the fundamental role of a two-phase (boiling) zone developing inside the porous media when the temperature reaches the saturation temperature. The specificity of the phase-change effect appears clearly (in temperature-time curves) under a form of plateau positioned around the boiling temperature. A finite volume model is proposed to predict the coupled effects of heat and mass transfer in porous media subject to high temperatures. The hydro-thermal model formulation is obtained by applying the conservation laws, the principles of thermodynamics in continuous open media, and by adopting some simplified assumptions specific to building materials [16-20]. In the present model, a method is developed to generate automatically the isotherm sorption curves for different temperatures using the sorption curve obtained at ambient temperature. Moreover, a parametric study (initial water content, intrinsic permeability and isotherm sorption curve) is performed to show the influence of these parameters on the hydro-thermal response of a thin wall subjected to fire. The theoretical predictions (temperature-time curves) have been compared with the experimental measures collected from walls tested at Scientific Center and Technical of Building.

2. THEORETICAL ASPECTS OF THE HYDRO-THERMAL MODEL

2.1. The model's Hypothesis

The principal objective to establish the hydro-thermal model is to investigate the mechanical behavior of masonry wall subjected to high temperatures (up to 1100 °C). This wall is built with hollow blocks which have the mortar (granulates, cement and water) as a constitutive material. A sample made of this material is shown in Figure 1. Such material is porous enough (porosity equal to $\phi_0 = 0.25$) to consider that the system evolution is almost quasi static and the inertial effects are neglected. The main features on which is based the hydro-thermal developed model are described below:

- H1: the porous media is composed by three phases (solid phase “index s ”, liquid phase “index l ”, gaseous phase, “index g ” obtained by mixing air “index a ” and vapor “index v ”).
- H2: the porous medium is considered as isotropic and homogeneous.
- H3: the system evolution is quasi-static.
- H4: the solid phase is incompressible and is inert to fluid in the porous media.
- H5: the gaseous phase is considered as an ideal perfect gas.
- H6: the liquid phase is assumed incompressible and its apparent density is constant.
- H7: the single mass transfers occurs in the

porous media corresponds to the liquid-vapor phase change. H8: the hysteresis phenomenon in the sorption curve is not taken into account. H9: the porosity and permeability of the porous media are considered to be constant.



Figure 1. Photo of the sample cut off from the hollow block.

2.2. Constitutive Equations

The constitutive equations of the hydro-thermal model can be divided into two groups: the conservation and the behavior laws.

2.2.1. Conservation Laws

The equations of fluid mass conservation of three phases are given by [18, 19]:

2.2.1.a. Liquid Water Mass Conservation

$$\dot{m}_\ell + \text{div } w_\ell = -m_{\ell-v} \quad (1)$$

2.2.1.b. Vapor Mass Conservation

$$\dot{m}_v + \text{div } w_v = m_{\ell-v} \quad (2)$$

2.2.1.c. Dry Air Mass Conservation

$$\dot{m}_a + \text{div } w_a = 0 \quad (3)$$

2.2.1.d. Entropy Equation

The inequality of Clausius Duhem is defined by the equation given herein [18]:

$$\frac{DS}{Dt} \geq - \int_{\Omega_t} \frac{\vec{q} \cdot \vec{n}}{T} d\Omega_t + \int_{\Omega_t} \frac{r}{T} d\Omega_t \quad (4)$$

2.2.2. Constitutive Equations

The constitutive equations adopted in this problem are extended and presented here after:

2.2.2.a. Darcy's Law for Liquid Water Flow

$$w_\ell = k_{D\ell} (-\text{grad } p_\ell + \rho_\ell g) \quad (5)$$

2.2.2.b. Darcy's Law for Gas Mixture Flow

$$w_g = k_{Dg} (-\text{grad } p_g + \rho_g g) \quad (6)$$

2.2.2.c. Fick's Laws

$$\frac{p_v p_a}{p_g^2} (\vec{v}_v - \vec{v}_a) = -\tau \cdot D_{va} \overrightarrow{\text{grad}} \left(\frac{p_v}{p_g} \right) \quad (7)$$

2.2.2.d. Fourier's Law

$$q = -\lambda \text{grad } T \quad (8)$$

2.2.2.e. Liquid Vapor Phase-Change Law

$$\frac{dp_\ell}{\rho_\ell} = \frac{dp_v}{\rho_v} - \frac{L_{\ell \rightarrow v}}{T} dT \quad (9)$$

2.2.3. State Equations

$$\dot{S} = s_i^m \dot{m}_i - 3\alpha_i^p \dot{p}_i + \frac{C_\varepsilon^d}{T_0} \dot{T} \quad (10)$$

$$\dot{m}_i = \rho_i N_{ij} \dot{p}_j - 3\rho_i \alpha_i^p \dot{T} \quad (11)$$

where N_{ij} is the tangent capillary modulus. The expression of this parameter will be discussed later in the Appendix 1.

3. GOVERNING EQUATIONS OF THE HYDRO-THERMAL MODEL

The introduction of the constitutive equations ((5), (6), (7), (8), (9), (10)) and (11) into the conservation laws ((1), (2), (3) and (4)) allows to obtain three principal differential equations of the model: vapor and liquid diffusion, dry air diffusion and heat diffusion equations. The temperature T , the vapor pressure p_v and the dry air pressure p_a are the variables of the coupled problem.

3.1. Water and Vapor Mass Diffusion

$$\mathbf{A}_{11} \operatorname{div} \operatorname{grad} p_v + \mathbf{A}_{12} \operatorname{div} \operatorname{grad} p_a + \mathbf{A}_{13} \operatorname{div} \operatorname{grad} T + \mathbf{B}_{11} \dot{p}_v + \mathbf{B}_{12} \dot{p}_a + \mathbf{B}_{13} \dot{T} = \mathbf{C}_1 \quad (12)$$

3.2. Dry Air Mass Diffusion

$$\mathbf{A}_{21} \operatorname{div} \operatorname{grad} p_v + \mathbf{A}_{22} \operatorname{div} \operatorname{grad} p_a + \mathbf{B}_{21} \dot{p}_v + \mathbf{B}_{22} \dot{p}_a + \mathbf{B}_{23} \dot{T} = \mathbf{C}_2 \quad (13)$$

3.3. Energy Diffusion

$$\mathbf{A}_{31} \operatorname{div} \operatorname{grad} p_v + \mathbf{A}_{33} \operatorname{div} \operatorname{grad} T + \mathbf{B}_{31} \dot{p}_v + \mathbf{B}_{32} \dot{p}_a + \mathbf{B}_{33} \dot{T} = \mathbf{C}_3 \quad (14)$$

4. NUMERICAL FORMULATION OF THE MODEL

4.1. Presentation of Equations Under Matrix Form

The resulting equations ((12), (13) and (14)) can be presented under the matrix form:

$$\begin{bmatrix} \mathbf{A}_{11} & \mathbf{A}_{12} & \mathbf{A}_{13} \\ \mathbf{A}_{21} & \mathbf{A}_{22} & 0 \\ \mathbf{A}_{31} & 0 & \mathbf{A}_{33} \end{bmatrix} \times \begin{bmatrix} \Delta p_v \\ \Delta p_a \\ \Delta T \end{bmatrix} + \begin{bmatrix} \mathbf{B}_{11} & \mathbf{B}_{12} & \mathbf{B}_{13} \\ \mathbf{B}_{21} & \mathbf{B}_{22} & \mathbf{B}_{23} \\ \mathbf{B}_{31} & \mathbf{B}_{32} & \mathbf{B}_{33} \end{bmatrix} \times \begin{bmatrix} \dot{p}_v \\ \dot{p}_a \\ \dot{T} \end{bmatrix} = \begin{bmatrix} \mathbf{C}_1 \\ \mathbf{C}_2 \\ \mathbf{C}_3 \end{bmatrix} \quad (15)$$

The components $\mathbf{A}_{ij}$, $\mathbf{B}_{ij}$, $\mathbf{C}_i$ ($i, j = 1, 2, 3$) and the different physical units are developed in the Appendix 2 and 3, respectively.

4.2. Finite Volume Discretization

4.2.1. Principle of the Finite Volume Method

The finite volume method, which is developed by Spalding and Patankar [21], shows a great simplicity in implementation leading thus to its important progress since the years – 1970-1980). It is the basis of the majority of computer codes in Cartesian geometry. For example, the discretization of the equation of energy diffusion (14) is presented. The general form of this equation without hydrous effect can be deduced as follows:

$$A \operatorname{div}(\lambda \operatorname{grad} T) + B \frac{dT}{dt} + S = 0 \quad (16)$$

The principle of the finite volume method consists to integrate the equation (16) on each volume of control. The discretization in the domain is made by a one-dimensional regular

grid oriented positively in the right direction. To write the discretization scheme in P point, we indicate by E and W the nodes situated immediately on the right and left directions of the P point (see Figure 2). The width of the volume of control is Δx and the points situated on the limits of this volume are w and e . The integration of equation (16) in this domain (space) and in the time is:

$$\int_t^{t+\Delta t} \int_w^e \text{div}(\lambda \text{grad } T) dx dt + B_p \int_t^{t+\Delta t} \int_w^e \frac{dT}{dt} dx dt + \frac{1}{A_p} \int_t^{t+\Delta t} \int_w^e S dx dt = 0 \quad (17)$$

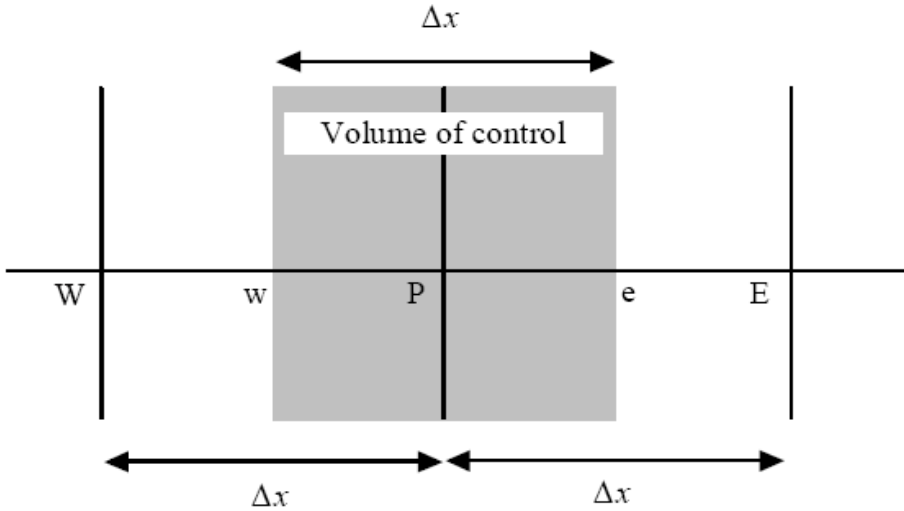


Figure 2. Definition of the volume of control.

The temperature T is supposed to be constant in the volume of control. This assumption allows to write the second term of equation (17) according to the expression given herein:

$$B_p \int_t^{t+\Delta t} \int_w^e \frac{dT}{dt} dx dt = B_p \Delta x (T_P^{t+\Delta t} - T_P^t) \quad (18)$$

After the spatial integration, the other terms of equation (17) can be integrated under the general form:

$$\int_t^{t+\Delta t} f(t) dt = [\theta f(t + \Delta t) - (1 - \theta) f(t)] \Delta t \quad (19)$$

where $f(t)$ is the function to integrate. ($\theta = 0$: explicit scheme, $\theta = 1$: implicit scheme, $\theta = 0.5$: Crank-Nicolson semi-implicit scheme).

Finally the discretization of the equation (17) using the implicit scheme ($\theta = 1$) leads to the expression:

$$\left(\frac{\lambda_e}{\Delta x} \right) T_E^{t+\Delta t} - \left(\frac{\lambda_w + \lambda_e}{\Delta x} \right) T_P^{t+\Delta t} + \left(\frac{\lambda_w}{\Delta x} \right) T_W^{t+\Delta t} + B_p \frac{\Delta x}{\Delta t} (T_P^{t+\Delta t} - T_P^t) + \frac{\bar{S}}{A_p} \Delta x = 0 \quad (20)$$

or under the simple form:

$$\alpha_P T_P^{t+\Delta t} = \alpha_E T_E^{t+\Delta t} + \alpha_W T_W^{t+\Delta t} + b \quad (21)$$

$$\text{where : } \alpha_E = \frac{\lambda_e}{\Delta x}, \alpha_W = \frac{\lambda_w}{\Delta x}, \alpha_P = \alpha_E + \alpha_W - B_P \frac{\Delta x}{\Delta t}, b = \frac{\bar{S}}{A_P} \Delta x - B_P \frac{\Delta x}{\Delta t} T_P^t,$$

4.2.2. Discretization of Model's Equations

The use of the finite volume method in the equation (15) of the hydro-thermal model allows for the following discrete system:

$$\left[\underline{\underline{A}}^t \right] \begin{bmatrix} \vec{p}_v^{t+\Delta t} \\ \vec{p}_a^{t+\Delta t} \\ \vec{T}^{t+\Delta t} \end{bmatrix} = \left[\vec{V}^t \right] \quad (22)$$

$$\text{where : } \left[\underline{\underline{A}}^t \right] = \begin{bmatrix} \underline{\underline{M}}_1^t & \underline{\underline{M}}_2^t & \underline{\underline{M}}_3^t \\ \underline{\underline{M}}_4^t & \underline{\underline{M}}_5^t & \underline{\underline{M}}_6^t \\ \underline{\underline{M}}_7^t & \underline{\underline{M}}_8^t & \underline{\underline{M}}_9^t \end{bmatrix}, \left[\vec{V}^t \right] = \begin{bmatrix} \vec{V}_1^t \\ \vec{V}_2^t \\ \vec{V}_3^t \end{bmatrix},$$

$$\left[\underline{\underline{M}}_1^t \right] = \begin{matrix} & j=2 & j & j=n-1 \\ \begin{matrix} i=2 \\ i \\ i=n-1 \end{matrix} & \begin{bmatrix} \frac{(\mathbf{B}_{11})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} & 0 \\ \frac{(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{11})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} \\ 0 & \frac{(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{11})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{11})_i^t \theta}{\Delta x^2} \end{bmatrix} \end{matrix}$$

$$\left[\underline{\underline{M}}_2^t \right] = \begin{bmatrix} \frac{(\mathbf{B}_{12})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} & 0 \\ \frac{(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{12})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} \\ 0 & \frac{(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{12})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{12})_i^t \theta}{\Delta x^2} \end{bmatrix}, \left[\underline{\underline{M}}_3^t \right] = \begin{bmatrix} \frac{(\mathbf{B}_{13})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} & 0 \\ \frac{(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{13})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} \\ 0 & \frac{(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{13})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{13})_i^t \theta}{\Delta x^2} \end{bmatrix}$$

$$\left[\underline{\underline{M}}_4^t \right] = \begin{bmatrix} \frac{(\mathbf{B}_{21})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{21})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{21})_i^t \theta}{\Delta x^2} & 0 \\ \frac{(\mathbf{B}_{21})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{21})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{21})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{21})_i^t \theta}{\Delta x^2} \\ 0 & \frac{(\mathbf{B}_{21})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{21})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{21})_i^t \theta}{\Delta x^2} \end{bmatrix}, \left[\underline{\underline{M}}_5^t \right] = \begin{bmatrix} \frac{(\mathbf{B}_{22})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} & 0 \\ \frac{(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{22})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} \\ 0 & \frac{(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{22})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{22})_i^t \theta}{\Delta x^2} \end{bmatrix}$$

$$[M_6^t] = \begin{bmatrix} \frac{(\mathbf{B}_{23})_i^t}{\Delta t} & 0 & 0 \\ 0 & \frac{(\mathbf{B}_{23})_i^t}{\Delta t} & 0 \\ 0 & 0 & \frac{(\mathbf{B}_{23})_i^t}{\Delta t} \end{bmatrix}, [M_7^t] = \begin{bmatrix} \frac{(\mathbf{B}_{31})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} & 0 \\ \frac{(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{31})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} \\ 0 & \frac{(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} & \frac{(\mathbf{B}_{31})_i^t}{\Delta t} - \frac{2(\mathbf{A}_{31})_i^t \theta}{\Delta x^2} \end{bmatrix}$$

$$(V_1)_i^t = \frac{(\mathbf{C}_1)_i^t + (\mathbf{C}_1)_{i+1}^t}{2} + \frac{(\mathbf{B}_{11})_i^t}{\Delta t} p_{vi}^t + \frac{(\mathbf{B}_{12})_i^t}{\Delta t} p_{ai}^t + \frac{(\mathbf{B}_{13})_i^t}{\Delta t} T_i^t - \frac{(\mathbf{A}_{11})_i^t (1-\theta)}{\Delta x^2} (p_{vi-1}^t - 2p_{vi}^t + p_{vi+1}^t) \\ - \frac{(\mathbf{A}_{12})_i^t (1-\theta)}{\Delta x^2} (p_{ai-1}^t - 2p_{ai}^t + p_{ai+1}^t) - \frac{(\mathbf{A}_{13})_i^t (1-\theta)}{\Delta x^2} (T_{i-1}^t - 2T_i^t + T_{i+1}^t)$$

$$(V_2)_i^t = \frac{(\mathbf{C}_2)_i^t + (\mathbf{C}_2)_{i+1}^t}{2} + \frac{(\mathbf{B}_{21})_i^t}{\Delta t} p_{vi}^t + \frac{(\mathbf{B}_{22})_i^t}{\Delta t} p_{ai}^t + \frac{(\mathbf{B}_{23})_i^t}{\Delta t} T_i^t - \frac{(\mathbf{A}_{21})_i^t (1-\theta)}{\Delta x^2} (p_{vi-1}^t - 2p_{vi}^t + p_{vi+1}^t) \\ - \frac{(\mathbf{A}_{22})_i^t (1-\theta)}{\Delta x^2} (p_{ai-1}^t - 2p_{ai}^t + p_{ai+1}^t)$$

$$(V_3)_i^t = \frac{(\mathbf{C}_3)_i^t + (\mathbf{C}_3)_{i+1}^t}{2} + \frac{(\mathbf{B}_{31})_i^t}{\Delta t} p_{vi}^t + \frac{(\mathbf{B}_{32})_i^t}{\Delta t} p_{ai}^t + \frac{(\mathbf{B}_{33})_i^t}{\Delta t} T_i^t - \frac{(\mathbf{A}_{31})_i^t (1-\theta)}{\Delta x^2} (p_{vi-1}^t - 2p_{vi}^t + p_{vi+1}^t) \\ - \frac{(\mathbf{A}_{33})_i^t (1-\theta)}{\Delta x^2} (T_{i-1}^t - 2T_i^t + T_{i+1}^t)$$

5. NUMERICAL SIMULATIONS AND EXPERIMENTAL TESTS

5.1. Experimental Test Description

The aim of this part is to compare the numerical results with the experimental ones carried out at Scientific Center and Technical of Building (CSTB France) where the temperature was measured inside the wall. The latter was built by the hollow blocks made of material presented in Figure 1. It should be noted that the vapor pressure inside the wall is not measured, so the results corresponding to this variable were only commented. The principle of the experimental test which consist to applied the thermal loading throught a square wall (280x280x20 cm3) is described in [14] and also shown in Figure 3.

The standard temperature (T_{iso}) is composed by a vertical furnace which use the gas combustion (CH4). The temperature in the wall was measured using thermocouples located in several points of the hollow block partitions as indicated in Figure 3. The result of temperature measurement in point (1)(see Figure 3) is compared to the theoretical predictions and discussed in the paragraph 5.5.1.

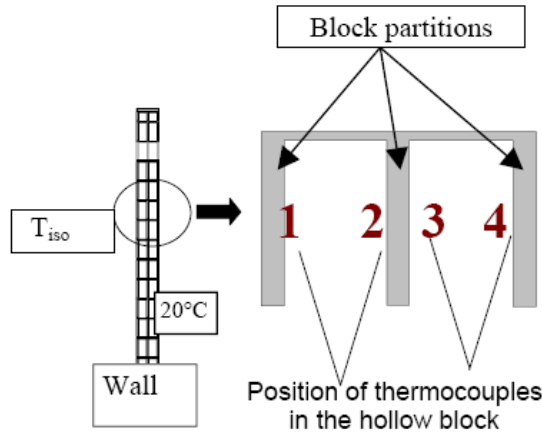


Figure 3. Principle of the experimental tests.

5.2. Thermal Boundary Conditions

5.2.1. Face Exposed to Fire

The temperature is imposed by using the standard curve (T_{iso})(see Figure 4)[22]:

$$T_{out} = T_{iso} = T_0 + 345 \log_{10} (8t + 1) \quad (23)$$

The thermal exchange with the wall depends on the convection coefficient h_T , which is given in [22]:

$$q_T = h_T (T - T_{out}) \quad (24)$$

where T is the temperature in the wall and T_{out} is the temperature outside the wall.

5.2.2. Face Non Exposed to Fire

The temperature on this face is taken equal to $T = 20^\circ\text{C}$ (see Figure 4).

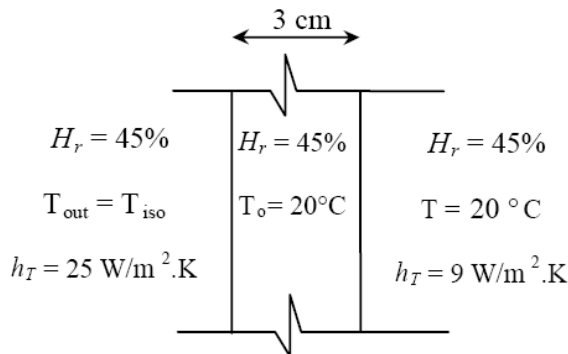


Figure 4. Geometry and boundary conditions for the thin wall.

5.3. Hydrous Boundary Conditions

The vapor pressure on the two faces (exposed or not to fire) is assumed to be constant during heating and equal to:

$$P_v = P_{v0} \quad (25)$$

where P_v is the vapor pressure on the two faces of the wall and P_{v0} is the initial vapor pressure.

5.4. Numerical Simulation

5.4.1. Drying a Thin Wall by Elevated Temperatures

In Figure 4 are shown the geometry of the thin wall, as well as initial and boundary conditions.

5.4.2. Material Properties

The material properties used to perform the simulations are reported in table 1.

Table 1. Values of different parameters of the model

Given parameters	Values	Unit
Thickness of wall	0.03	m
Initial temperature on the face non exposed to fire	20.	°C
Initial relative humidity (on the thin wall and outside)	0.45	-
Initial porosity (taken as constant)	0.25	-
Thermal conductivity of the solid phase	1.5	W/(m . °C)
Mass density of the porous media at dry state	1500.	Kg/m ³
Specific heat of the solid phase	850	J/(Kg . °C)
Convection coefficient on the face exposed to fire	25	W/(m ² . °K)
Convection coefficient on the face not exposed to fire	9	W/(m ² . °K)
Intrinsic permeability	1.10 ⁻¹⁵	m ²

5.5. Results and Discussions

5.5.1. Comparison between Theoretical and Experimental Results

Figure 5 allows the comparison between the theoretical curves (simulated using the thermal model [14] and the hydro-thermal model) with the experimental results. The last ones were obtained by the temperature measurement in point (1) located in first partition of hollow block (see Figure 3) during the heating of masonry wall.

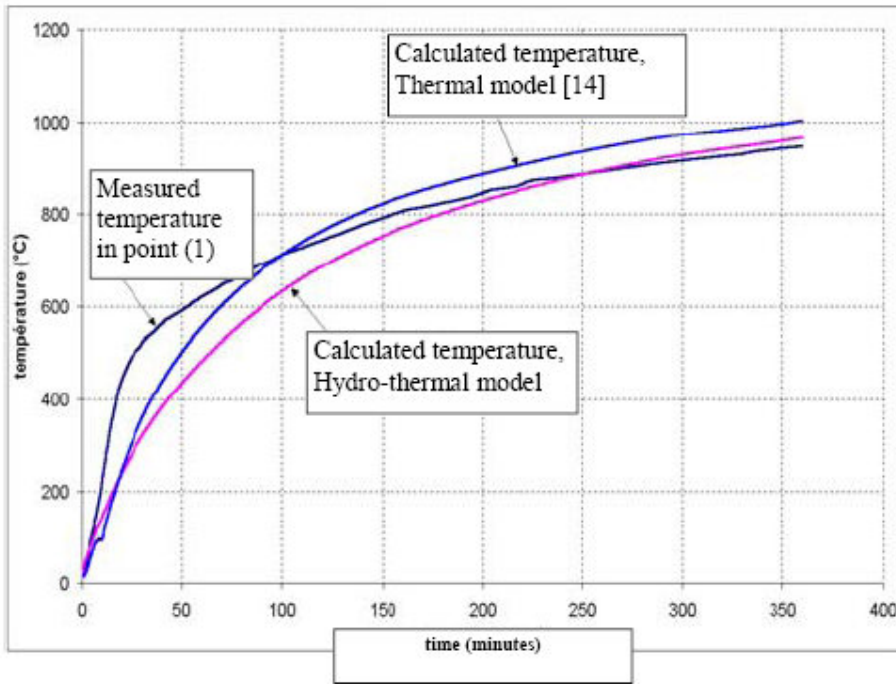


Figure 5. Comparison between theoretical and experimental results: temperature evolution in point (1) of the hollow block first partition (thick = 1.5 cm).

It can be seen that qualitatively the theoretical model estimates correctly the temperature in this point. Also, one can observe that there is no presence of plateau of phase-change phenomenon in the temperature-time curve calculated by the hydro-thermal model. This observation is in accordance with that obtained experimentally (see Figure 5). However, the thermal model still predicts this plateau at temperature equal to $T = 100\text{ °C}$ (see Figure 5). Beyond 50 minutes, a difference of 30 °C can be observed between the curves calculated by the two models. This discrepancy is probably due to the fact that the loss energy carried by the vapor coming out of the first partition of hollow block is taken into account in the hydro-thermal model.

5.5.2. Numerical Results

Figure 4 simulates the drying of a thin wall subjected from one side to a temperature as a function of time according to the formula (23). The other side of wall is subjected to an ambient temperature (20 °C). Thermal exchange with the wall depends on the convection coefficient exchange h_T . Ambient moisture is subjected directly to the two wall sides, the initial relative humidity is equal to $Hr = 45\%$

5.5.1.a. Temperature Evolution

The temperature evolution within the thin wall is presented in Figure 6 where $x = 0\text{ cm}$ is the side exposed to the standard temperature curve ($T_{out} = T_{iso}$) and $x = 3\text{ cm}$ corresponds to the face not exposed to fire. A plateau around a saturation temperature of $T = 100\text{ °C}$ is correctly appeared. This plateau is due to the energy absorption controlled by a phase-change phenomenon (liquid-vapor).

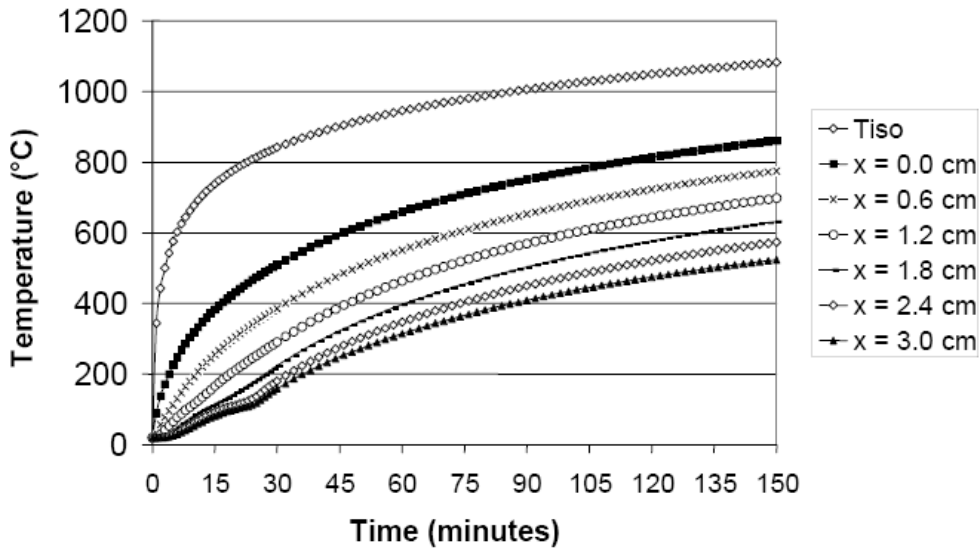


Figure 6. Temperature evolution as a function of the time in the thin wall.

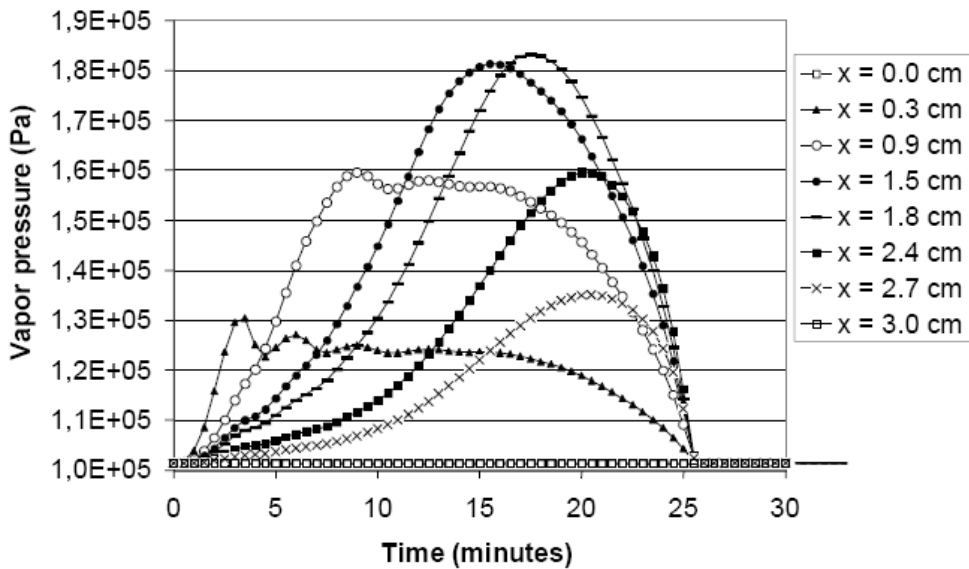


Figure 7. Vapor pressure evolution as a function of the time in the thin wall.

The length of the plateau becomes more important when the studied points are far from the side exposed to fire. This can be interpreted by vapor flow accumulation coming from the left points. It can be noted that the saturation temperature can be higher than 100 °C when the pore pressure increases. As an example, the plateau corresponding to point ($x = 1.8 \text{ cm}$) is situated at temperature equal to 150 °C (see Figure 6). An examination of Figure 7 displays that the vapor pressure in this point ($x = 1.8 \text{ cm}$) is equal to two times the atmospheric pressure. Based on this figure, it is worth intriguing that the phase-change phenomenon has disappeared for points located near the face exposed to fire ($x = 0 \text{ cm}$, $x = 0.6 \text{ cm}$ and

$x = 1.2 \text{ cm}$), this can be interpreted by the fact that the phase-change phenomenon occurs instantaneously on these points.

5.5.1.b. Vapor Pressure Evolution

The vapor pressure evolution in several points in the thin wall is well demonstrated in Figure 7. The pressure peaks appear in this figure showing that the vapor pressure is increased from atmospheric pressure to a maximum value for points located in the middle of wall. It is interesting to notice that the vapor pressure peaks appear at the time where the phase-change phenomenon finishes. As a typical example, the pore pressure peak for a point situated at $x = 2.4 \text{ cm}$ (see Figure 7) appears after 22 minutes which corresponds to the end of the plateau of phase-change phenomenon in the same point (see Figure 6).

5.6. Effects of Some Parameters on the Hydro-Thermal Response of Thin Wall

The objective of this paragraph is to present the influence of some parameters on the hydrous thermal response of laterally heated thin wall. In these simulations, the data which will be used are the same ones as that used previously except that the initial water content, the intrinsic permeability and the isotherm sorption curves are taken as variables.

5.6.1. Initial Water Content Effect

The different values of initial water content related to the relative humidity are presented in table 2:

Table 2. Values of initial water content

$H_r \%$	0	20	40	60	80	100
Water content (w)	0	0.0097	0.0175	0.0291	0.050	0.087

The intrinsic permeability of thin wall is equal to: $K = 1.10^{-15} \text{ m}^2$ and the isotherm sorption curve is given by fitting the curve of Perrin [23]:

$$w(T_0, H_r) = 0.123 \times [H_r(T_0, w)]^3 - 0.0994 \times [H_r(T_0, w)]^2 + 0.0639 \times H_r(T_0, w) \quad (26)$$

where w is the water content, T_0 the initial temperature and H_r the relative humidity. The results of simulations are reported in Figure 8. They show that the initial water content in the material plays an important role on the plateau length of phase-change phenomenon. Moreover, the end of plateau appears at the same temperature and for different values of time. In other words, the length of the plateau becomes higher when the initial water content is more important. This can be explained obviously by the energy needed to evaporate the liquid water, which will be more important if the quantity of liquid water is more important.

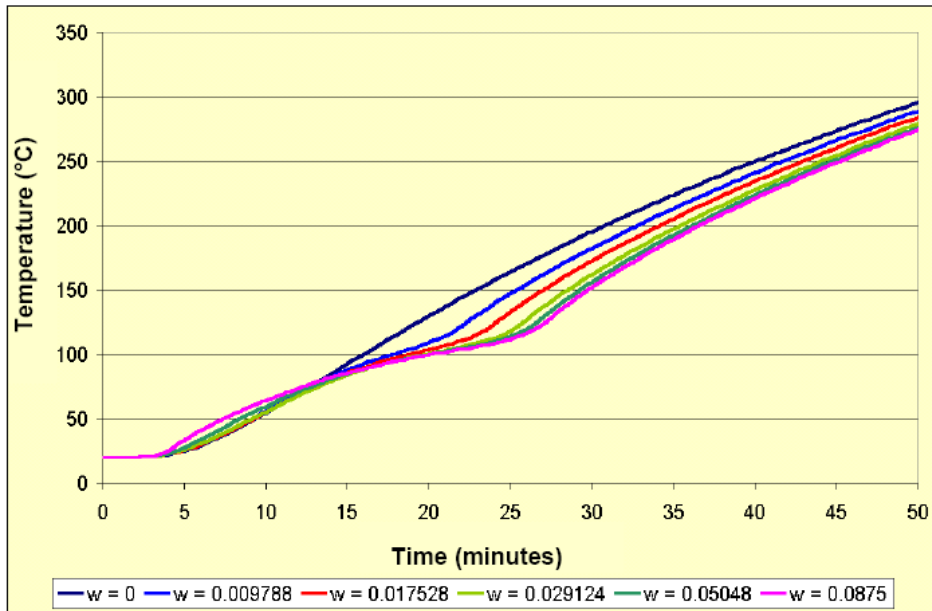


Figure 8. Initial water content effect on the length of plateau of phase-change phenomenon.

5.6.2. Intrinsic Permeability Effect

The different used values of intrinsic permeability are: $K = 5.10^{-17} m^2$, $K = 1.10^{-16} m^2$ and $K = 1.10^{-15} m^2$, with an initial water content equal to $w = 0.022$ and the isotherm sorption curve given by the expression (26).

Figure 9 gives the evolution of temperature with respect to the time in point $x = 2.7 cm$ and for different values of intrinsic permeability.

From this figure, one can observe that the saturation temperature changes from 100 °C (corresponding to the curve obtained for an intrinsic permeability equal to $K = 5.10^{-15} m^2$) to 160 °C (corresponding to the curve obtained for an intrinsic permeability equal to $K = 5.10^{-17} m^2$).

This can be elucidated by the fact that the vapor pressure corresponding to the temperature equal to 160 °C is greater than that corresponding to the saturation temperature equal to 100°C (see Figure 10).

In Figure 11, the curves of temperature versus time for the dried and wet materials are reported.

The difference between these curves is related to the energy absorbed during the phase-change phenomenon which starts at $T = 80 °C$ and finishes at $T = 170 °C$. The increase of vapor pressure induces a progressive increase of the boiling point or a progressive absorption of energy until the total evaporation of the liquid water in the porous media. This energy absorption extends over all the duration of vaporization (see Figure 11).

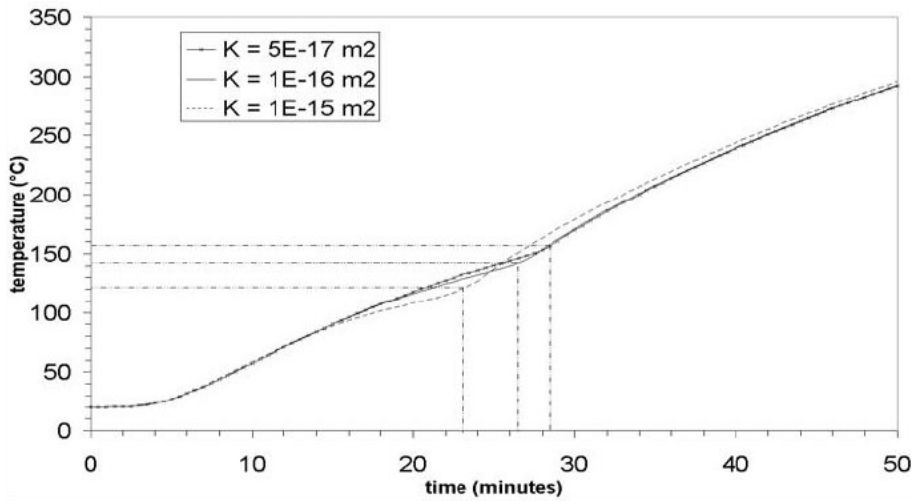


Figure 9. Intrinsic permeability effect on the hydro-thermal response of thin wall.

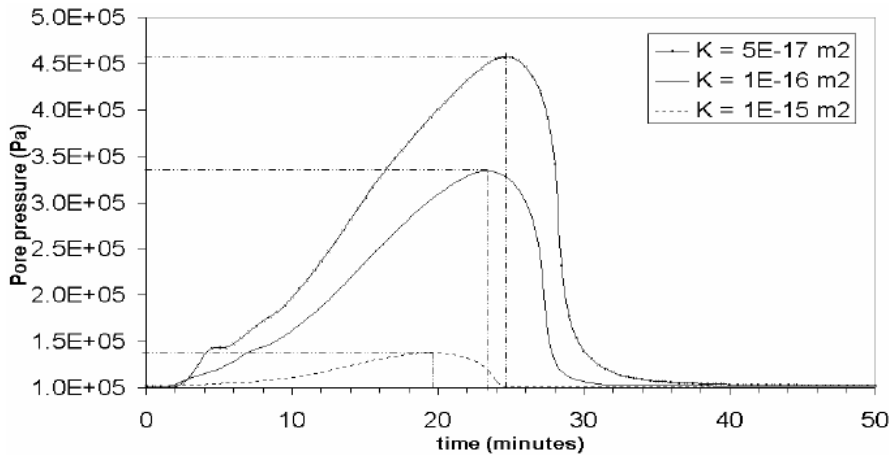


Figure 10. Vapor pressure evolution versus time for different values of intrinsic permeability.

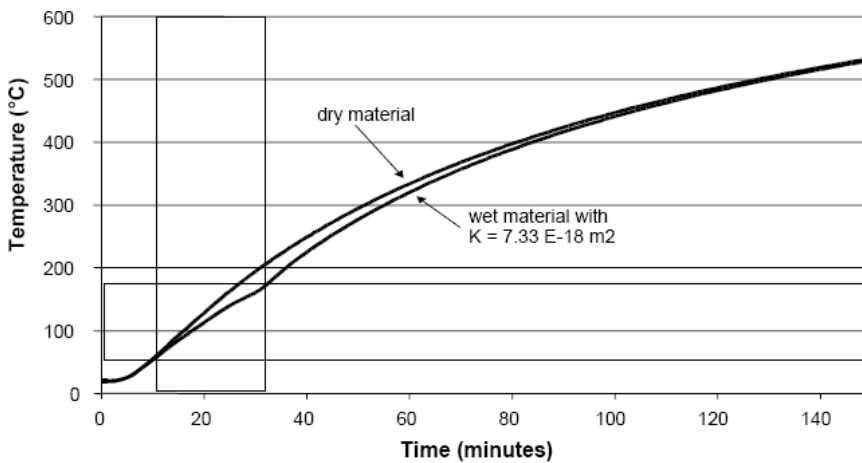


Figure 11. Energy absorption during the phase-change phenomenon liquid to vapor.

5.6.3. Effect of the Form of Isotherm Sorption Curve

In this paragraph, the effect of two isotherm sorption curves (see Figure 12) on the hydro-thermal response of a thin wall heated laterally is studied. The initial water content used in the simulation is equal to $w = 0.022$ and the intrinsic permeability is equal to $K = 5.10^{-15} m^2$. The obtained results using these two curves are reported in Figure 13. It is obviously noticed that the plateau length of the phase-change phenomenon given by using the Obeid sorption curve [24, 25] is less than that corresponding to the isotherm sorption curve by Perrin [23]. This remark can be interpreted by the fact that for a given relative humidity the initial water content corresponding to the curve of Perrin [23] is more important than that corresponding to the curve of Obeid [24, 25]. Infact, this observation confirm that a water content plays an important role in the phase-change phenomenon and in the resistance to fire of masonry structures.

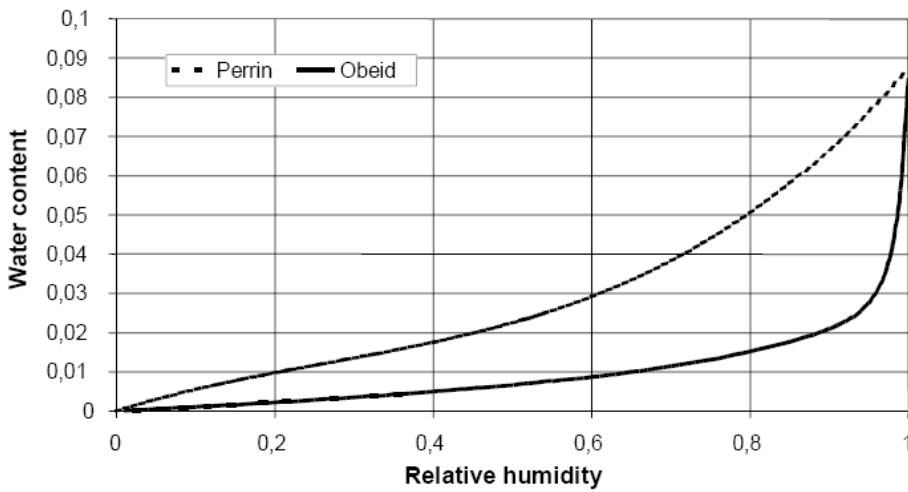


Figure 12. Isotherm sorption curves given by Perrin [23] and Obeid [24].

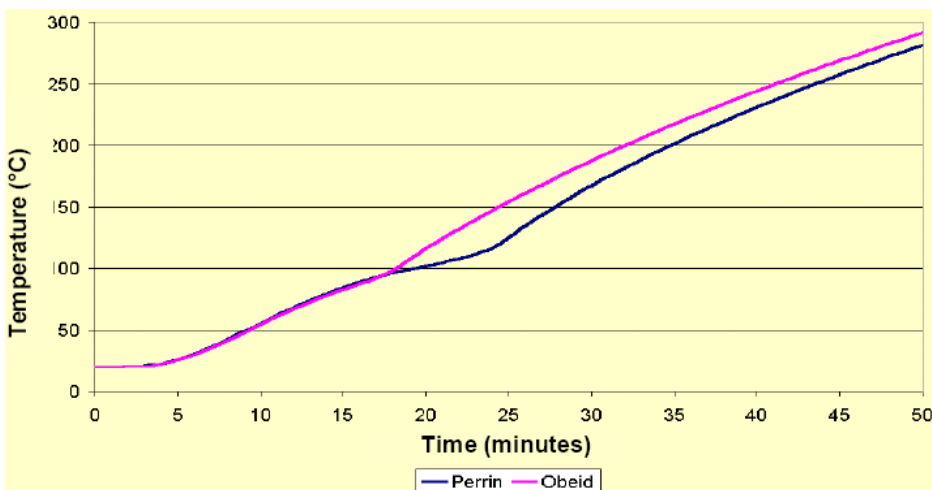


Figure 13. Effect of the form of the isotherm sorption curve.

CONCLUSIONS

Accounting for coupling between phase-change phenomenon, fluid flow and heat transfer, a hydro-thermal model using the finite volumes method is established. With this model, the important effect of phase-change phenomenon on the hydro-thermal response of a thin wall subjected to high temperatures is correctly predicted. This phenomenon is characterized by temperature stagnation at the level of boiling temperature. This last one can have several levels in the temperature-time curve according to the vapor pressure in the studied point. Compared to the experimental curves obtained in Scientific Center and Technical of Building (CSTB France), the hydro-thermal model gave results that showed reasonable agreement for the temperature-time curve. Also, the result of phase-change phenomenon predicted by this model is in accordance with the experimental observations. The parametric study shows the influence of: -the initial water content which plays an important role on the plateau length of the phase-change phenomenon, -the intrinsic permeability which shows that the saturation temperature changes from 100 °C to 160 °C, and -the form of isotherm sorption curve which affect the length of the plateau of phase-change (liquid-vapor) on the hydro-thermal response of wall.

ACKNOWLEDGEMENTS

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APPENDIX 1.

Expression of the tangent capillary modulus (N_{ij}) and Biot's coefficient (b_i):

$$b_g + b_\ell = 1 - \frac{K_d}{K_s} \quad N_g + N_\ell = \frac{b_g - \phi_g}{K_s} \approx 0$$

$$N_\ell + N_{\ell\ell} = \frac{b_\ell - \phi_\ell}{K_s} + \frac{\phi_\ell}{K_\ell} \approx \frac{\phi_\ell}{K_\ell} \quad N_\ell + N_{vv} = \frac{b_g - \phi_g}{K_s} + \frac{\phi_g}{K_v} \approx \frac{\phi_g}{K_v}$$

$$N_\ell + N_{aa} = \frac{b_g - \phi_g}{K_s} + \frac{\phi_g}{K_a} \approx \frac{\phi_g}{K_a} \quad b_v = b_a = b_g \quad N_{a\ell} = N_{v\ell} = N_\ell$$

$$N_{av} = N_{va} = N_g \quad N_{vv} = \frac{\phi_g}{K_v} + N_g \quad N_{aa} = \frac{\phi_g}{K_a} + N_g$$

The previous expressions can be written under the matrix form:

$$N_{ij} = \begin{bmatrix} N_{\ell\ell} & N_{\ell v} & N_{\ell a} \\ N_{v\ell} & N_{vv} & N_{va} \\ N_{a\ell} & N_{av} & N_{aa} \end{bmatrix} = \begin{bmatrix} \frac{\phi_\ell}{K_\ell} - N_\ell & N_\ell & N_\ell \\ N_\ell & \frac{\phi_g}{K_v} - N_\ell & -N_\ell \\ N_\ell & -N_\ell & \frac{\phi_g}{K_a} - N_\ell \end{bmatrix}$$

where the tangent capillary modulus of liquid N_ℓ is given by the expression:

$$N_\ell = -H \frac{M_v}{RT} \cdot \frac{\rho_d}{\rho_\ell^2} \left(\frac{\partial w}{\partial H} \right)_T + H \frac{M_v}{RT} \cdot \frac{3b_\ell}{\rho_\ell} \left(\frac{\partial \varepsilon_x}{\partial H} \right)_T$$

and $(\partial w / \partial H)_T$ is the slop of sorption isotherm curve as a function of the temperature [26] which is reported herein:

$$\left(\frac{\partial w}{\partial H_r} \right)_T = \left(\frac{\partial w}{\partial H_r} \right)_{T_0} \times \frac{\gamma(T_0)}{\gamma(T)} \times \frac{T}{T_0} \times [H_r(T_0, w)]^{1 - \frac{\gamma(T)}{\gamma(T_0)} \times \frac{T_0}{T}}$$

The water surface tension $\gamma(T)$ is given by the following expression: $\gamma(T) = (128 - 0.185T)$. The evolution of N_ℓ is represented in Figure 14, where $(\partial w / \partial H)_T$ is based on the isotherm sorption curve of Perrin [23].

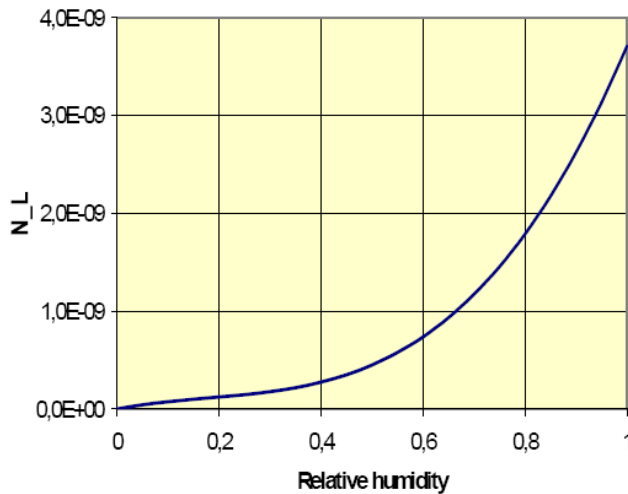


Figure 14. Evolution of parameter N_l as function of the relative humidity.

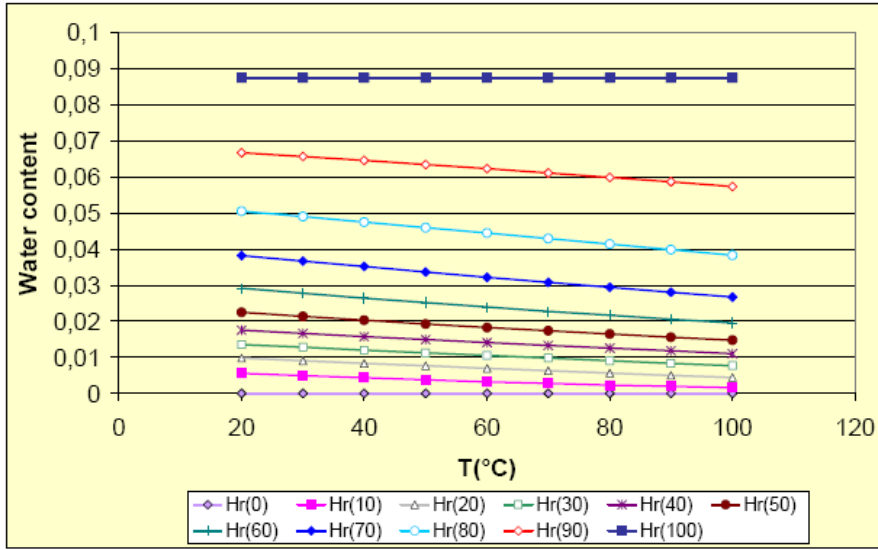


Figure 15. Water content evolution with respect to temperature for different values of the relative humidity.

After fitting of experimental results of Perrin [23] at ambient temperature (T_0), the obtained isotherm sorption curve [14] is represented in Figure 12. It is possible to generate the other isotherm sorption curves at different temperatures using the formula given here after [26]:

$$H_r(T, w) = H_r(T_0, w) \left(\frac{\gamma(T) \times T_0}{\gamma(T_0) \times T} \right)$$

This result is based on the assumption that the change of the sorption curve with temperature is governed only by the change of the water surface tension with the temperature. The isotherm sorption curves generated by this equation are reported in Figure 15.

APPENDIX 2. COMPONENTS RESULTING FROM THE EQUATIONS REPRESENTED UNDER THE MATRIX FORM

$\mathbf{A}_{11} = - \left[k_{D\ell} \frac{\rho_\ell}{\rho_v} + k_{Dv} + k_{Fv} \frac{p_a}{(p_v + p_a)^2} \right]$	$\mathbf{A}_{12} = - \left[k_{Dv} - k_{Fv} \frac{p_v}{(p_v + p_a)^2} \right]$
$\mathbf{A}_{13} = k_{D\ell} \rho_\ell \frac{L}{T}$	$\mathbf{B}_{11} = \left[- \frac{(\rho_\ell - \rho_v)^2}{\rho_v} N_\ell + \rho_v \frac{\phi_g}{K_v} \right]$
$\mathbf{B}_{12} = (\rho_\ell - \rho_v) N_\ell$	$\mathbf{B}_{13} = - \left[(\rho_v \rho_\ell - \rho_\ell^2) \frac{L}{T} N_\ell + 3(\rho_\ell \alpha_\ell^p + \rho_v \alpha_v^p) \right]$

$\mathbf{C}_1 = \text{grad} \left[k_{D\ell} \frac{\rho_\ell}{\rho_v} + k_{Dv} + k_{Fv} \frac{p_a}{(p_v + p_a)^2} \right] \cdot \text{grad } p_v +$ $\text{grad} \left[k_{Dv} - k_{Fv} \frac{p_v}{(p_v + p_a)^2} \right] \cdot \text{grad } p_a -$ $\text{grad} \left(k_{D\ell} \rho_\ell \frac{L}{T} \right) \cdot \text{grad } T - g \text{ grad} (k_{D\ell} \rho_\ell)$	
$\mathbf{A}_{21} = - \left[k_{Da} - k_{Fa} \frac{p_a}{(p_v + p_a)^2} \right]$	$\mathbf{A}_{22} = - \left[k_{Da} + k_{Fa} \frac{p_v}{(p_v + p_a)^2} \right]$
$\mathbf{B}_{21} = \frac{\rho_a}{\rho_v} (\rho_\ell - \rho_v) N_\ell$	$\mathbf{B}_{22} = \rho_a \left(\frac{\phi_g}{K_a} - N_\ell \right)$
$\mathbf{B}_{23} = - \left(\rho_\ell \rho_a N_\ell \frac{L}{T} + 3 \rho_a \alpha_a^p \right)$	$\mathbf{A}_{31} = L k_{D\ell} \frac{\rho_\ell}{\rho_v}$
$\mathbf{C}_2 = \text{grad} \left[k_{Da} - k_{Fa} \frac{p_a}{(p_v + p_a)^2} \right] \cdot \text{grad } p_v + \text{grad} \left[k_{Da} + k_{Fa} \frac{p_v}{(p_v + p_a)^2} \right] \cdot \text{grad } p_a$	
$\mathbf{A}_{33} = - \left(\lambda + k_{D\ell} \rho_\ell \frac{L^2}{T} \right)$	$\mathbf{B}_{31} = - \left(\begin{aligned} &3T \frac{\rho_\ell}{\rho_v} \alpha_\ell^p + 3T \alpha_g^p - \\ &L \rho_\ell N_\ell \frac{\rho_\ell}{\rho_v} + L \rho_\ell N_\ell \end{aligned} \right)$
$\mathbf{B}_{32} = - (3T \alpha_g^p + L \rho_\ell N_\ell)$	$\mathbf{B}_{33} = \left(C_\varepsilon^d \frac{T}{T_0} + 6 \alpha_\ell^p \rho_\ell L - N_\ell \rho_\ell^2 \frac{L^2}{T} \right)$
$\mathbf{C}_3 = \left[\text{grad } \lambda + L \text{ grad} \left(k_{D\ell} \rho_\ell \frac{L}{T} \right) \right] \cdot \text{grad } T - w_i T \text{ grad} (s_i^m)$ $- L \text{ grad} \left(k_{D\ell} \frac{\rho_\ell}{\rho_v} \right) \cdot \text{grad } p_v + L g \text{ grad} (k_{D\ell} \rho_\ell)$	

APPENDIX 3. VARIATION OF DIFFERENT PHYSICAL UNITS

Water content at saturation state $w_{sat} = \phi_0 \frac{\rho_\ell}{\rho_d}$	Water vapor saturation pressure (Kunzel, [27]) $p_{v\_sat} = 611. \times \exp \left(\frac{17.08 \times T - 273.15}{234.18 + T - 273.15} \right)$

Appendix 3. (Continued)

Sorption curve at ambient temperature (Perrin, [23]) $w = 0.123 \times [H_r(T_0, w)]^3 - 0.0994 \times [H_r(T_0, w)]^2 + 0.0639 \times H_r(T_0, w)$	Latent heat of water vaporisation (Coussy, [18]) $L = L_0 - (c_{p\ell} - c_{pv}) \times (T - T_0)$
Incompressibility modulus of dry air or vapor (Coussy, [18]) $K_\alpha = p_\alpha$	Coefficient of thermal expansion of dry air or vapor (Coussy, [18]) $\alpha_\alpha = 1/3T$
Specific heat (Obeid, [24]) $C = C_s + 21.0108 \times w$	Apparent thermal conductivity (Dangla, [19]) $\lambda = \lambda_s^{(1-\phi_0)} \times \lambda_\ell^{S_\ell \cdot \phi_0} \times \lambda_g^{(1-S_\ell) \cdot \phi_0}$
$\left(\frac{\partial \varepsilon}{\partial H} \right)_{T,\sigma} = 4 \times 10^6$	$b_\ell = H \frac{3M_v K^d}{RT \rho_\ell} \left(\frac{\partial \varepsilon_x}{\partial H} \right)_{T,\sigma}$
$N_\ell = -H \frac{M_v}{RT} \cdot \frac{\rho_d}{\rho_\ell^2} (\partial w / \partial H)_T + H \frac{M_v}{RT} \cdot \frac{3b_\ell}{\rho_\ell} (\partial \varepsilon_x / \partial H)_T$	$\alpha_\ell^p = -\frac{1}{3} \frac{\rho_d}{\rho_\ell} \left(\frac{\partial w}{\partial T} \right)_{H,\sigma}$
Hygro-thermal expansion coefficient for the gaseous phase (Coussy, [18]) $\alpha_g^p = -\alpha_\ell^p + (1 - \phi_0) \alpha_s + \phi_g \alpha_g + \phi_0 S_\ell \alpha_\ell$	Diffusivity coefficient of vapor in the air (Ferraille-Fresnet, [28]) $D_{va} = 0.217 \times 10^{-4} \times \frac{p_{atm}}{p_g} \times \left(\frac{T}{T_0} \right)^{1.88}$
Relative permeability to liquid (Van Genuchten, [29])	Relative permeability to gas (Mualem, [30]) $k_{rg} = (1 - S_\ell)^{0.5} \times (1 - S_\ell^2)$
Diffusivity coefficient of vapor in the gas mixture (dry air and vapor) (Dangla, [19]) $D_{vg} = \phi_g \cdot \tau \cdot D_{va}$	Surface tension $\gamma(T) = (128 - 0.185 T_{Kelvin})$
Relative humidity in porous media $H_r(T, w) = H_r(T_0, w) \left(\frac{\gamma(T)}{\gamma(T_0)} \times \frac{T_0}{T} \right)$	Slop of (water content – relative humidity) curve for a given temperature $(\partial w / \partial H_r)_T = (\partial w / \partial H_r)_{T_0} \times (\gamma(T_0) / \gamma(T)) \times (T / T_0) \times [H_r(T_0, w)]^{1 - \frac{\gamma(T)}{\gamma(T_0)} \times \frac{T_0}{T}}$

Slop of (water content – temperature) curve for a given humidity

$$\left(\frac{dw}{dT}\right)_{H_r} = -H_r(T_0, w) \times \ln[H_r(T_0, w)] \left(\frac{\gamma'(T)}{\gamma(T)} - \frac{1}{T} \right) \times \left(\frac{\partial w}{\partial H_r} \right)_{T_0, w}$$

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Chapter 9

AGRICULTURAL WASTES AS BUILDING MATERIALS: PROPERTIES, PERFORMANCE AND APPLICATIONS

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ABSTRACT

While recycling of low added-value residual materials constitutes a present day challenge in many engineering branches, attention has been given to cost-effective building materials with similar constructive features as those presented by materials traditionally employed in civil engineering. Bearing in mind their properties and performance, this chapter addresses prospective applications of some elected agroindustrial residues or by-products as non-conventional building materials as means to reduce dwelling costs.

Such is the case concerning blast furnace slag (BFS), a glassy granulated material regarded as a by-product from pig-iron manufacturing. Besides some form of activation, BFS requires grinding to fineness similar to commercial ordinary Portland cement (OPC) in order to be utilized as hydraulic binder. BFS hydration occurs very slowly at ambient temperatures while chemical or thermal activation (singly or in tandem) is required to promote acceptable dissolution rates. Fibrous wastes originated from sisal and banana agroindustry as well as from eucalyptus cellulose pulp mills have been evaluated as raw materials for reinforcement of alternative cementitious matrices, based on ground BFS.

Production and appropriation of cellulose pulps from collected residues can considerably increase the reinforcement capacity by means of vegetable fibers. Composites are prepared in a slurry dewatering process followed by pressing and cure under saturated-air condition. Exposition of such components to external weathering

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leads to a significant long-term decay of mechanical properties while micro-structural analysis has identified degradation mechanisms of fibers as well as their mineralization. Nevertheless, these materials can be used indoors and their physical and mechanical properties are discussed aiming at achieving panel products suitable for housing construction whereas results obtained thus far have pointed to their potential as cost-effective building materials.

Phosphogypsum rejected from phosphate fertilizer industries is another by-product with little economic value. Phosphogypsum may replace ordinary gypsum provided that radiological concerns about its handling are properly overcome as it exhales radon-222, a gaseous radionuclide whose indoor concentration should be limited and monitored. Some phosphogypsum properties of interest (e.g., bulk density, consistency, setting time, free and crystallization water content, and modulus of rupture) have indicated its large-scale exploitation as surrogate building material.

INTRODUCTION

Developing countries usually face grave housing deficits and the following hurdles against dwelling construction have been typically pointed out: high interest rates, elevated social taxes, high informal labor indexes, and bureaucracy. Lack of loan is an additional problem¹ as banks may not be interested on funding or because governmental programs are scarce. As a result, a considerable percentage of the population in developing countries still lives at sub-dwelling units. In 2006, estimates suggested that around 7.9 million dwellings were needed in Brazil, most of them (83.3%) located in urban areas, particularly in the so-called Metropolitan Regions² surrounding Brazilian state capitals (2.2 million dwellings) [1]. Metropolitan Regions around São Paulo and Rio de Janeiro cities present the greatest housing deficits, adding together to almost 1.2 million dwellings [1].

Aiming at lowering costs, scientific attention has been given to non-conventional building materials with similar features as those presented by construction materials traditionally used in civil engineering. Quest for such surrogate materials can be two-fold interesting as (i) it may help to reduce dwelling deficits (particularly in developing countries) inasmuch as cheaper houses become economically feasible and (ii) it can be environmentally friendly as low-value wastes can be recycled or exploited. Accordingly, this chapter is particularly interested in agroindustrial residues or by-products as prospective non-conventional construction materials.

VEGETABLE FIBERS AS NON-CONVENTIONAL BUILDING MATERIAL

Vegetable fibers are widely available in most developing countries. They are suitable reinforcement materials for brittle matrix even though they present relatively poor durability performance. Accounting for the mechanical properties of the fibers as well as their broad

¹ This is particularly true during economic and financial crisis such as the worldwide crisis started in 2008.

² Metropolitan Regions of major interest in Brazil refer to the following capitals (corresponding state in brackets): Belém (Pará), Fortaleza (Ceará), Recife (Pernambuco), Salvador (Bahia), Belo Horizonte (Minas Gerais), São Paulo (São Paulo), Rio de Janeiro (Rio de Janeiro), Curitiba (Paraná), and Porto Alegre (Rio Grande do Sul).

variation range, one may develop building materials with suitable properties by means of the adequate mix design [2], [3].

The purpose of the fiber reinforcement is to improve mechanical properties of a given building material, which would be otherwise unsuitable for practical applications [4]. A major advantage concerning fiber reinforcement of a brittle material (e.g., cement paste, mortar, or concrete) is the composite behavior after cracking. Post-cracking toughness produced by fibers in the material may allow large-scale construction use of such composites [4].

There are two approaches for the development of new composites in fiber-cement [5]. The first one is based on the production of thin sheets and other non-asbestos components. The later components are similar to asbestos-cement ones and they are produced by well-known industrial-scale processes such as Hatschek and Magnani methods commercially used with high acceptance for building purposes [6]. The second approach consists of producing composites for different types of building components like load-bearing hollowed wall, roofing tiles, and ceiling plates, which are not similar to components commercially produced with asbestos-cement.

Estimated as several million of tons per year [7], consumption of fiber-reinforced cement building components is rapidly increasing, especially in developed countries. This is because such type of material allows one to produce lightweight building components with good mechanical performance (mainly regarding impact energy absorption) and suitable thermal-acoustic insulation, while being economically attractive [4]. Fibers naturally occur in tropical and equatorial countries, where they have been essentially targeted to cordage, textile, and papermaking sectors. Their heterogeneity and perishing allied to restricted market for their use have lead to intense generation of residues with high pollution potential. For example, each ton of commercially used sisal fibers yields three tons of residual fibers, whose dumping has originated environmental hazards [8].

Table 1. Physical or mechanical properties of some fibers.

Fiber	Property of interest				
	Density (g/cm ³)	Tensile strength (MPa) ^e	Modulus of elasticity (GPa)	Elongation at failure (%)	Water absorption (%)
Jute (<i>Corchorus capsularis</i>) ^a	1.36	400 - 500	17.4	1.1	250
Coir (<i>Cocos nucifera</i>) ^b	1.17	95 - 118	2.8 ^d	15 - 51	93.8
Sisal (<i>Agave sisalana</i>) ^b	1.27	458	15.2	4	239
Banana (<i>Musa cavendishii</i>) ^a	1.30	110 - 130	---	1.8 - 3.5	400
Bamboo (<i>Bambusa vulgaris</i>) ^b	1.16	575	28.8	3.2	145
E-glass ^c	2.50	2500	74	2 - 5	---
Polypropylene ^c	0.91	350 - 500	5 - 8	8 - 20	---

^a [11], ^b [5], ^c [12], ^d [13]; ^e tensile strength strongly depends on the type of the fiber, being a bundle or a single filament.

As reported in Coutts [9], vegetable fibers contain cellulose (which is a natural polymer) as the main reinforcement material. The chains of cellulose form microfibrils, which are held together by hemicellulose and lignin in order to form fibrils. The later are then assembled in

various layers to build up the fiber structure. Fibers or cells are cemented together in the plant by lignin, which can be dissolved by the cement matrix alkalinity [10]. The usual denomination for fibers is indeed a reference to strands with significant consequences on durability studies.

Banana fibers cut from the plant pseudo-stem and sisal by-products from cordage industries are examples of widely available fibers. Eighteen types of potential fibers have been identified, including cellulose pulp recovered from newspaper, malva, coir, and sisal [5]. However, if costs and availability issues are accounted for, the number of suitable fiber types reduces drastically. Coir, sisal chopped strand fibers, and eucalyptus residual pulp have already been identified as fibrous waste materials suitable for cement reinforcement [8] and Table 1 presents some of their mechanical and physical properties of interest.

The present chapter is particularly interested in three different types of fibrous residues typically found in Brazil, namely:

- Sisal (*Agave sisalana*) field by-product: This material is readily available (e.g., 30,000 tons per year from a given producers' association) and it has presently no commercial value. Its use offers an interesting additional income for rural producers and simple manual cleaning via a rotary sieve provides a suitable starting-point material.
- Banana (*Musa cavendishii*) pseudo-stem fibers. This by-product has high potential availability from fruit production (e.g., 95,000 ton per year, based on Brazil's main producing area). This material has no market value and a simple low-cost fiber extraction process is required.
- *Eucalyptus grandis* waste pulp. Accumulating from several Kraft and bleaching stages, this resource has low commercial value (USD 15/ton) and is readily available (e.g., 17,000 ton per year from one pulp industry in Brazil's southeast region). Disadvantages of this material include short fiber length and high moisture content (about 60% of dry mass).

Although chopped fibrous residues can be directly introduced into the cement matrix for reinforcement, further chemical processing of these residual fibers has proved to improve the performance of the building products [14]. Pulped fibers are preferred for composites production using slurry vacuum de-watering technique, which is a laboratory-scale crude simulation of Hatschek process. During the de-watering stage, pulp forms a net that retains cement grains. Small fibers remain homogeneously distributed in two directions (2-D) into the matrix [15] and this fact suggests some advantages of using sisal pulp (individualized fibers) in relation to sisal strand fibers [14]. Reinforcement is distributed into the composite leading to the effective capacity of reinforcing and bridging cracks during bending tests. Cellulose pulps can be produced from residual crops (non-wood) fibers or wood species, reaction with alkaline liquors (e.g., sodium hydroxide, i.e., Kraft process), or organic solvents (e.g., ethanol).

Low performance of natural fiber reinforced composites (NFRC) has been associated to the use of chopped strand fibers as reinforcement for ordinary brittle cement matrices produced by conventional dough mixing methods [5]. This has been identified as the main reason for the low acceptance of these products by the industry. Consequently, in several

developing countries asbestos-cement remains the major composite in use although health hazards have become a major concern [16]. In view of that, agricultural residual fibers discussed in this chapter were further prepared in order to fit their use and to achieve improved performance in the composites.

PHOSPHOGYPSUM AS NON-CONVENTIONAL BUILDING MATERIAL

Another research line has pointed to the replacement of ordinary gypsum (calcium sulphate hemihydrate). Basically composed by calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), gypsite is the raw material for the production of ordinary gypsum through thermal dehydration. Gypsum has been mainly consumed as constructive boards (panels) and as wall covering (on minor extent) but its large-scale use in developing countries may become restricted or economically unfeasible due to transportation costs from production sites (mines) to potential consumption places (e.g., large cities), which is the scenario observed in Brazil.

According to the Brazilian National Department of Mineral Production (subordinated to the Ministry of Mining and Energy) [17], around 98% of Brazil's gypsite mines adding up to 1.3×10^9 tons are located in northern or north-eastern states, namely, Pará (30.3%), Bahia (42.7%), and Pernambuco (25.1%). Altogether in 2007, their corresponding gypsite production comprised 1.9×10^6 tons so that 89% (1.7×10^6 tons) was due to Pernambuco state alone, located more than 2,400 km away from either Rio de Janeiro or São Paulo Metropolitan Regions (both in Brazil's southeast region). Compared to the USA (world's largest gypsum consumer and producer), Brazilian consumption is very low, not only due to the aforesaid transportation costs and logistics associated to gypsite mines but also due to related energy costs and lack of necessary facilities.

Conversely, growing demands for phosphate fertilizers have yielded enormous amounts of phosphogypsum for years worldwide [18]. Despite being essentially $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, such material has currently little economic value due to environmental issues notably regarding radon-222 (^{222}Rn) exhalation. Together with its decay products, ^{222}Rn is a radioactive noble gas responsible for most human natural exposure to radiation and assessment of its exhalation rate is crucial for radiological protection design [19].

Half-life of ^{222}Rn ($= 3.824$ days) is long enough to allow its transport through porous media or open air. If inhaled, its progeny is relatively short-lived allowing its eventual decay to ^{210}Pb (half-life $= 22.3$ years) before removal by physiological clearance mechanisms. Lung cancer risk related to dangerous exposure to the radiation released from ^{222}Rn and from its short-lived decay products was addressed in the 1950s among uranium miners while indoor-air ^{222}Rn concentration issues were claimed in the 1970s. Since then, scientific attention to ^{222}Rn exposure has increased [20]. Initial evidence had pointed to soil as a major natural source for high indoor concentrations [21] but building materials can also play an important role [22].

Phosphogypsum has been simply piled up nearby phosphate fertilizers industrial units [23], this way requiring considerable open-air space. For inactive phosphogypsum stacks in the US territory, US EPA (Environmental Protection Agency) has once restricted ^{222}Rn exhalation rates to $0.74 \text{ Bq} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ [24]. Even so, large-scale application of phosphogypsum is a motivating dilemma and research has been conducted to overcome difficulties related to

the disposal and handling of this waste. Feasible solutions have suggested its exploitation as soil amendment in agriculture, mine recovery, road base, and embankment filling.

Of particular interest, encouraging (i.e., radioactively safe) evidence has already become available for phosphogypsum use as a non-conventional building material with similar features as ordinary gypsum [25]. Bearing in mind indoor air ^{222}Rn concentration, a major concern refers to the maximum amount of phosphogypsum (pure or blended to building materials) to be present in constructive elements such as pre-fabricated blocks or panels for cost-effective dwellings. Relying on protection procedures as air renewal and/or building openings (doors and windows), limits must be set so as to avoid hazardous radiological impacts, thus enabling occupants to be exposed to tolerable levels³, i.e., without considerably increasing naturally occurring doses.

In line with its agroindustrial expansion, the Brazilian phosphogypsum scenario could not be different so that millions of tons have been similarly piled-up close to fertilizers plants [23]. These fertilizers plants are located in Brazil's southeast (basically in Minas Gerais and São Paulo states), hence close to the biggest Metropolitan Regions of the country. Aiming at cost-effective dwellings, such strategic coincidence might be convenient while motivating for prospective application of phosphogypsum as a surrogate building material.

Engineering precaution should then be exercised in terms of both constructive aspects and of protection against ionizing radiation whose level should be as low as those recognized by federal regulations or international standards. For instance, the International Commission on Radiological Protection (ICRP) has recommended 200 up to 600 $\text{Bq}\cdot\text{m}^{-3}$ for indoor-air ^{222}Rn concentrations at residences and workplaces [26]. In Brazil, the National Commission for Nuclear Energy (CNEN) is the organization responsible for setting upper limits for indoor-air ^{222}Rn concentrations at these two aforesaid human environments.

VEGETABLE FIBER-CEMENT: COMPONENT, COMPOSITE, AND PERFORMANCE

A main drawback of using vegetable fibers is their durability in a cementitious matrix and the compatibility between both phases. Alkaline media weaken most natural fibers, especially the vegetable ones, which are actually strands of individual filaments liable to get separated from one another. The mineralization phenomenon proposed elsewhere [27], [28] can be associated to the long-term loss of the composite tenacity. The severe degradation of exposed composites can also be attributed to the interfacial damages due to continuous volume changes exhibited by the porous vegetable fibers inside the cement matrix [29].

Settled at the Construction and Thermal Comfort Laboratory (Faculty of Animal Science and Food Engineering – FZEA, University of São Paulo – USP, Brazil), the Research Group on Rural Construction has adopted two approaches to improve the durability of vegetable fibers. One is based on fibers protection by coating to avoid the water effect, mainly alkalinity. The other approach aims at reducing the free alkalis within the matrix by

³ Those more acquainted to human comfort may realize that, as opposing to thermal environment, a “radiological comfort zone” concept is not applicable here as the ideal lower level will be always zero rather than a minimum value (below which there would be discomfort). Accordingly, one may think of a “radiological stress zone” whose lower threshold would correspond to a maximum acceptable ^{222}Rn concentration.

developing low alkaline binders based on industrial and/or agricultural by-products [30]. Similar reduced alkalinity effect can be reached by fast carbonation process as presented in [31], [32]. Studies and strategies to improve durability of vegetable fibers have been basically carried out on two types of building components, namely, roofing tiles and flat sheets for wall panels. Methodologies and results obtained for each type of component are presented and discussed in the following sections.

ROOFING TILES

Cement-based roofing tiles containing vegetable fibers or particles for rural constructions have been reported elsewhere [33], [34], [35]. Better results for fiber-cement materials were found using refined pulp and slurry dewatering process, followed by pressing [36]. The improved composites performance may justify the increase in energy consumption during these procedures. Such production is based on vacuum dewatering followed by pressing and it can be worthy for undulated tile fabrication in the near future by using of natural fibers or agricultural residues.

Improving Tiles Performance By Accelerated Carbonation

The present study was carried out as an attempt to produce durable fiber-cement roofing tiles (approximate dimensions: 500 mm long, 275 mm wide, 8 mm thick) by slurry dewatering technique and using sisal (*Agave sisalana*) Kraft pulp as reinforcement. Effects of accelerated carbonation on physical and mechanical performances of vegetable fiber-reinforced cementitious tiles were evaluated along with their consequent behaviors after ageing. Cement raw materials mixture was prepared with approximately 40% of solids (comprising 4.7% sisal pulp, 78.8% cement, and 16.5% ground carbonate material).

Initial cure was carried out in controlled environment (i.e., temperature: $25 \pm 2^\circ\text{C}$, relative humidity - RH: $70 \pm 5\%$) so that roofing tiles remained in moulds protected with plastic bags for two days. Afterwards, roofing tiles were removed from moulds and immersed in water for further 26 days. After total curing period (28 days), tiles were submitted to both physical and mechanical tests. Remaining tiles series were intended to soak and dry-accelerated ageing tests as well as to accelerated carbonation so that roofing tiles were tested in saturated condition after immersion in water for at least 24 h. Accelerated carbonation of roofing tiles was carried out in a climatic chamber providing environment saturated with carbon dioxide (CO_2) and controlled temperature (20°C) and humidity (75% RH). Roofing tiles were submitted to climatic chamber environment during one week until complete carbonation of samples. Carbonation degree was estimated via exposure to 2% phenolphthalein solution diluted in anhydrous ethanol as described in [4].

Figure 1 shows cross-sections of tiles after the application of phenolphthalein solution so that violet regions refer to non-carbonated areas. Tiles that were not fast carbonated underwent carbonation in peripheral regions only (tile 1 in Figure 1), which probably occurred during exposure inside the laboratory environment itself. Cross-section of tile 2

(Figure 1) was not violet colored, indicating that it was fully carbonated after being exposed to accelerated carbonation.

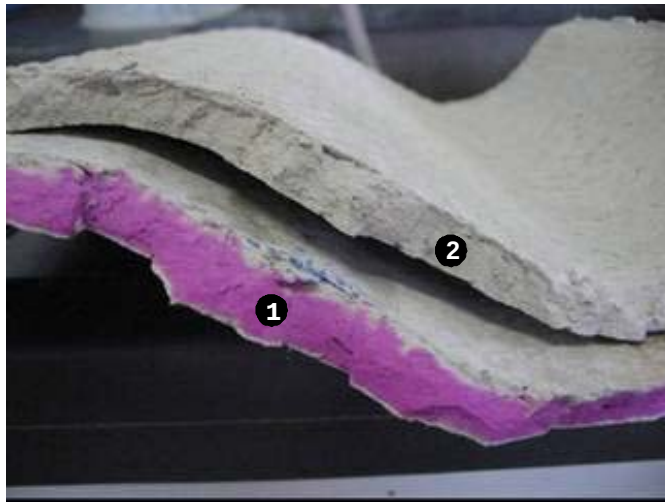


Figure 1. Cross-sections of tiles after the application of phenolphthalein solution: (tile 1) inner non-carbonated areas and (tile 2) areas exposed to fast carbonation.

Results for physical properties of undulated roofing tiles are presented in Table 2. Values for water absorption (WA), apparent void volume (AVV), and bulk density (BD) of roofing tiles for 28 days ageing (condition A) were similar to those found in [35] concerning the evaluation of roofing tiles produced with binder based on ground blast furnace slag (GBFS) reinforced with 3% by mass of sisal pulp and processed by vibration. Results in [35] for WA, AVV, and BD were 31.0%, 42.3%, and 1.35 g/cm^3 , respectively.

Table 2. Average values and standard deviations for water absorption (WA), apparent void volume (AVV), and bulk density (BD) of roofing tiles under different conditions.

Condition	WA (%)	AVV (%)	BD (g/cm^3)
A (28 days)	32.8 ± 1.1	44.2 ± 0.7	1.35 ± 0.03
B (100 cycles)	33.3 ± 0.9	44.0 ± 0.9	1.32 ± 0.01
C (fast carbonation and 100 cycles)	23.3 ± 0.7	35.8 ± 1.8	1.56 ± 0.01

In general, ageing cycles contributed to mitigate leaching and to reduce porosity of roofing tiles. Accelerated carbonation followed by 100 cycles (condition C) was the treatment that most affected physical properties of roofing tiles. Porosity reduction provided by carbonation can be responsible for mechanical properties improvement while accelerated carbonation reduced tiles apparent void volume (AVV) by approximately 20%. Significant water absorption reduction and carbonated roofing tiles densification suggested the effective carbon dioxide absorption as well as the formation of new hydration products in the cement matrix. An estimated 15% reduction of cellulose fiber-cement porosity after its accelerated carbonation was also reported elsewhere [37].

Figure 2 presents typical load-deflection curves of roofing tiles. The maximum load (ML) supported by roofing tiles did not experience a significant reduction after ageing cycles. These results are considerably above the 425 N limit as recommended in [38] for 8 mm thick tiles. Ageing (condition B) did not cause significant decrease in ML and toughness (TE) of roofing tiles in relation to non-aged tiles tested with 28 days (condition A). Moreover, ML and TE were superior to those found in preceding works with roofing tiles produced by vibration (Figure 2). ML and TE values around 550 N and 1.6 kN□mm, respectively, for roofing tiles reinforced with 2% (volume basis) of unrefined coir, sisal macro-fibers and eucalyptus waste pulp at 28 days of age were reported in [8].

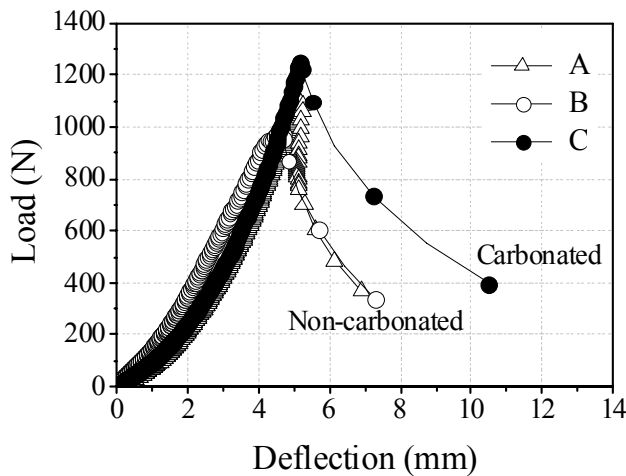


Figure 2. Load-deflection curves for tiles at different treatment conditions.

Pulp refinement and dispersion in the composite seem to contribute to homogeneous fibers distribution during roofing tiles molding, leading to better fibers anchorage in the matrix and thus improving the product strength. Among other variables, fibers net was more efficient at retaining cement particles during vacuum dewatering process, hence providing suitable packing during the pressing stage as well as more effective fiber-matrix bond. Figure 3 presents an image of the carbonated tile with refined sisal Kraft fiber, obtained via scanning electron microscope (SEM) and back-scattered electron (BSE) detector. The SEM-BSE image shows the advantage of refined fiber in generating a high contact area with the matrix.

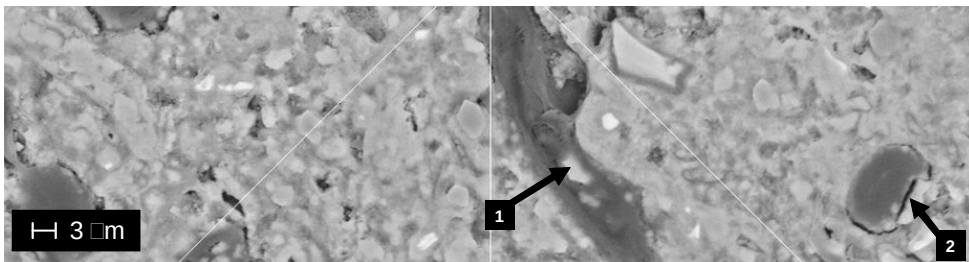


Figure 3. SEM-BSE image of fast carbonated and aged tile (condition C in Table 2).). Fibers are well adhered to matrix, suggesting good composite packaging. Arrows point to precipitated calcium hydroxide (1) inside fiber lumen and (2) around fiber surface.

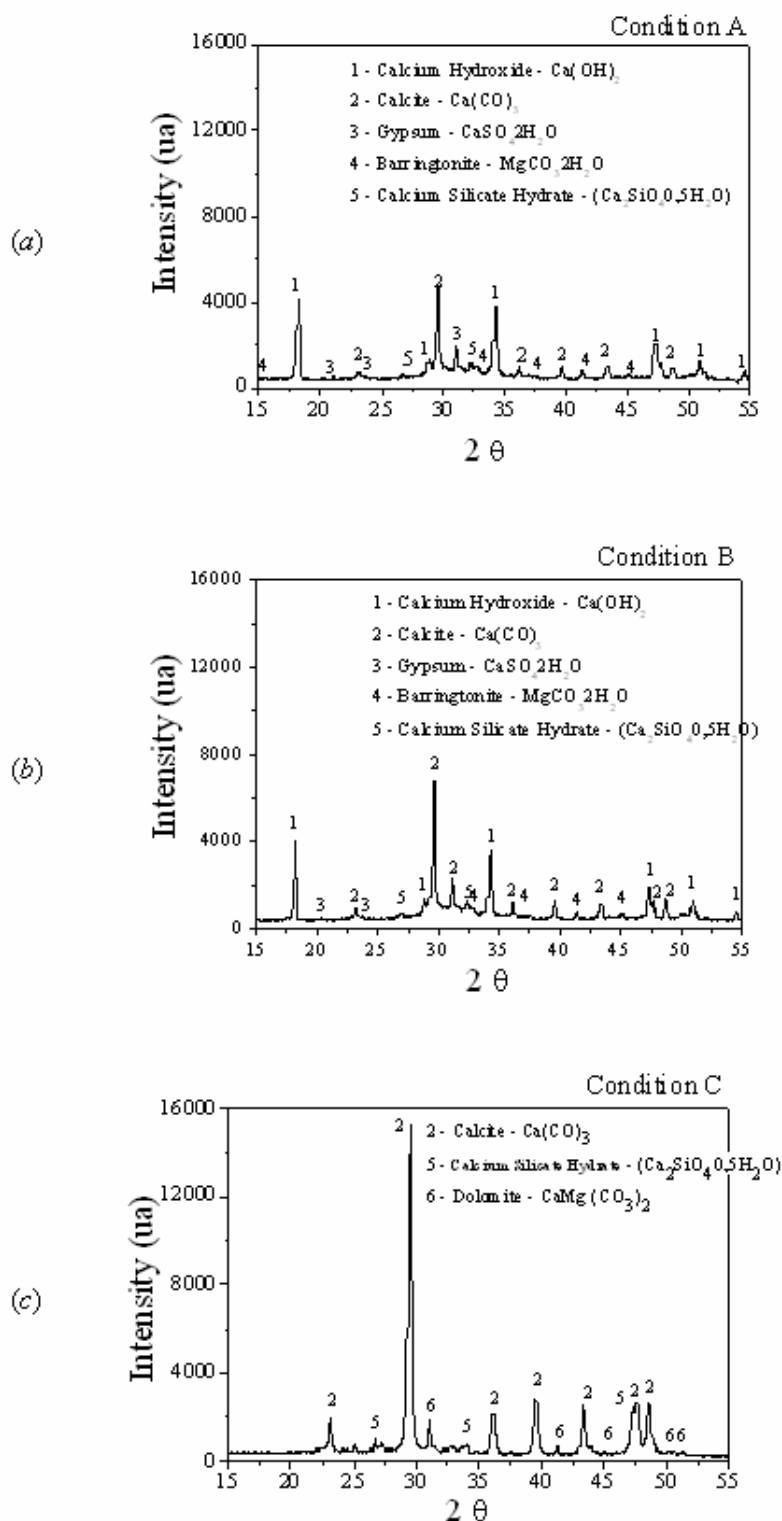


Figure 4. X-ray diffraction pattern of tiles: (a) non-aged (condition A), (b) after 100 ageing cycles (condition B), and (c) fast carbonated after 100 ageing cycles (condition C).

The cementitious phases of samples at each condition were analyzed by X-ray diffraction so that patterns in Figure 4(a) and (b) show the presence of calcium hydroxide, Ca(OH)_2 , in samples not submitted to accelerated carbonation (conditions A and B). Conversely, Ca(OH)_2 was not identified in fast carbonated samples (condition C). The formation of greater amount of calcium carbonate instead of other carbonates can be associated to high percentage of calcium (about 60%) in the ordinary Portland cement used herein [39]. Such result suggests a successful CO_2 adsorption in the cement based matrix while high carbonation can be associated to the consumption of hydroxyls (OH) present within the cement matrix due to CO_2 adsorption after its diffusion into composite pores. High apparent porosity (AVV) of roofing tiles (around 44% at 28 days) contributed to such fast diffusion [40].

Series of accelerated carbonated roofing tiles after 100 ageing cycles (condition C) showed better mechanical performance in comparison to other series, including notably higher toughness ($5.9 \pm 1.9 \text{ kN}\cdot\text{mm}$) and deflection at toughness ($\text{DTE} = 9.1 \pm 2.5 \text{ mm}$) in relation to non-aged (condition A) and fast-aged (condition B) series. The strength increase of aged material achieved in [41] was attributed to calcium hydroxide elimination due to carbonation treatment (109 days in a CO_2 incubator), mechanical performance improvement of flat sheets reinforced with 12% (mass basis) of Eucalyptus pulp after accelerated carbonation and ageing cycles was reported in [37].

In addition to chemical analysis, calcium carbonate (CaCO_3) microstructure in tile fracture surfaces was visualized via SEM - secondary electron (SE) images. In Figure 5 regarding fast carbonated tiles, one may observe CaCO_3 formation in crystals as well as packed in layers. As reported in [42], morphology of CaCO_3 crystalline state plays an important role in determining binder strength so that the improved strength was then attributed to the layered morphology of CaCO_3 .

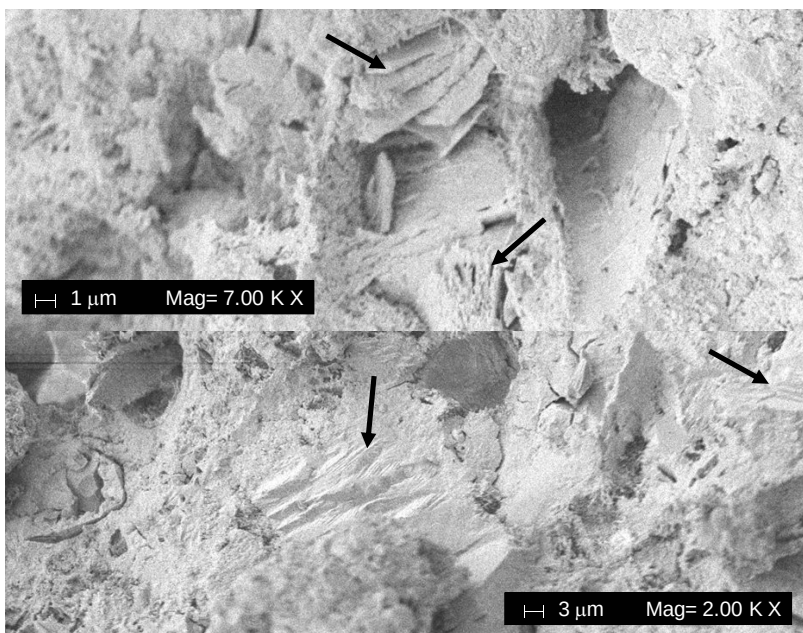


Figure 5. SEM of fracture surfaces of fast carbonated and aged tiles (condition C). Arrows indicate layered CaCO_3 .

Last but not least, Figure 6 shows roofing tiles exposed to natural ageing. Such undulated shape is typically employed in Brazil.

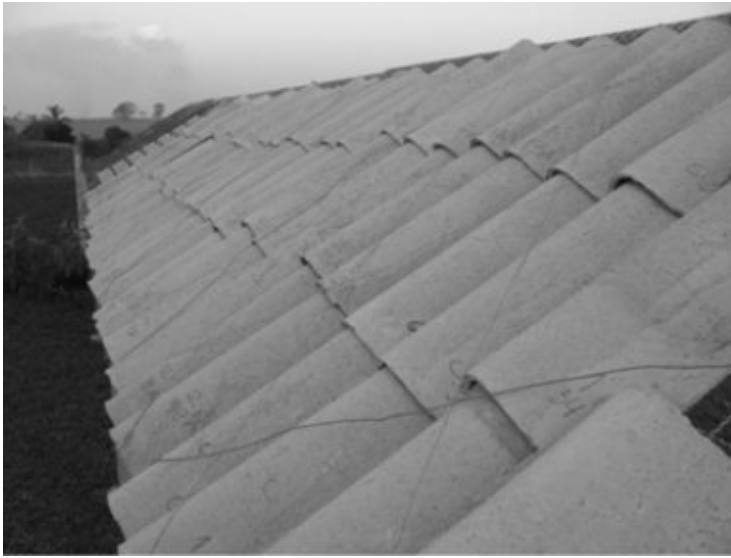


Figure 6. Roofing tiles exposed to natural ageing in Brazil.

Thermal Properties of Undulated Tiles

Table 3 lists values for thermal conductivity k , specific heat c , and thermal diffusivity $\alpha = k/(\rho \cdot c)$ of composites, obtained by parallel hot wire method as described in [43]. Aforesaid thermal properties were determined at room temperature (i.e., 25°C) as well as at 60°C.

Table 3. Values for thermal conductivity k , specific heat c , and thermal diffusivity $\alpha = k/(\rho \cdot c)$ of composites, obtained by parallel hot wire method.

Mix design	Test temperature (°C)	k [W/(m·K)]	c [J/(kg·K)]	α (10^{-7} m ² /s)
Sisal fiber-cement (S4_7)	25	0.716	1278.7	3.060
	60	1.214	1071.5	6.191
Sisal + PP fiber-cement (S3PP1_7)	25	0.816	1201.1	3.951
	60	0.823	1294.4	3.694
Asbestos cement	25	0.837	1167.6	4.048
	60	0.967	1315.8	4.150

One notes that composites have different thermal behavior at room temperature ($\sim 25^\circ\text{C}$) and at 60°C. At the former, S4_7 formulation exhibited more favorable thermal properties for

thermal comfort, namely, lower thermal conductivity k and higher specific heat c , thus leading to lower thermal diffusivity α . At 60°C, formulation with PP fibers (S3PP1_7) presented more adequate values for thermal comfort. At both test temperatures, the mix-design with asbestos presented less appropriate values in comparison to the formulations without asbestos.

Raising test temperature to 60°C increased thermal conductivity and thermal diffusivity of composites with sisal (S4_7) up to 45% and 100%, respectively, compared to the other mix-design. One may point to the presence of moisture within prismatic specimens used to influence measurements, which may increase thermal conductivity for higher temperatures [44]. The fact that non-asbestos mix-design (S4_7) shows larger cellulose fiber content (thus presenting greater water absorption) may explain such thermal conductivity increase. Thermal behavior was also evaluated with respect to downside surface temperatures of non-asbestos roofing tiles produced (sisal fiber-cement – S4_7) compared with ceramic and asbestos-cement corrugated roofing sheets currently available in Brazilian market. Thermal behavior of roofing elements might also be influenced by product dimensions, shape, and color; however, a comprehensive discussion on those aspects is beyond the scope of the present chapter.

Thermal performance analysis of the roofing tiles considered the prospective influence of both cross-sectional area A and thickness Δx of the tile, its thermal conductivity k , and the temperature difference $\Delta T = T_{\text{air}} - T_{\text{down}}$, where T_{air} is the prevailing temperature of outside air while T_{down} is the downside surface temperature of the tile. Absolute values $dQ/dt = |\dot{Q}|$ for the heat transfer rate across the tile were calculated according to a one-dimensional approach of Fourier's law [45]:

$$\dot{Q} = -Ak \frac{dT}{dx} \Rightarrow \frac{dQ}{dt} = \left| Ak \frac{\Delta T}{\Delta x} \right| \quad (1)$$

At the hottest hours of the day, ceramics roofing tiles presented temperatures T_{down} up to 10°C lower than those of asbestos-cement sheets and 6°C lower in relation to those of sisal fiber-cement tiles. Among fiber-cement roofing tiles, non-asbestos tiles presented downside surface temperatures 3°C lower. Heat transfer resistance is directly related to the material microstructure (which can be assessed by its thermal diffusivity) and to its dimensions (mainly thickness) so that observed differences might be explained. Ceramic, non-asbestos, and asbestos roofing elements presented thicknesses around 12 mm, 8 mm, and 4 mm respectively. Heat transfer rates dQ/dt were calculated employing thermal conductivity data at 25°C as presented in Table 3 for fiber-cement tiles while literature values were assigned to ceramic tiles, namely, 1.05 W/(m·K) [46].

Solar radiation flux and heat transfer rate along different hours of the day are shown in Figure 7 for the hottest day over the evaluated period in summer. As one may see, heat transfer rates through asbestos-cement sheets were higher than rates related to ceramic and non-asbestos tiles. As a consequence, such higher rates lead to a hotter indoor environment. Related to the thermal diffusivity, thermal inertia is an important attribute for roofing tiles as it tends to reduce the amplitude of the thermal variation inside the building. For thermal inertia analysis, one may divide results into two periods, namely, morning and afternoon. In Figure 7, one observes that the highest radiation flux peak (about 1100 W/m²) occurred at

10:00 am and at 11:30 am, whose effect was observed 1 h later with the increase of heat transfer rates through tiles. Ceramic tiles presented maximum heat transfer rate 15 min later than non-asbestos tiles and 30 min later than asbestos cement tiles, which can be attributed to the thermal inertia of the tiles. Furthermore, bearing in mind a barrier for thermal radiation, results suggested a better performance of ceramic and non-asbestos fiber-cement tiles.

In view of their lower heat transfer rates, sisal fiber-cement tiles rendered good capacity of lowering outdoor temperature peaks (more efficiently than asbestos fiber-cement ones). One may then claim resultant advantages concerning the reduction of thermal radiation penetration, which is a result in accordance to previous studies. Differences were found for sisal-reinforced fiber-cement roofing tiles (produced by vibration) around 11.5°C lower (at 12:00 pm) compared with asbestos-cement corrugated tiles [35] while significant differences were also observed for animal thermal comfort as the micro-environment of non-asbestos fiber-cement roofing tiles presented superior performance in relation to asbestos fiber-cement counterparts [47]. Employing fiber-cement roofing components based on blast furnace slag and vegetable pulps (*Eucalyptus*), differences of 7°C between internal and external surface temperatures were presented in [48].

Ceramic tiles showed slightly lower heat transfer rates compared to sisal fiber-cement ones, indicating a possible influence of tiles surface reflectance [49]. Although darker coloration of red ceramics tile suggests greater absorption (66%) in the visible spectrum, infrared reflectance is high enough (78%) to provide a total reflectance of about 67%. The opposite was observed for light gray non-asbestos fiber-cement tiles, with a total reflectance of approximately 40% [49].

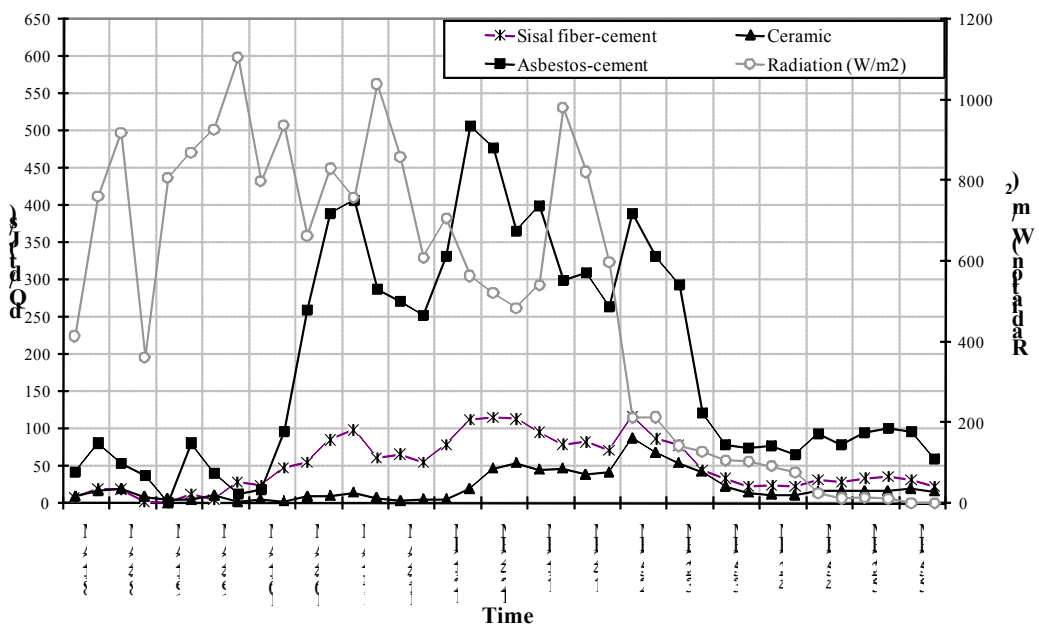


Figure 7. Variation of solar radiation and heat transfer rate through distinct roofing elements as a function of time. Data collected on December 22, 2005.

STRATEGIES FOR IMPROVING THE PERFORMANCE OF THE COMPOSITES

Flat composites were fabricated in order to evaluate the performance of the fiber-reinforced cement-based composites under various ageing conditions. Production method followed the slurry vacuum de-watering process aiming at the viable utilization of such materials in civil construction. Matrix materials were added to an appropriate amount of moist fibers pre-dispersed in water so as to form slurries within a 20-30% range (solid mass basis). After homogeneously stirred, slurry was immediately transferred to an evacuable box. Water was drawn off under vacuum until the pad appeared dry on the surface, whereupon it was flattened carefully with a tamper. Pads were then pressed at 3.2 MPa for 5 min and sealed inside a plastic bag for cure under saturated-air condition or water immersion for future mechanical tests at a total age of 28 days.

In some cases, further samples were prepared to evaluate their performance after natural or accelerated ageing experiments. Tests were carried out so as to evaluate prospective effects due to (i) matrix modification by less alkali blends, (ii) different fiber contents, (iii) decrease of fiber mineralization by chemical modification, (iv) improvement of fiber-to-cement bonding, and (v) decrease of the distance between fibers. Related results are presented and discussed in the sequence.

Effects due to Matrix Modification by Less Alkali Blends

In order to improve the durability of the composites, diminution of the matrix alkalinity was attempted. The main component to produce the paste matrix was the alkaline granulated iron blast-furnace slag (BFS) ground to $500 \text{ m}^2 \cdot \text{kg}^{-1}$ Blaine fineness, presenting the following oxide composition (mass-basis) as provided in [50]: SiO_2 - 33.78%, Al_2O_3 - 13.11%, Fe_2O_3 - 0.51%, CaO - 42.47%, MgO - 7.46%, SO_3 - 0.15%, Na_2O - 0.16%, K_2O - 0.32%, free CaO - 0.10%, and CO_2 - 1.18%. In Brazil, more than 6 million tons of basic ground-BFS (GBFS) are available every year, generated by the steel industry [51]. GBFS costs can be as low as USD 10.00 per ton.

For the cement production, slag must be ground to fineness at least similar to that of the ordinary Portland cement, which adds a further cost of approximately USD 15.00 per ton, and it must be activated by alkaline compounds. Gypsum for agricultural purposes and lime (calcium hydroxide) for civil construction were elected as chemical alkali-activators for BFS respectively in proportions of 10% and 2% (binder mass basis), as discussed in [52]. Standard commercial ordinary Portland cement (OPC), Adelaide Brighton brand type "general purpose" (GP), minimum compressive strength of 40 MPa at 28 days (Australian Standards AS 3972 and AS 2350.11) was adopted as the reference matrix to compare with BFS cement.

As detailed in [14], waste strand fibers generated during crop stages of both sisal (*Agave sisalana*) and banana (*Musa cavendishii* - *nanicao* cultivar) were initially cut to around 30 mm in length. Via filtration from drainage lines prior to effluent biological treatment, waste *Eucalyptus grandis* pulp from Kraft and bleaching stages was also collected (at about 0.5% by mass) from a commercial production of a cellulose mill.

Aiming at cheaper price and economical viability at small-scale production (if compared with chemical pulps), strand fibers underwent low-temperature chemithermomechanical pulping (CTMP) in line with [53], [54]. Additionally mechanical beating provided important internal and external fibrillation of filaments, leading to conformable fibers and thus to fiber-matrix bonding improvement. Initial preparation comprised soaking in cold water overnight, followed by simple and low-pollutant chemical pre-treatment based on 1-hour cooking in boiling saturated lime liquor. Such step effectively attacked residual slivers, which could be easily broken by fingers, thus showing adequate preparation for subsequent mechanical treatments. Appropriate chemical attack is of utmost importance for reducing energy consumption, which represents one of the major concerns related to mechanical pulps [6]. Some pulp and fiber properties are summarized in Table 4.

Table 4. Some pulp and fiber properties of interest.

Fiber	By-produced sisal CTMP ^(f)	Banana CTMP ^(f)	<i>E. grandis</i> Kraft waste
Screened yield (%)	43.38	35.57	N/A
Kappa number ^(a)	50.5	86.5	6.1
Freeness (mL) ^(b)	500	465	685
Length-weighted average length (mm) ^(c)	1.53	2.09	0.66
Fines (%) ^(d)	2.14	1.55	7.01
Fiber width (μm) ^(e)	9.4	11.8	10.9
Aspect ratio	163	177	61

^(a) Appita P201 m-86 [55]; ^(b) AS 1301.206s-88; ^(c) Kajaani FS-200; ^(d) Arithmetic basis; ^(e) Average from 20 determinations by SEM; ^(f) Chemithermomechanical pulping (CTMP); N/A: not available.

Asplund laboratory defibrator provided 103 kPa steam gauge pressure corresponding to 121°C in presence of the pre-treatment solution with pre-steaming by 120 s and defibration by additional 90 s. At those conditions [6], well fibrillated softwood fibers could be obtained from low temperature (i.e., 125-135°C) CTMP instead of yield smooth, lignin encased and un-fibrillated fibers from high temperature (i.e., 150-175°C) pulping. The pulp in preparation passed through a Bauer 20 cm laboratory disc refiner equipped firstly with straight open periphery plates (1 pass at 254 μm clearance) and subsequently with straight closed periphery plates (1 pass at 127 μm and 1 pass at 76 μm). Partial de-watering before each refinement step provided pulp with adequate consistency for the improvement of the defibration process.

Sisal and banana pulps passed through a 0.229 mm slotted Packer screen for separation of shaves and then through a supplementary Somerville 0.180 mm mesh screening and subsequent washing to reduce particles with length below 0.2 mm. Fibers shortening and fines generation are expected although undesirable results from beating procedures can be controlled via appropriate energy applied to the stock during the mechanical treatment [53]. Finally, the produced pulps were vacuum de-watered, pressed, crumbed, and stored in sealed plastic bags under refrigeration. *Eucalyptus grandis* waste pulp was employed just as received

after a 2 min disintegration and washing in hot (nearly boiling) water using a closed-circuit pump system.

Figure 8 shows results from mechanical and physical tests on composites reinforced with 8% of produced sisal and banana pulps as well as with waste *Eucalyptus grandis* pulp from Kraft and bleaching stages. Flexural strength around 18 MPa for 8% residual fiber-BFS composites is considered an acceptable achievement when using mechanically pulped fibrous raw materials in comparison with similar results [54] for sisal Kraft pulp as reinforcement of air-cured BFS based matrices in 17 MPa and $1.4 \text{ kJ}\cdot\text{m}^{-2}$ ranges for flexural strength and toughness, respectively. Current results may also be considered a significant advance over a previous work [56] using disintegrated paper reinforced OPC with flexural strength up to 7 MPa at least 30% less than the corresponding control matrix under dough mixing method for fabrication.

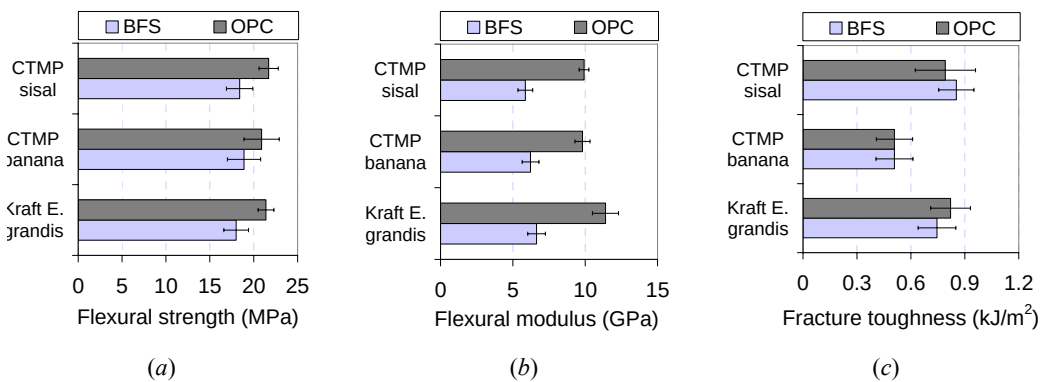


Figure 8. Average values and standard deviations for mechanical properties of composites as a function of the type of pulp fibers and matrix.

OPC-based composites performed superior mechanical strength around 21 MPa at 28 days of age associated to lower water absorption in comparison to BFS composites with all tested fibers in 8% content. BFS matrix seemed to lack hydration improvement, which could be achieved by high-temperature cure up to 60°C [57] or by adopting another alkaline activator (e.g., sodium silicate) as proposed in [58].

The high standard deviation associated with the flexural strength could be justified by the heterogeneity of the reinforcement fibers based on the following facts:

- Fibrous wastes generally present high moisture content and are thus expected to undergo fast biological decay [59], [60], leading to weak fibers in the pulp;
- Mechanical refinement often originates bunches of individual fibers mutually linked by non-cellulose compounds (e.g., lignin), as indicated in Table 4 by high Kappa numbers for sisal and banana CTMP. Strand fibers thus tend to perform poor distribution in the cement matrix.

BFS composites reinforced with banana fiber showed lower values for fracture toughness compared to both sisal and *Eucalyptus grandis* composites. It is a result of high length and aspect ratio of banana fiber, which leads to a stronger anchorage in the matrix and to the predominance of fiber fracture during mechanical test before any further fiber displacement

could occur, as depicted in Figure 9(b). Figures 9(d) and 9(e) show images of by-product sisal CTMP in OPC with the desirable coexistence between fractured and pulled out filaments, pointing to the proximity of critical length [61] of that fiber in the specified matrix under ambient moisture condition. Twisted and bent fibers reinforce the idea of optimum interaction between both phases as well as of high energy dissipation during fiber pullout. Such favorable microscopic behavior explains the suitable compromise between flexural strength (21.7 MPa) and toughness ($0.792 \text{ kJ}\cdot\text{m}^{-2}$) for 8% sisal CTMP in OPC (Figure 8).

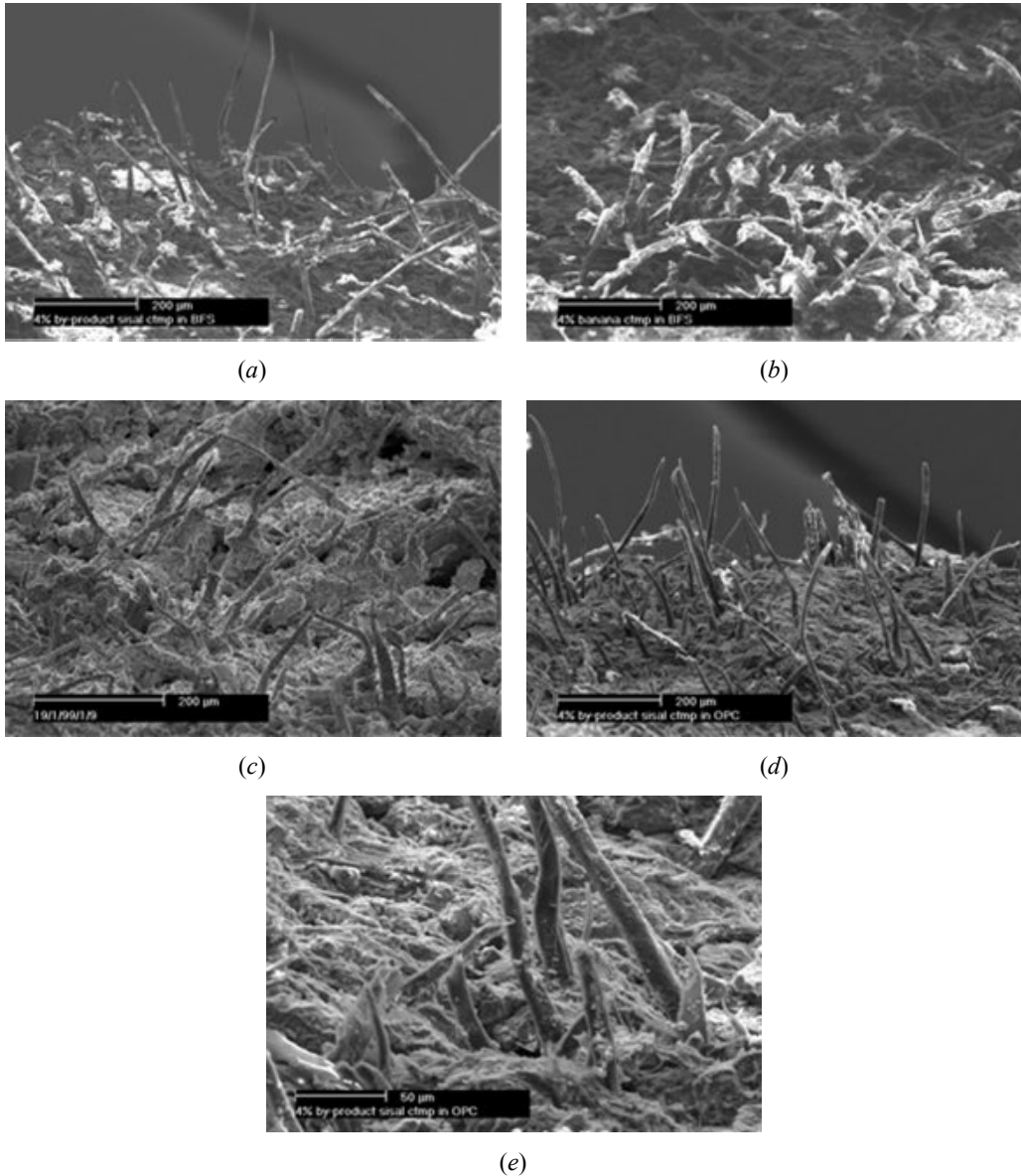


Figure 9. Sequence of scanning electron microscope (SEM) images (hydration age between brackets): (a) 4% sisal CTMP in BFS matrix (73 days); (b) 4% banana CTMP in BFS matrix (32 days); (c) 4% *Eucalyptus grandis* waste Kraft in BFS matrix (51 days); (d) 4% sisal CTMP in OPC matrix (67 days); (e) 4% sisal CTMP in OPC matrix - higher magnification (67 days).

Freeness values within 465- 685 mL range (Table 4) provide adequate water drainage and prevent cement particles loss during suction stage of industrial systems based on Hatschek model for panels fabrication as pointed in [62], [63]. Low Kappa number value (Table 4) for *Eucalyptus grandis* Kraft pulp is an indication of bleached fiber with low lignin content. On the other hand, high values for mechanical pulps suggest damaged and fibrillated filaments or even remaining slivers expected to present exposed lignin to undesirable alkaline attack inside cement matrices.

As also concluded in similar research [64], [54], density, water absorption, and porosity are interrelated properties. Low densities are preferable to reduce transportation costs and carriage effort while they are normally connected to higher water absorption values with the inconvenient increase of the self-bearing load during utilization and to risk of excessive permeability. As a reference, Brazilian standards (NBR 12800 and NBR 12825) limit water absorption to 37% (mass basis) for fiber-cement corrugated roofing sheets.

Elevated presence of fines in waste *Eucalyptus grandis* Kraft (Table 4) could contribute to packing effect inside cement matrices, thus leading to denser materials with lower water absorption and apparent porosity, if compared to other OPC and BFS composites for the same fiber content (Figure 10). Such observation is consistent with results from wastepaper fiber-cement composites research reported in [65].

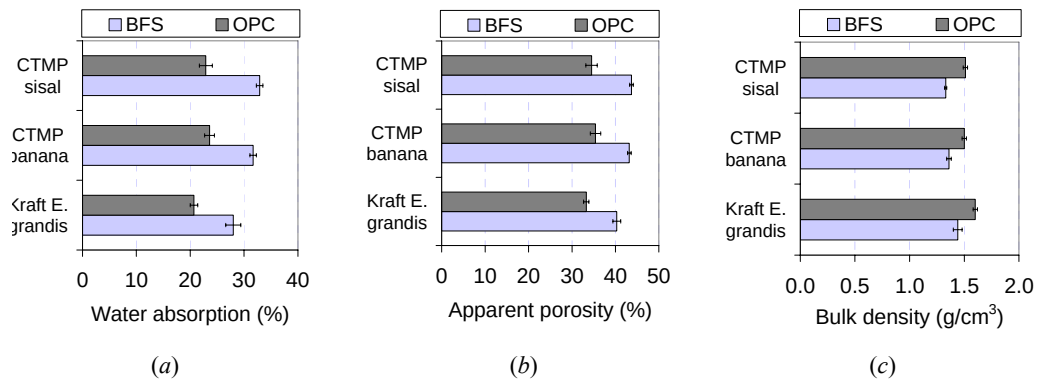


Figure 10. Average values and standard deviations of the physical properties of the composites in function of the type of pulp fibers and matrix.

Effects due to Different Fiber Contents

Figure 11 and Figure 12 present the effect of the fiber content respectively on mechanical and physical performance of composites. The formulations follow those for BSF composites as presented in the previous section, except for variable fiber content. All BFS composites showed a considerable increase (at least 20%) in flexural strength within the 8-12% fiber content interval if compared to the corresponding 4% fiber content composites (Figure 11).

The short length of *Eucalyptus grandis* (Table 4) allowed the inclusion of up to 16% of fiber by binder mass although losing flexural strength, which could be associated to the high volume of permeable voids. As *Eucalyptus grandis* fiber content increased from 4% to 16%, the elastic modulus in bending of BFS composites decreased from 9 GPa to 4 GPa, a behavior that was equally observed for the other similar fiber-cements. Materials with 8% fiber OPC

showed significantly higher modulus than corresponding BFS ones, likely due to insufficient hydration attributed to the BFS binder as previously commented.

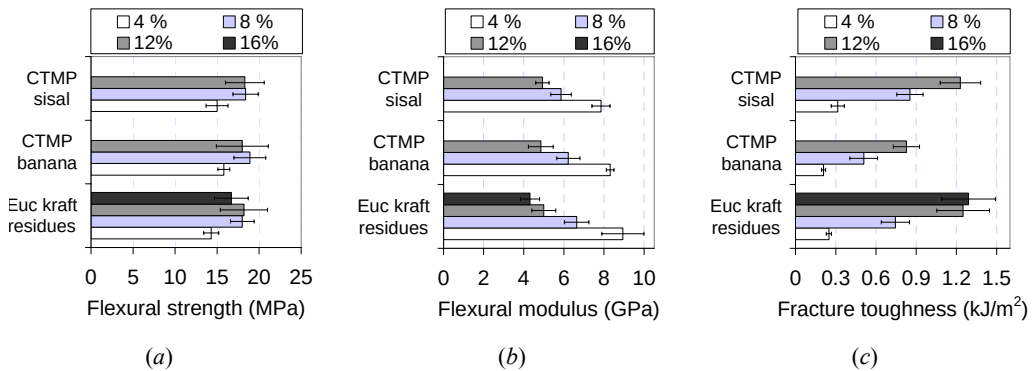


Figure 11. Variation of mechanical properties as a function of fiber content (%, mass basis) for composites with different pulp fibers.

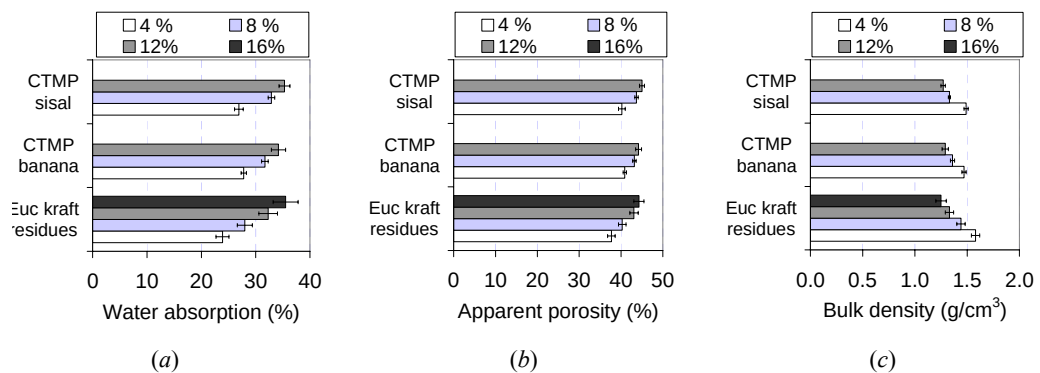


Figure 12. Variation of physical properties as a function of fiber content (%, mass basis) for composites with different pulp fibers.

The fracture toughness was greatly enhanced up to 5-fold by fiber reinforcement from 4 to 12% load interval. As observed in Figure 11(c) for *Eucalyptus grandis* BFS composites, best energy absorption seems to fall between 12 and 16% of fiber content with toughness in the vicinity of $1.3 \text{ kJ} \cdot \text{m}^{-2}$. Predominance of fiber pullout for sisal and *Eucalyptus grandis* composites (see Figures 9(a) and 9(c)) is related to the high frictional energy absorption. In the specific case of *Eucalyptus grandis* fibers, the short length is compensated by larger number of filaments for a fixed fiber content and, hence, by higher probability of matrix micro-crack interception in its initial stage of propagation. Increase of fiber content leads to poor packing during composites preparation, especially at the pressing stage. Cellulose fibers are highly conformable and play a spring effect inside the cement matrix immediately after the press release. Owing to compaction reduction in combination with fibers of low bulk density ($\sim 1,500 \text{ kg} \cdot \text{m}^{-3}$) and high water absorption, permeable voids volume and water absorption increase linearly with fiber content.

Effects due to Decrease of Fiber Mineralization by Chemical Modification

Eucalyptus Kraft pulp fibers were submitted to chemical treatment in order to reduce their hydrophilic character. The procedure for surface treatment of Eucalyptus pulp fibers and the option for silanes were based in studies as developed in [66]. The silanes employed were methacryloxypropyltri-methoxysilane (MPTS) and aminopropyltri-ethoxysilane (APTS), in a proportion of 6% by mass of cellulose pulp. Silanes were pre-hydrolyzed during 2 h under stirring in 80/20 volume basis ethanol-distilled water solution. Cellulose pulp was introduced (5% by mass basis) followed by further 2 h of stirring. Composites were prepared by the same procedure as described in the previous section, using 5% by mass of (untreated or treated) pulp in a matrix composed by 85% of OPC and 15% of carbonate filler.

Effect of treating pulp fibers on their mineralization was analyzed using scanning electron microscope (SEM) and back-scattered electron (BSE) detector to view cut and polished surfaces. BSE images allow easy identification of composite phases via atomic number contrast. Figure 13 presents SEM micrographs of composites whose pulp fibers are either impregnated with or free from silane coupling agents, where black areas are cross-sections of pulp fibers. In composites with untreated and APTS treated pulp fibers, Figures 13(a) and 13(b) respectively, one observes that the majority of lumens were filled up with reprecipitated products from cement hydration, while in composites with MPTS treated pulp fibers, Figure 13(c), fiber lumens are free from hydration products.

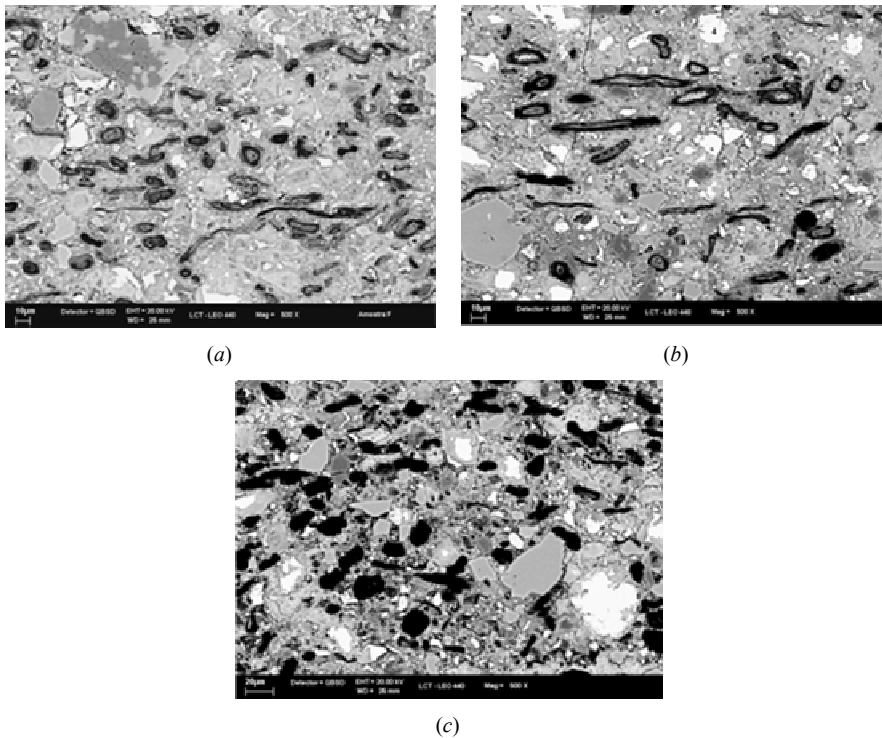


Figure 13. SEM-BSE images of composites reinforced with Eucalyptus bleached pulps: (a) untreated, (b) APTS treated, and (c) MPTS treated (after 200 ageing cycles).

Table 5 shows the effect of pulp treatment on the mechanical performance of composites. At 28-days cure, composites with APTS silaned pulp presented significantly higher modulus of rupture (MOR) than composites with untreated pulp or MPTS silaned pulp whereas toughness of the composites was not influenced by silane treatment. Similar results for composites reinforced with silane-treated fibers were found in [67], [68].

Table 5. Average values and standard deviations for properties of composites: limit of proportionality (LOP), modulus of rupture (MOR), modulus of elasticity (MOE) and toughness (TE).

Fiber treatment	Condition	LOP (MPa)	MOR (MPa)	MOE (GPa)	TE (kJ/m ²)
Untreated	28 days	6.9 ± 1.1	9.9 ± 1.4	13.3 ± 1.2	0.86 ± 0.25
MPTS		6.5 ± 1.0	10.7 ± 1.3	16.3 ± 1.7	0.83 ± 0.46
APTS		7.8 ± 1.3	12.1 ± 1.4	16.3 ± 2.5	0.82 ± 0.29
Untreated	200 cycles	6.3 ± 0.9	7.5 ± 0.5	17.7 ± 1.1	0.13 ± 0.07
MPTS		7.2 ± 0.9	8.0 ± 1.0	18.6 ± 4.6	0.30 ± 0.12
APTS		6.9 ± 1.7	8.3 ± 1.0	18.4 ± 3.8	0.13 ± 0.07

Average MOR values notably decreased after 200 ageing cycles for composites with either treated or untreated fibers compared to those after 28 days cure. MOR differences after ageing were not observed between composites with treated or untreated fibers. As suggested in Table 5, the fact that MPTS-treated pulp did not present fibers filled up with products from cement hydration seems to influence the higher toughness of the corresponding composites after 200 ageing cycles. Yet, for untreated and APTS-treated pulps, composite capacity to absorb energy was markedly decreased most likely due to reprecipitation of hydration products into fibers permeable voids with consequent composite embrittlement.

Table 6. Average values and standard deviations for properties of composites: water absorption (WA), apparent void volume (AVV), and bulk density (BD).

Fiber treatment	Condition	WA (%)	AVV (%)	BD (g/cm ³)
Untreated	28 days	16.4 ± 0.9	29.0 ± 1.0	1.77 ± 0.04
MPTS		17.7 ± 1.3	30.8 ± 1.5	1.75 ± 0.04
APTS		16.7 ± 0.8	29.9 ± 1.0	1.79 ± 0.03
Untreated	200 cycles	15.2 ± 1.2	26.5 ± 1.9	1.75 ± 0.03
MPTS		16.2 ± 1.7	27.9 ± 2.4	1.72 ± 0.08
APTS		13.5 ± 0.5	24.6 ± 0.7	1.83 ± 0.03

The effect of silane treatment on composites physical properties is presented in Table 6. Significant differences were not observed between composites with treated or untreated pulp

at 28 days. However, after 200 ageing cycles, composites with APTS-treated pulp presented lower water absorption and apparent porosity in relation to composites with untreated pulp and MPTS-treated pulp. Bulk density of composites with APTS-treated pulp was significantly higher after 200 ageing cycles. This behavior suggests that chemical treatment increased the interaction with cement, which influenced physical properties of the composite. Lower porosity of composites reinforced with silanated carbon fibers was reported in [69]. In such study, authors attributed this behavior to the hydrophilic character of the silane used, which improved fiber-matrix bond. The fact that fibers are filled up with cement hydration products also explains the porosity decrease of composites.

The chemical composition of virgin pulp fibers seems to exert significant influence on composites durability as well. Lignin is an amorphous chemical species with high solubility in alkaline medium and its removal is essential part of pulping process [4]. Further lignin extraction from pulps is normally referred to as bleaching treatment. Figure 14 presents the influence of bleaching Eucalyptus pulp fibers in order to improve adhesion between fibers and matrix. Bleaching process makes fiber more susceptible to mineralization as it extracts compounds from fiber cell wall structure.

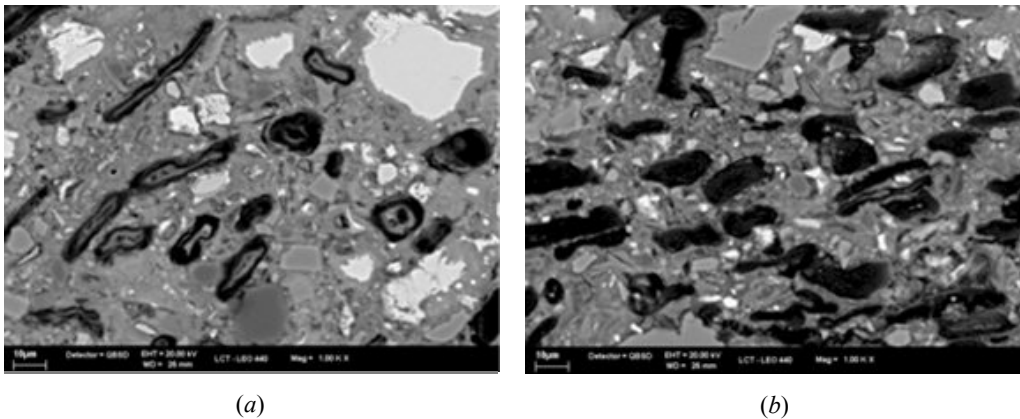


Figure 14. SEM-BSE images of composites reinforced with Eucalyptus: (a) bleached and (b) unbleached (28 days).

Effects due to Improvement of Fiber-to-Cement Bonding

One possible treatment to enhance mechanical performance of composites reinforced with cellulose pulp is the refining process, which is carried out in the presence of water, usually by passing the suspension of pulp fibers through a disc refiner composed by a relatively narrow gap between rotor and stator [70], [71]. Cellulose fibers are intrinsically strong and refinement improves their ability to be processed, which is necessary if the composite is manufactured using Hatschek production method [72]. The main effect of refinement in cellulose fiber structure as a result of mechanical treatment is the fibrillation of fibers surface [73]. These fibrillated and short fibers are responsible for the formation of a net inside the composite mixture with the consequent retention of cement matrix particles during de-watering stage of manufacturing process. Better fiber-matrix interface adhesion and

mechanical performance can be achieved by increasing the specific surface area of the fiber, by reducing the fiber diameter and producing a rough surface proportioning better mechanical anchorage in the matrix [72].

Figure 15(a) presents the poor adhesion of unrefined sisal pulp fibers and depicts void sizes up to $3\text{ }\mu\text{m}$ at the interface between fiber and matrix. In composites with refined pulp fibers, external layers were partially pulled out from cell wall after refining and these external layers then improve fibers anchorage into the cementitious matrix. In Figure 15(b), one may see external layers of refined fibers largely bonded to the cementitious matrix. The refined fiber-cement paste bond seems to be stronger than the unrefined fiber-cement paste bond, as asserted in [74]. The large superficial contact performed by refined cellulose pulp has enhanced the mechanical performance and has improved the load transfer from matrix to fibers [75].

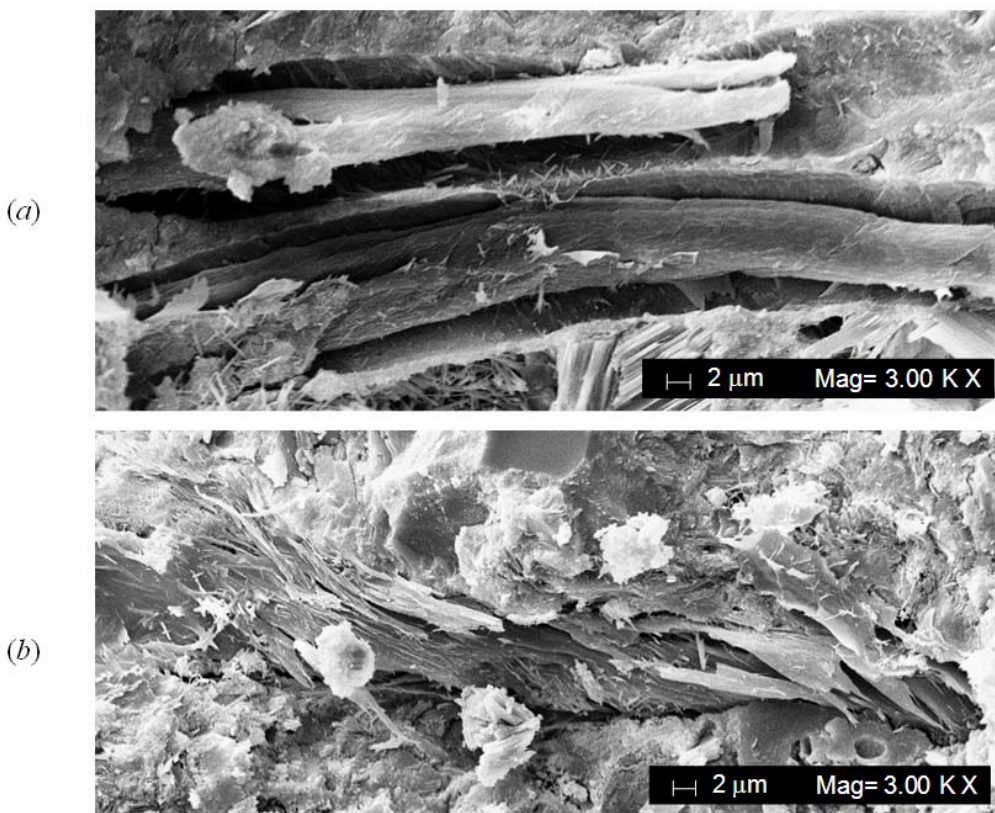


Figure 15. SEM micrographs of fractured surfaces of sisal fiber-cement composites with (a) unrefined pulp (CSF 680 mL) - voids at the fiber-matrix interface after 100 soak / dry ageing cycles; (b) pulp refined at CSF 20 mL and after 100 soak / dry ageing cycles.

The state of the surface structure of vegetable pulp fibers may vary due to their natural source or due to the pulping process. Roughness of unrefined and unbleached Eucalyptus and Pinus pulps were evaluated via atomic force microscopy (AFM). The surface of Eucalyptus fibers presented some fibrillar structure in most samples (arrow in Figure 16(a)). In Pinus fibers, typical surface structure was granular (arrow in Figure 16(b)), possibly related to

amorphous non-carbohydrates (lignin and extracts) in the fiber surface. Fibrillar surface structures of Eucalyptus fibers suggest a higher potential for Eucalyptus fibers to anchorage in the cement matrix.

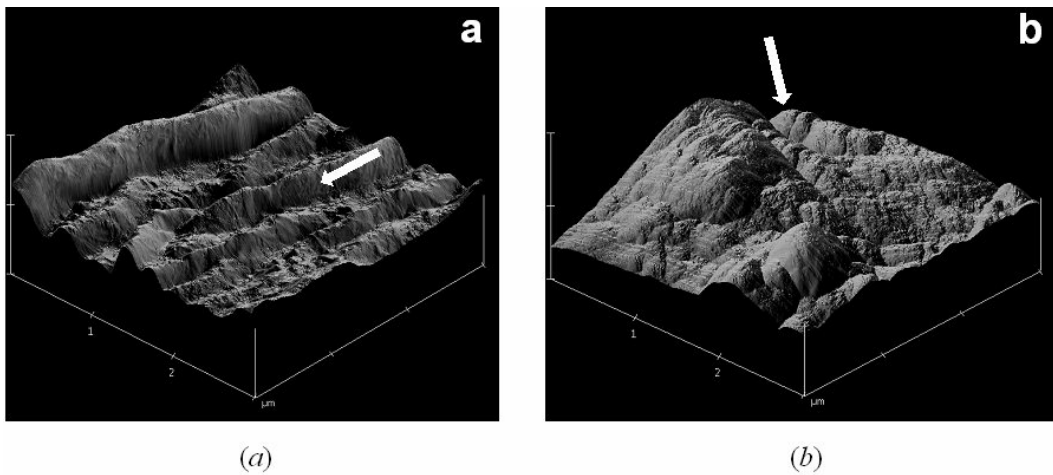


Figure 16. AFM topography images of (a) unbleached Eucalyptus fibers and (b) unbleached Pinus fibers. Image sizes are $3\ \mu\text{m} \times 3\ \mu\text{m}$; m; vertical axis in the images is 500 nm long.

Similar to the procedure previously cited, the interface between pulp fibers and cement matrix was analyzed utilizing SEM-BSE. In composites cross-sections after accelerated ageing cycles, arrows in Figure 17 show improved interface of (a) Eucalyptus fibers compared with (b) Pinus fibers.

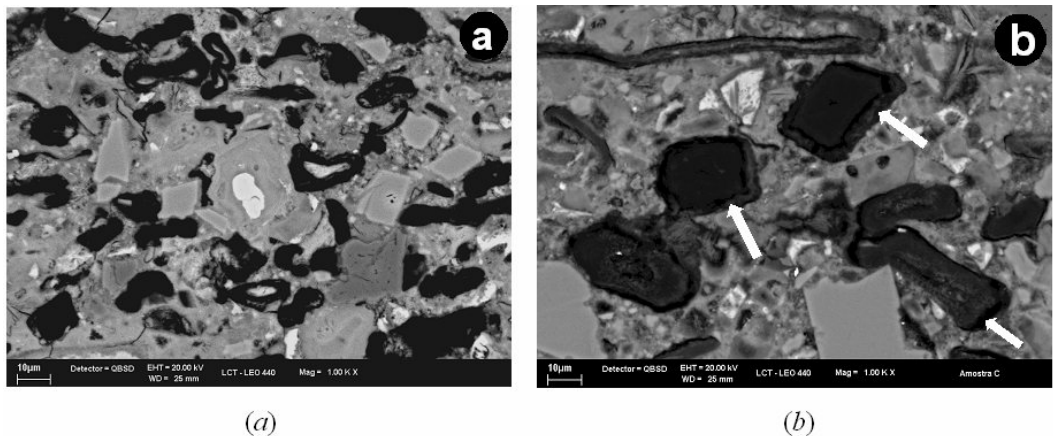


Figure 17. SEM-BSE image of composites reinforced with (a) Eucalyptus pulps and (b) Pinus pulps, after accelerated ageing.

A subsequent mercury intrusion porosimetry (MIP) analysis evidenced a higher content of larger pores (within the 1000–3000 nm range) in composites reinforced with Pinus fibers, as shown in Figure 18. One might then attribute such result to voids in the corresponding fiber-matrix interface.

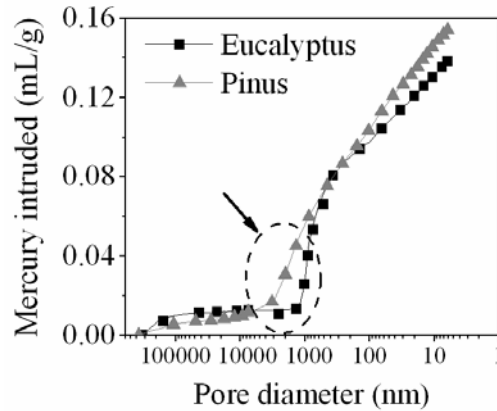


Figure 18. Composites reinforced with Eucalyptus and Pinus pulps: corresponding cumulative mercury intrusion porosimetry (MIP) analysis.

Effects due to Decrease of the Distance Between Fibers

Mechanical properties of fiber-cement composites are very sensitive to the uniformity of fibers volume distribution (dispersion) whereas the distance (spacing) between fibers is a critical geometrical parameter for composites performance [76]. As a rule, cracks initiate and advance from a composite section that has larger fiber-free matrix regions and fiber clumping [77]. Crack initiation requires less energy if it increases the size and the number of matrix regions that are not reinforced by fibers and such phenomenon becomes more pronounced in view of the progressive cement matrix embrittlement throughout its ageing.

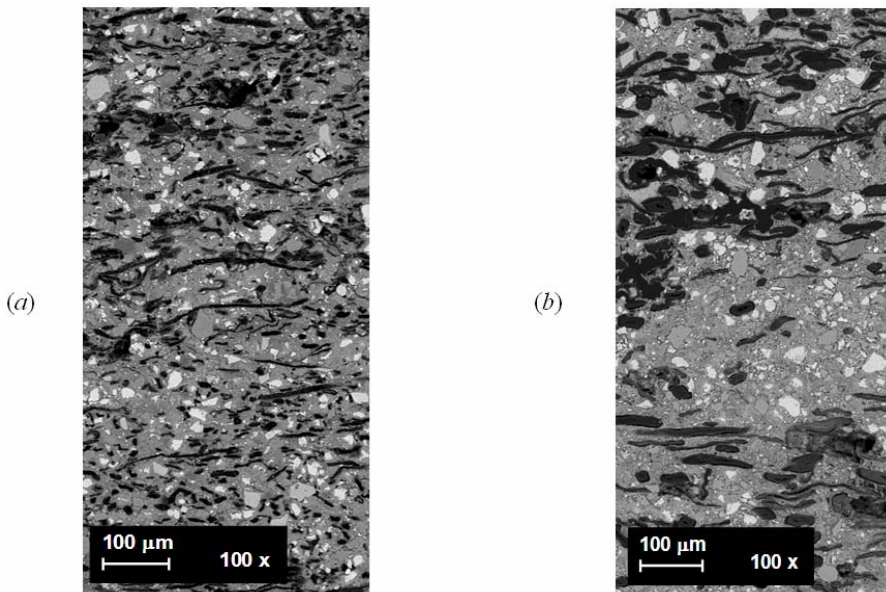


Figure 19. SEM-BSE image of composites reinforced with (a) Eucalyptus pulp and (b) Pinus pulp.

Likely to be more homogeneous in length, Eucalyptus pulp presents shorter fibers (0.83 ± 0.01 mm) than Pinus pulp (2.40 ± 0.09 mm). As the use of short fibers might lead to higher number of fibers per volume or weight in relation to long fibers, the former may reduce fiber-free areas, i.e., the distance between fibers. Additionally, the smaller the fiber length is (which usually refers to lower aspect ratio), the easier the fiber dispersion becomes [78].

Comparing Figures 19(a) and 19(b), short Eucalyptus fibers are better distributed than Pinus fibers. Bridging fibers share and transfer the load to other parts of the composite, which increases composite MOR and toughness. Calculated fiber spacing is at least two times higher for Pinus fibers relative to Eucalyptus ones [76]. Furthermore, due to their longer length, fibers in Pinus pulp are prone to cling to one another, thus jeopardizing the reinforcement.

PHOSPHOGYPSUM: RADIOLOGICAL CONCERNS AND PERFORMANCE

In line with the agricultural boom experienced during the past decades, Brazilian demands for phosphate fertilizers have increased accordingly. As a consequence, considerable amounts of phosphogypsum have been by-produced, whose large-scale exploitation as a non-conventional building material has challenged and motivated many research lines. Difficulties to be overcome refer not only to the constructive aspects but also to the radioactively safe use of phosphogypsum in substitution of ordinary (i.e., commercial) gypsum. With respect to the environmental issue related to this agricultural waste, concerns are addressed to radon-222 (^{222}Rn) exhalation from phosphogypsum-bearing building materials

Most of the total radiation received by humans has to do with ^{222}Rn , which is a decay product from uranium, actinium, and thorium. As such radioactive noble gas can naturally occur in soil formations, it can penetrate into dwellings through microscopic cracks in the building structure. Exposure risks to inhabitants can equally be attributed to ^{222}Rn exhaled from building materials themselves, in which case phosphogypsum-bearing materials are likely to fall. Belonging to ^{238}U decay chain, ^{222}Rn results from α -decay of ^{226}Ra , which is an impurity frequently observed in phosphogypsum. Hence, ^{226}Ra trapped in phosphogypsum-bearing materials eventually decays to ^{222}Rn and such gaseous radionuclide may percolate the porous matrix, reach up open air (local atmosphere or indoor air), and be eventually inhaled by nearby humans or animals.

Radon exposure belongs to the scope of environmental toxicology and its exhalation rate closely depends on the prevailing distribution in the porous medium. Research has been conducted in order to measure and correlate those rates to known physical parameters regarding the porous medium such as emanation rates from ^{226}Ra , moisture content, grain size, porosity, permeability, species (^{222}Rn) diffusivity, and temperature [20].

Though radiological issues concerning phosphogypsum management still remain, there is a broad interest in finding its large-scale exploitation. Accordingly, besides the constructive performance viewpoint, the use of such agroindustrial waste as a substitute for ordinary gypsum deals with ^{222}Rn exhalation. Comprehensive understanding of ^{222}Rn generation and its transport can be useful to assess related radiation exposure, to set up acceptable radiological standards, and to devise radiological protection based on human health threats.

MODELING AND SIMULATION OF RADON-222 EXHALATION

Similar to several other applications [79], [80], ^{222}Rn exhalation from phosphogypsum-bearing materials involves transport phenomena in porous media. Besides diffusion and convection, ^{222}Rn accumulation in dwellings can be concurrently affected by emanation (from ^{226}Ra), adsorption, absorption, and self-decay [81], [82]. Initial model frameworks have considered diffusion and convection with interstitial air flow driven by prescribed pressure differences in line with Darcy's law [83], [84], [85], [86]. Including pressure fluctuations [87], such approach has been adopted until lately [88] as it yields a Poisson equation (for transient transport) or a Laplace equation (for steady-state transport) to be solved for pressure, which simplifies the numerical implementation of governing equations into a computational code⁴. Including entry rates from water and building materials, a steady-state balance for indoor ^{222}Rn concentration was proposed in [89] whereas a transient model for exposure to phosphogypsum panels was recently presented in [90]. Further theoretical contributions comprise transient models for ^{222}Rn diffusion and decay in activated charcoal [91] and for ^{222}Rn and ^{210}Pb transport through the atmosphere [92].

Accounting for sources (e.g., from distinct building materials [22]), time-dependent model frameworks have attempted to assess ^{222}Rn entry rates and its accumulation inside building or enclosures based on bulk values. With respect to spatial coordinates, such models are forcibly of zero-order so that indoor ^{222}Rn concentration is allegedly uniform throughout the entire domain. Whenever point-to-point variation must be analyzed, failure of zero-order approaches is expected because they solely provide volume-averaged ^{222}Rn concentrations. Detailed ^{222}Rn indoor distributions can only be achieved by means of higher order model frameworks in space [93].

Comprehensive models for indoor-air ^{222}Rn exhalation and accumulation become stiffer as more and more influencing processes are entailed. Experimental data do help to assess and depict real and complex behavior but field or laboratory data acquisition might be risky or should be avoided due to safety concerns, technological constraints, or economic issues (costly human or material resources). Since such situation is applicable to the alternative use of phosphogypsum, numerical simulation may then play an important role by rapidly (and safely) investigating any prospective scenario, evoking as few simplifying assumptions as possible while accounting for effects sometimes conveniently neglected or simply ignored.

Nuclear physicists or engineers may rely on simulation if, for instance, non-linear and/or transient behavior, three-dimensional domains, or irregular geometry should be analyzed. Such real-world problems (for which computational time was prohibitive years ago) may help one to define proper radiological protection standards or design. A finite-difference method to predict ^{222}Rn entries into house basements from underneath soil gas was implemented following Darcy's law in [84] while a simulator for ^{222}Rn transport in soil was developed in [86]. Assuming air flow driven by user-defined pressure differences, a finite-volume method code was developed in [88] including time variation, three-dimensional domains, and several controlling parameters whereas fluctuations in such driving pressure differences were numerically investigated in [87].

⁴ Otherwise, one should additionally evoke and solve complete (and stiffer) momentum equations.

Modeling ^{222}Rn Exhalation from Phosphogypsum-Bearing Materials: Primitive Variables

A porous medium is a solid matrix with an interconnected void system (i.e., interstices) through which fluids may flow [79]. If only one fluid saturates the void space, single-phase flow occurs; in a two-phase flow liquid and gaseous phases share the interstices [80]. Macroscopic measurements are normally achieved on regions or samples comprising several pores so that space-averaged physical quantities are assumed to continuously vary on time and on spatial coordinates. Porosity ε of a medium is a dimensionless quantity measuring the total volume fraction occupied by void space and such definition takes for granted that interstices are in fact connected. A basic concept behind such average is the representative elementary volume (REV), whose characteristic length is much larger than the pore scale but significantly smaller than the macroscopic domain length. Governing equations are derived for quantities at REV center and resulting values are allegedly independent from REV size. A REV in phosphogypsum-bearing porous materials may contain solid grains (or lattice) as well as pore space filled with air and/or water (for wet conditions) so that its porosity ε may encompass both air-based ε_a and water-based ε_w counterparts ($\varepsilon = \varepsilon_a + \varepsilon_w$).

A basic radiological concept is the activity (of a radioactive source), which is the amount of radionuclides decaying during a given time. In radioactive decay, an unstable isotope attempts to reach stability by emitting radiation in the form of particles and/or electromagnetic waves. After decay, the former isotope is referred to as parent nuclide while the newer is known as daughter nuclide. The number of particles expected to decay ($-dN$) during a small time (dt) is proportional to the number of particles in the sample (N) and these quantities are related to each other as:

$$\frac{dN}{dt} = -\lambda N \quad (2)$$

where constant λ is the so-called decay constant, whose value is unique for each radioisotope. SI unit for radioactive decay is becquerel (Bq), which is defined as 1 Bq = 1 disintegration per second (dps); yet, curie (Ci) and disintegration per minute (dpm) have also been used.

Knowledge of ^{222}Rn activity concentration profile in phosphogypsum-bearing materials is vital to evaluate resultant exhalation rates. Accordingly, ^{222}Rn transport depends on related mobile activity in the REV, which is properly evaluated and expressed in terms of the partition-corrected porosity ε_c and air-borne activity concentration c_a . For a dry medium without solid sorption, one shows that $\varepsilon_c = \varepsilon$ [88]. Internal sinks of ^{222}Rn activity refers to its decay while internal sources are associated to ^{226}Ra concentration, which can be inferred by assuming that such radioactive impurity is evenly distributed all over the phosphogypsum-bearing material. Corrected emanation rates into the pore system are assessed considering that some ^{222}Rn particles still undergo decay until they finally reach the interstices.

Diffusion-dominant ^{222}Rn transport across porous medium layers is a relatively simple approach valid for low-porosity materials, in which convective transport is neglected while additional simplifying assumptions could include steady-state process and one-dimensional species transfer. The later implies that porous medium is stratified with regard to a coordinate

axis parallel to the main and sole transport direction so that ^{222}Rn concentration becomes uniform at any normal plane. Further steps in the model framework include expansion of the solution domain up to two or three dimensions and time dependence. The later is appropriate for indoor ^{222}Rn accumulation while the former allows one to study edge effects.

Depending on the length scales, one may adopt distinct approaches for the mathematical role of ^{222}Rn exhaling material. A first rationale may assume that the phosphogypsum-bearing material is very slim such as housing panels or boards placed against walls or as part of the building envelope itself [90], [93], [94]. For constant ^{222}Rn diffusivity D_a in open air and disregarding air motion (i.e., neglecting convective mass transfer), ^{222}Rn activity distribution can be governed by the following time-varying diffusive-dominant transport equation [95]:

$$\frac{\partial c_a}{\partial t} = D_a \left(\frac{\partial^2 c_a}{\partial x^2} + \frac{\partial^2 c_a}{\partial y^2} + \frac{\partial^2 c_a}{\partial z^2} \right) - \lambda c_a \quad (3)$$

where x , y and z are Cartesian coordinates, t is time, and sink term $(-\lambda c_a)$ is due to ^{222}Rn self-decay. There is no source term (due to emanation) in Eq. (3) as air presumably lacks ^{226}Ra . One may assume that such later radionuclide is uniformly distributed in the phosphogypsum-bearing material thus yielding a fixed and homogeneous ^{222}Rn exhalation rate j_{Rn} into neighboring air. From the mathematical viewpoint, ^{222}Rn exhalation hence becomes a boundary condition rather than a source term in the governing species equation.

Conversely, a distinct approach should be adopted if the solution domain comprises a blunt (i.e., finite thickness) ^{222}Rn exhaling solid as, for instance, a phosphogypsum-bearing building block (brick) in a still-air detection test chamber [94]. In this case, the porous sample partially fills up the solution domain so that ^{222}Rn transport may occur under two distinct “conditions”, namely, in open air and within the REV. Corresponding species diffusivities D_a and $\tilde{D}$ can be allegedly constant and conveniently related to each other as:

$$\tilde{D} = \delta D_a \quad \Leftrightarrow \quad \delta = \tilde{D} / D_a \quad (4)$$

where $\tilde{D}$ is the species bulk diffusivity, which should be used whenever species flux j refers to the geometric cross-sectional area A . If Fick’s law for ^{222}Rn diffusion is set up in terms of interstitial cross-sectional area, an “interstitial diffusivity”⁵ should be used instead [21], [86].

Bearing in mind Eq. (4) and recalling that ^{222}Rn sources (^{226}Ra particles) exist only inside the solid matrix while ^{222}Rn sink (i.e., self-decay) occurs everywhere⁶, Eq. (3) is extended to the following diffusive-dominant ^{222}Rn transport equation:

$$\varepsilon^n \frac{\partial c_a}{\partial t} = \delta^n D_a \left(\frac{\partial^2 c_a}{\partial x^2} + \frac{\partial^2 c_a}{\partial y^2} + \frac{\partial^2 c_a}{\partial z^2} \right) + n \tilde{G} - \varepsilon_c^n \lambda c_a \quad (5)$$

⁵ Such transport coefficient has also been referred to as “effective diffusivity” although such term may cause confusion with the usual meaning attributed to “effective” in the porous media literature, which refers the REV averaging procedure previously discussed. “Interstitial diffusivity” should be preferred as it is unambiguous.

⁶ Yet, ^{222}Rn self-decay must be properly adjusted with respect to the interstitial volume content.

where $\tilde{G}$ is mobile ^{222}Rn activity generation rate per REV unit and the dimensionless parameter n denotes whether ^{222}Rn transport occurs outside ($n = 0$) or inside ($n = 1$) the porous matrix [96]. Uniform distribution of ^{226}Ra particles (yielding homogeneous generation rate $\tilde{G}$) and constant partition-corrected porosity ε_c are implicitly assumed in Eq. (5), which can then be regarded an extension to the governing equation proposed in [88].

Radon-222 can be additionally transported by convection, either forced or natural [97]. The former refers to the action of fans, pumps, blowers, or wind while the later is induced by fields (e.g., gravity) acting on density gradients due to thermal and/or solutal variations. Applications point to ^{222}Rn exhaling building envelopes subjected to indoor air currents (thermally induced or not) or to air flow over phosphogypsum-bearing embankments or stacks (piles) [98], [99]. Apart from ^{222}Rn activity governing equation suitably extended to include convective terms, the model framework must equally incorporate bulk fluid continuity and momentum equations to be solved for flow field velocity components. If thermal effects should be accounted for, energy equation is invoked to be usually solved for temperature field. If local thermodynamic equilibrium prevails inside the REV, temperatures are the same for all phases (e.g. solid, air, and water and so that $T_s = T_a = T_w = T$), which is reasonable if internal energy sources are negligible.

Aforesaid governing equations are typically coupled to one another and the corresponding solution domain may encompass both porous medium and open air. With respect to momentum equations, outside the porous material fluid flow can be governed by Navier-Stokes equations, which for Newtonian fluids and incompressible flow (constant density $\rho_a = \rho_\infty$) can be expressed in terms of fluid (air) dynamic viscosity μ_a as:

$$\rho_a \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) = \mu_a \nabla^2 \vec{v} - \nabla p + \rho_a \vec{g} \quad (6)$$

where p is pressure and $\vec{g}$ is gravity acceleration. The so-called seepage (or filtration) velocity $\vec{v}$ has components assessed as $v = \dot{V}/A$, where $\dot{V}$ is the volumetric flow rate through a REV with geometric cross-sectional area A , while components of the so-called interstitial velocity are given as $v_{\text{int}} = \dot{V}/A_f$, based on the cross-sectional area $A_f = \varepsilon A$ related to the pore system. Referred to as Dupuit-Forchheimer relation [79], [80], these two velocities are related to each other as:

$$v = \varepsilon v_{\text{int}} \quad \Leftrightarrow \quad v_{\text{int}} = v / \varepsilon \quad (7)$$

Regarding natural convection, Boussinesq approximation can be introduced so that thermo-physical properties become constant except for bulk air density ρ_a in buoyant forces [97]. Hence, incompressible flow presumably holds while a linear dependence of ρ_a upon local temperature T is supposed solely for the buoyancy term in momentum equations:

$$\rho_a(T) = \rho_\infty [1 - \beta_T (T - T_\infty)] \quad , \quad \beta_T = \frac{1}{\rho_\infty} \left(\frac{\partial \rho_a}{\partial T} \right)_\infty \quad (8)$$

where β_T is the coefficient of thermal volumetric expansion and both density ρ_∞ and temperature T_∞ are reference values such as related to atmospheric air condition sufficiently far from the stack (pile or embankment) or related to indoor air sufficiently far from the building wall. Thinking of thermosolutal natural convection [100], one could claim for radon-induced bulk fluid (air) density variations but corresponding contributions are definitely smaller if compared to entire air mass content so that solutal variations in ρ_a can be safely ignored.

For fluid flow within the porous medium, a classical steady-state approach is Darcy's law relating the fluid velocity $\vec{v}$ and the pressure gradient $\vec{\nabla}p$, namely:

$$\vec{v} = -\frac{1}{\mu_a} \vec{K} \cdot \vec{\nabla}p \quad (9)$$

where $\vec{K}$ is the permeability tensor [79], [80]. For simplicity, phosphogypsum-bearing materials can be treated as isotropic so that permeability becomes a scalar K and Eq. (9) reduces to:

$$\vec{v} = -\frac{K}{\mu_a} \vec{\nabla}p \quad \Leftrightarrow \quad \vec{\nabla}p = -\frac{\mu_a}{K} \vec{v} \quad (10)$$

It can be further assumed that K is constant throughout. In addition, porosity $\varepsilon = \varepsilon_c$ (dry porous medium without solid sorption) can be supposedly constant all over as well.

Extensions to Darcy's law have been attempted so as to bear some resemblance to Navier-Stokes equations [80]. For the so-called Darcy-Brinkman-Forchheimer approach and in line with [79], [96], [100], [101], [102], [103], one may put forward the following governing equations for bulk fluid mass (continuity), momentum, energy (with local thermal equilibrium but neglecting internal heat sources, viscous dissipation and radiative effects) and species (^{222}Rn activity):

$$\vec{\nabla} \cdot \vec{v} = 0 \quad (11)$$

$$\frac{1}{\varepsilon^n} \frac{\partial \vec{v}}{\partial t} + \frac{\vec{v} \cdot \vec{\nabla} \vec{v}}{(\varepsilon^2)^n} = \Gamma^n \mathbf{v}_a \cdot \nabla^2 \vec{v} - \frac{\vec{\nabla}p}{\rho_\infty} - n \left(\frac{\mathbf{v}_a}{K} + \frac{c_f |\vec{v}|}{\sqrt{K}} \right) \vec{v} + \bar{g} \beta_T (T_\infty - T) \quad (12)$$

$$\left[(1 - \varepsilon^n) \rho_s c_s + \varepsilon^n \rho_\infty c_{p,a} \right] \frac{\partial T}{\partial t} + \rho_\infty c_{p,a} \vec{v} \cdot \vec{\nabla} T = \left[(1 - \varepsilon^n) k_s + \varepsilon^n k_a \right] \nabla^2 T \quad (13)$$

$$\varepsilon^n \frac{\partial c_a}{\partial t} + \vec{v} \cdot \vec{\nabla} c_a = \delta^n D_a \nabla^2 c_a + n \tilde{G} - \varepsilon^n \lambda c_a \quad (14)$$

where $\nu_a = \mu_a / \rho_\infty$ is air kinematic viscosity, c_f is a dimensionless form-drag coefficient [80] also referred to as Ergun's coefficient [79], c_s is specific heat of solid matrix, $c_{p,a}$ is constant-pressure specific heat of air while k_s and k_a are thermal conductivities of solid matrix and air, respectively. Depending on porous medium characteristics [79], [80] [102], thermal conductivities of solid (k_s) and air (k_a) can be lumped in a REV-averaged (effective) thermal conductivity obeying a specific expression other than the linear relation in Eq. (13). Analogous to Eq. (4) for ^{222}Rn diffusivity, REV-to-fluid property ratios can also be introduced respectively for kinematic viscosity, thermal conductivity, and heat capacity, as expressed by [101]:

$$\Gamma = \tilde{\nu} / \nu_a, \quad \Lambda = \tilde{k} / k_a, \quad \sigma = (\tilde{\rho} \tilde{c}_p) / (\rho_\infty c_{p,a}) \quad (15)$$

Modeling ^{222}Rn Exhalation from Phosphogypsum-Bearing Materials: Dimensionless Variables

Relying on Buckingham's Π -theorem and similarity rationale [95], transport phenomena models can be expressed by means of dimensionless differential governing equations so that simultaneous influencing parameters can be lumped into fewer controlling parameters. Such practice may help to reduce the number of required experiments, tests, scale-up steps, or optimization procedures. If forced convection prevails regarding open air flow condition, one may choose the free stream velocity u_∞ as a reference value. Applying the previously presented model framework for ^{222}Rn generation and transfer for a two-dimensional domain (without loss of generality), dimensionless variables for time τ , Cartesian coordinates X and Y , velocity components U and V , pressure P , temperature θ , and ^{222}Rn activity concentration C can be defined as:

$$\tau = \frac{t}{\Delta t}, \quad X = \frac{x}{L}, \quad Y = \frac{y}{L}, \quad U = \frac{u}{u_\infty}, \quad V = \frac{v}{u_\infty}, \quad P = \frac{p}{\Delta p}, \quad \theta = \frac{T - T_\infty}{\Delta T},$$

$$C = \frac{c_a - c_\infty}{\Delta c} \quad (16)$$

where L is a characteristic length while c_∞ is a reference level for ^{222}Rn activity concentration (e.g. in air away from the porous medium) allegedly to fulfill the condition $c_\infty > 0$. Depending on the problem physics, reference scales Δc and ΔT for ^{222}Rn activity concentration and temperature can be suitably defined while proper choices for time and pressure scales are:

$$\Delta t = L / u_\infty \quad \text{and} \quad \Delta p = \rho_\infty u_\infty^2 \quad (17)$$

By introducing Eqs. (16) and (17) into Eqs. (11) to (14) and assuming $\vec{g} = -g \hat{j}$, one may write the following set of coupled dimensionless governing equations:

$$\frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} = 0 \quad (18)$$

$$\frac{1}{\varepsilon^n} \frac{\partial U}{\partial \tau} + \frac{1}{(\varepsilon^2)^n} \left(U \frac{\partial U}{\partial X} + V \frac{\partial U}{\partial Y} \right) = \frac{\Gamma^n}{\text{Re}} \left(\frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U}{\partial Y^2} \right) - \frac{\partial P}{\partial X} - n \left(\frac{1}{\text{Re Da}} + \frac{c_f |\vec{V}|}{\sqrt{\text{Da}}} \right) U \quad (19)$$

$$\frac{1}{\varepsilon^n} \frac{\partial V}{\partial \tau} + \frac{1}{(\varepsilon^2)^n} \left(U \frac{\partial V}{\partial X} + V \frac{\partial V}{\partial Y} \right) = \frac{\Gamma^n}{\text{Re}} \left(\frac{\partial^2 V}{\partial X^2} + \frac{\partial^2 V}{\partial Y^2} \right) - \frac{\partial P}{\partial Y} - n \left(\frac{1}{\text{Re Da}} + \frac{c_f |\vec{V}|}{\sqrt{\text{Da}}} \right) V + \frac{\text{Gr}}{\text{Re}^2} \theta \quad (20)$$

$$\sigma^n \frac{\partial \theta}{\partial \tau} + U \frac{\partial \theta}{\partial X} + V \frac{\partial \theta}{\partial Y} = \frac{\Lambda^n}{\text{Re Pr}} \left(\frac{\partial^2 \theta}{\partial X^2} + \frac{\partial^2 \theta}{\partial Y^2} \right) \quad (21)$$

$$\varepsilon^n \frac{\partial C}{\partial \tau} + U \frac{\partial C}{\partial X} + V \frac{\partial C}{\partial Y} = \frac{\delta^n}{\text{Re Sc}} \left(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} \right) + \frac{1}{\text{Re Sc}} [nS - \varepsilon^n R(C - C_\infty)] \quad (22)$$

where $C_\infty = -c_\infty / \Delta c$ is the C value given by the last of Eqs. (16) for null air-borne ^{222}Rn activity concentration ($c_a = 0$). Dimensionless parameters regarding convective heat and mass transfer in porous media arise as expected such as Reynolds (Re), Darcy (Da), Grashof (Gr), Prandtl (Pr) and Schmidt (Sc) numbers, expressed in terms of air properties respectively as:

$$\text{Re} = \frac{u_\infty L}{\nu_a}, \quad \text{Da} = \frac{K}{L^2}, \quad \text{Gr} = \frac{g \beta_\tau \Delta T L^3}{\nu_a^2}, \quad \text{Pr} = \frac{\nu_a}{\alpha_a}, \quad \text{Sc} = \frac{\nu_a}{D_a} \quad (23)$$

where $\alpha_a = k_a / (\rho_\infty c_{p,a})$ is the thermal diffusivity of air.

Besides those parameters, Eq. (22) introduces two unusual dimensionless numbers referred to as decay-to-diffusion (R) and emanation-to-diffusion (S) ratios⁷, respectively related to ^{222}Rn decay and emanation processes [93], [94], [98], [99], [104], defined as:

$$\text{R} = \frac{\lambda L^2}{D_a} \quad \text{and} \quad \text{S} = \frac{\tilde{G} L^2}{D_a \Delta c} \quad (24)$$

⁷ R and S respectively assess the relative importance of ^{222}Rn decay and emanation in relation to its mass diffusion.

In the model framework for time-dependent pressure-driven ^{222}Rn migration inside soil proposed in [21], two dimensionless groups were introduced in the species (^{222}Rn activity) concentration equation: a convection-to-decay ratio (N) and a mass-transfer Péclet number⁸ (Pe_m , measuring the relative importance of convection with respect to diffusion). Recalling the previous definition for the decay-to-diffusion ratio R, Eq. (24), and bearing in mind definitions proposed⁹ for N and Pe_m , it is interesting to verify that indeed:

$$\frac{\text{Pe}_m}{N} = \frac{\text{convection} / \text{diffusion}}{\text{convection} / \text{decay}} = \frac{\text{decay}}{\text{diffusion}} \Rightarrow \frac{\text{Pe}_m}{N} \cong R \quad (25)$$

A surrogate dimensionless group M can be additionally introduced¹⁰, namely:

$$M = \frac{S}{R} = \frac{\tilde{G}}{\lambda \Delta c} \quad (26)$$

which is interpreted as emanation-to-decay ratio [94], [98], [99], [104]. Despite still sensitive to scale Δc for ^{222}Rn activity concentration, M number is independent from both open-air diffusivity D_a and the characteristic length L . In terms of R and M, Eq. (22) can be recast as:

$$\varepsilon^n \frac{\partial C}{\partial \tau} + U \frac{\partial C}{\partial X} + V \frac{\partial C}{\partial Y} = \frac{\delta^n}{\text{Re Sc}} \left(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} \right) + \frac{R}{\text{Re Sc}} [nM - \varepsilon^n (C - C_\infty)] \quad (27)$$

In the absence of strong air currents (i.e., negligible forced convection), it might be rather cumbersome to identify a reference velocity u_∞ , which can be awkwardly small. Dimensionless variables formerly proposed in Eqs. (16) basically remain the same but suitably “re-scaled” by $u_\infty = v_a/L$ wherever required. In Eqs. (19) to (22) or (27), such velocity scale implies that Reynolds number, as defined in line with the first of Eqs. (23), numerically¹¹ reduces to unity ($\text{Re} = 1$).

PHOSPHOGYPSUM PROPERTIES

Phosphogypsum was characterized from chemical and radiological viewpoint in [105]. One aspect about the later refers to ^{222}Rn exhalation, which is important parameter to assess radiation doses onto occupants within dwellings. Indoor ^{222}Rn activity concentration can be experimentally measured using activated charcoal assembled inside relatively simple samplers as the cylindrical one (diameter = 90 mm, height = 45 mm) shown in Figure 20(a). Charcoal for measurements must be dried at 75°C for at least 7 days and samplers must be

⁸ There is also a corresponding and similar definition for heat-transfer Péclet number.

⁹ It seems the proposed definition for Péclet number should be altered to $\text{Pe}_m = K \Delta P_o (\varepsilon \mu D)^{-1}$, which appears to be the correct result after casting the proposed governing species transport equation into dimensionless form.

¹⁰ In fact, original definitions for R, S and M included the porosity (either geometric or partition-corrected) [104].

exposed to indoor air for up to 30 days. Retained (adsorbed) ^{222}Rn is counted through gamma spectrometry with NaI detector based on the 609.3 keV peak, which refers to ^{214}Bi radionuclide (a decay product of ^{222}Rn).

Alternatively, solid state nuclear track detectors (SSNTD) have been largely employed due to relatively low cost (related to both detector itself and measurement process), with particular attention to CR-39 polycarbonate (allyl diglycol-carbonate, $\text{C}_{12}\text{H}_{18}\text{O}_7$) detectors presenting higher efficiency. They basically consist of a plastic diffusion chamber that is permeable solely to ^{222}Rn (i.e., decay products of such radionuclide are not able to penetrate through it). As depicted in Figure 20(b), SSNTD is placed inside the diffusion chamber in order to register alpha particle emissions occurred during ^{222}Rn decay. A calibration factor correlates the quantity of detected tracks and ^{222}Rn concentration in indoor air.



Figure 20. Measurement devices for indoor ^{222}Rn activity concentration: (a) activated charcoal collector and (b) diffusion chamber with SSNTD.

As far as physical and mechanical properties of interest are concerned, preliminary tests were accomplished in [106] regarding phosphogypsum samples by-produced from 3 distinct phosphate fertilizer industries¹². Properties were determined considering Brazilian standards for bulk density (NBR 12127), consistency and setting time (NBR 12128, employing a Vicat equipment), modulus of rupture (NBR 12129, utilizing EMIC hydraulic press model PCE 100D - 1 MN load), and free water / crystallization water content (NBR 12130). Brazilian standard NBR 13207 recommends the bulk density of $700 \text{ kg}\cdot\text{m}^{-3}$ for ordinary gypsum. As preliminary results for phosphogypsum pointed to approximately $570 \text{ kg}\cdot\text{m}^{-3}$, results have been improved by properly separating small grains from samples.

The reference value for free water content is 1.3% as specified by NBR 13207. Samples were initially dried at 125°C for 4 h but results were unsatisfactory for both ordinary gypsum (4.2%) and phosphogypsum (6.2%). After drying samples at the same temperature (125°C) for a longer period (5 h), improved results were obtained for both phosphogypsum (sample #1 = 0.60%, sample #2 = 0.66%, sample #3 = 1.12%) and gypsum (1.37%). Table 7 shows results for crystallization water content for different drying periods. The phosphogypsum samples were dried up to 7 h in order to fulfill recommended standards (NBR 13207).

¹¹ It is important to stress this is only a numerical implication thanks to the choice of velocity scale.

¹² They are here referred to as numbers, namely, sample #1, sample #2, and sample #3.

Table 7. Crystallization water content (% by mass) for phosphogypsum samples.

Drying period (h)	Sample #1	Sample #2	Sample #3
4	14.43	12.77	n.a. **
5	10.00	9.54	n.a. **
6	9.36	6.77	n.a. **
7	4.91 *	6.22 *	1.34 *
24	5.90 *	6.19 *	1.62 *

* Values fulfilling standards recommended in NBR 13207; ** Not available or not measured.

Table 8 shows the test results for consistency whereas Table 9 shows the results for setting time for both ordinary gypsum and phosphogypsum samples. Regarding the later test, setting starts when the tip remains 1 mm from the base while test ends when tip no longer penetrates into the paste but it just leaves a slender imprint. Compared to ordinary gypsum and phosphogypsum sample #3, either sample #1 or sample #2 required an elevated water consumption, which jeopardized their performance in corresponding MOR tests (as shown ahead). If compared to ordinary gypsum, setting time occurred quite rapidly for phosphogypsum (in general basis), which may affect its handling as it loses its workability faster.

Table 8. Consistency results for ordinary gypsum and phosphogypsum samples.

Amount of gypsum (g)	Cone tip penetration (mm)		Amount of phosphogypsum (g)	Cone tip penetration (mm)		
	Test #1	Test #2		Sample #1	Sample #2	Sample #3
250.00	34	34	187.50	20	21	n.a. **
272.73	36	34	172.50	24	26	n.a. **
300.00	32 *	34	150.00	34	33	n.a. **
319.15	29 *	30 *	157.90	31.5 *	32 *	n.a. **
333.33	24	26	200.00	n.a. **	n.a. **	38
			215.00	n.a. **	n.a. **	29 *
			225.00	n.a. **	n.a. **	25

* Values fulfilling standards recommended in NBR 13207; ** Not available or not measured.

Specimens for MOR tests were prepared in molds with three cubic compartments so that three samples with 50 mm characteristic length were produced simultaneously for each material (ordinary gypsum and phosphogypsum samples). Accordingly, cross-sectional area then results 2500 mm^2 whereas the water/phosphogypsum ratio was the same for consistency tests. Results for each specimen are presented in Table 10. As already commented, higher water consumption of phosphogypsum in samples #1 and #2 jeopardized their MOR performance. Ordinary gypsum was then added to phosphogypsum as an attempt to improve

such property so that new MOR tests for 20% addition (mass basis) resulted in 8.7 MPa and 8.8 MPa for samples #1 and #2, respectively.

Table 9. Setting time results (min:s) for ordinary gypsum and phosphogypsum samples.

Gypsum	Test #1	Test #2	Phosphogypsum	Sample #1	Sample #2
Start	14:30 *	16:00 *	Start	06:00	08:30
End	31:00	31:00	End	09:00	16:26

* Values fulfilling standards recommended in NBR 13207.

Table 10. MOR results for ordinary gypsum and phosphogypsum samples.

Material	Specimen	Load (kN)	MOR (MPa)
Ordinary gypsum	1-G	31.8	12.72 *
	2-G	38.9	15.56 *
	3-G	30.9	12.36 *
Phosphogypsum sample #1	1-A	9.3	3.72
	2-A	5.4	2.16
	3-A	8.8	3.52
Phosphogypsum sample #2	1-B	15.0	6.00
	2-B	10.1	4.04
	3-B	12.3	4.92
Phosphogypsum sample #3	1-C	23.8	9.52 *
	2-C	24.7	9.88 *
	3-C	19.8	7.92 *

* Values fulfilling standards recommended in NBR 13207.

CONCLUSION

Non-conventional building materials have been extensively investigated as an alternative option for cost-effective housing in developing countries. The present chapter addressed and discussed some agroindustrial residues or wastes that are likely to provide a suitable as well as a sustainable solution.

Both waste sisal and banana chemithermomechanical pulps (CTMP) were suitable for cement composite manufacturing via laboratory method similar to counterpart processes broadly used in commercial production. Residual *Eucalyptus grandis* Kraft pulp presented similar behavior during the fabrication steps of fiber-cement with the advantage of being already available in pulp form and at relatively low costs in comparison to the traditional softwood pulps. The incorporation of these waste fibers at 8% by mass into the matrix based

on blast-furnace slag (BFS) resulted in composites with fracture strength approximately 18 MPa slightly lower than the correspondent materials based on ordinary Portland cement (OPC). Both 12% (mass basis) incorporation of sisal and *Eucalyptus grandis* into BFS composites rendered tough composites (approximately $1.2 \text{ kJ}\cdot\text{m}^{-2}$ of toughness), which is a reasonable performance if compared to previous investigations carried out on sisal chemical pulp as reinforcement for BFS composites.

Microscopy images depicted the importance of proper linkage between composite phases, providing the coexistence of fiber fracture and pullout. Such major outcome could then explain the strength sustained as well as better toughness results achieved by sisal CTMP composites in comparison to corresponding performance of banana CTMP. Physical properties indicated poor packing of high-content fiber composites with the consequent low density and high water absorption values, despite within acceptable standard limits. Both proposed waste fibers utilization and mechanical pulping methods together with low-energy cements as blast-furnace slag are likely to represent an attractive option for asbestos-free fiber-cements in the near future.

Another agroindustrial waste with prospective use as a non-conventional building material is phosphogypsum. Results from its characterization and performance have been quite promising and encouraging. Among possible large-scale exploitation of such by-product one may point to building blocks or housing panels, provided that radiological issues related to radon-222 exhalation and its accumulation in indoor air have been properly overcome. Comprehensive understanding of corresponding transport phenomena is likely to rely on experimental research supported by numerical simulation so as to yield reliable information concerning radiological impact and protection design of prospective safe scenarios.

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Chapter 10

RECYCLED AGGREGATE STRUCTURAL CONCRETE: A METHODOLOGY FOR THE PREDICTION OF ITS PROPERTIES*

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ABSTRACT

Structural concrete made with recycled aggregates from construction and demolition waste is an eco-efficient solution to reduce both the production of waste and the depletion of natural non-renewable materials. Even though this material shows great potential as an alternative to conventional concrete (made with primary aggregates), its large-scale use has been hampered by lack of regulation and technical documentation. Furthermore, some production procedures hinder the use of recycled aggregates under normal waste collection conditions.

In this Chapter, the specific problems of preparing concrete with recycled aggregates are addressed and the properties of recycled aggregates *versus* primary (natural stone) aggregates are compared.

A general methodology to predict the long-term performance (in terms of both mechanical properties and durability) of concrete made with recycled aggregates using the corresponding performance of equivalent conventional concrete (reference concrete) is proposed and validated. The approach employed includes an international literature review and a summation of experimental campaigns monitored / supervised by the author.

This methodology allows the early estimation of the properties of concrete made with recycled aggregates based on the properties of the aggregates mix and of young concrete, which can be used both by the structural designer and the contractor, thus effectively removing a barrier to the widespread use of this material.

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ABBREVIATIONS

CDW	construction and demolition waste;
CPA	coarse primary (natural) aggregates;
CRA	coarse recycled aggregates;
FPA	fine primary (natural) aggregates;
FRA	fine recycled aggregates;
MRA	mixed (concrete and masonry) recycled aggregates;
PA	primary (natural) aggregates;
RA	recycled aggregates;
RAC	recycled aggregate concrete;
RC	reference concrete (i.e. without recycled aggregates);
RCA	recycled concrete aggregates;
RMA	recycled (brick and/or stone) masonry aggregates.

INTRODUCTION

The Construction and Demolition Waste Problem

The construction industry, even though essential to the progress of Society, is also a serious contributor to major environmental impacts. One of the most visible aspects of these impacts is construction and demolition waste (CDW), which represents from 20% to 30% (including soils) of all the solid waste produced each year.

Even though innocuous in comparison with other types of waste, the absence of a viable reuse for CDW contributes to the depletion of natural non-renewable - even if abundant - resources (stone turned into gravel and sand), to the dramatic decrease of the landfills where they are dumped instead of other more dangerous industrial waste and, when dumped illegally as frequently happens, to an unacceptable onslaught on the environment and each person's individual freedom to enjoy Nature.

Therefore, this problem needs to be addressed and, as with other similar waste materials, the best solution is to reduce their production (e.g. by building constructions that last much longer). When that is not possible, the second-best strategy is to find and implement viable uses (from a technical and economic point of view) for this material. The construction elements may be reused as they are in other locations and with similar functions and, when that is not possible either (as happens with most of bulk CDW), the materials may be recycled.

This last option can be divided into three levels: *upcycling*, when the recycled use of the materials is of greater value than its original one (this is not usually possible with CDW); *cycling* or *recycling*, when the quality demand of the new use is similar to the original one; and *downcycling*, when the materials are used for a less demanding function than the original one, i.e. there is very little profit from their intrinsic value (in terms of cost or potential properties). This is the commonest way in which CDW is being recycled at the moment. Since most of bulk CDW consists of inert materials (concrete, brick masonry and mortars), CDW is largely recycled as aggregate in roads, streets and the floors of buildings, used in the

landscaping of spent mining infrastructures, or as drainage layers of landfills and in concrete production.

Unfortunately, in many countries none of these options is chosen (though this is happening increasingly less often) and the CDW ends up in landfills or dumped beside remote roads.

Production of CDW in Europe

Table 1 shows the average values of CDW production in various European countries, taken from a paper presented by the European Union in 2003 (Muthmann 2003) to which the average annual growth rates determined from Eurostat Environmental Statistics were added, as well as an estimation of *per capita* production. These statistics have the drawback of including data from the 1990s, probably outdated now, and also of resulting from different criteria for estimating the amount in each country (e.g. whether soil is taken into account or not, the use of enquiries or intelligent guesses).

Table 1. CDW production in the EU by country
(adapted from (Muthmann 2003) in (Gonçalves 2007))

Country	Average CDW production (1000 tonnes)	Average annual growth	Time scale	Population in 2005 (millions of inhabitants)	Per capita production (kg/person)
Belgium	6 559	n/a	1994	10.4	631
Denmark	2 787	6.05%	1992-2000	5.4	516
Germany	238 580	2.07%	1996-2000	82.5	2 892
Greece	1 898	3.90%	1996-2000	11.1	171
Spain	22 000	n/a	1991	43.0	512
France	24 300	-0.05%	1991-1997	59.9	406
Ireland	2 012	27.19%	1995-1998	4.1	491
Italy	26 226	-4.20%	1991-1999	58.5	448
Luxembourg	4 359	42.16%	1997-1999	0.5	8 717
Netherlands	15 604	4.33%	1990-2001	16.3	957
Austria	27 500	n/a	1999	8.2	3 354
Finland	33 545	4.12%	1997-1999	5.2	6 451
United Kingdom	70 625	0.39%	1990-1999	60.0	1 177
Norway	1 840	-3.74%	1990-2000	4.6	400
Switzerland	6 393	n/a	1998	7.5	852
Cyprus	555	-2.34%	1990-1999	0.7	793
Czech Republic	8 486	16.55%	1998-2001	10.2	832
Estonia	294	16.08%	1995-2000	1.3	226
Latvia	39	n/a	2001	2.3	17
Lithuania	231	10.00%	2000-2001	3.4	68
Malta	970	-2.29%	1990-2001	0.4	2 424
Poland	668	2.94%	1998-2001	38.2	17
Romania	623	27.68%	1995-2000	21.7	29
Slovakia	477	-6.80%	1998-2000	5.4	88
Slovenia	427	35.64%	1995-2001	2.0	213
Croatia	290	n/a	2000	4.4	66
Total	497 285			467.2	1 064

The result is that there are some dubious values, too low or too high, suggesting a figure of 1064 kg per person annually, which is most probably higher than the real one. Therefore, these results should be viewed with caution especially where they differ most from a previous estimate, put together in the so-called Symonds report (1999).

In Table 2 some more updated statistics for some European countries are presented, also containing their CDW recycling ratio. These values clearly represent a positive evolution compared with existing literature. For example, in the Symonds report (1999) it is stated that 180 million tonnes are produced in Europe every year, leading to a *per capita* yearly production of 480 kg, less than half the figure in Table 1, which may be explained by soil not being considered in the Symonds report and possibly also by an increasing trend.

The origin of this CDW, according to the Waste Centre of Denmark (WCD) (2005), is as follows: 5%-10% from new construction works, 20%-25% from rehabilitation works and 70%-75% from demolition sites. These percentages may vary widely from country to country, reflecting their level of development / stagnation (in less developed countries the relative influence of new construction is dramatically higher).

Table 2. Reuse of CDW in selected countries in Europe (UEPG 2006)

Country	CDW produced (M tonnes)	Recycling		Dumping		Source
		M tonnes	%	M tonnes	%	
Netherlands	25.8	24.6	95.3	0.9	3.5	Survey 2002-2003, 2005
United Kingdom	91.0	81.8	89.9	9.2	10.1	QPA, 2003
Germany	213.9	186.3	87.1	27.6	12.9	Monitoring-Bericht, 2002
Belgium	14.0	12.0	85.7	2.0	14.3	WS and FDERECO, 2005
France	309.0	195.0	63.1	114.0	36.9	Survey FNTF et Ademe, 2001

In terms of composition, CDW varies a lot and the first thing that matters is whether it results from new construction, rehabilitation work or demolition (Figure 1). In the last case, the age of the construction demolished has a great influence on the materials but there are major differences in buildings of similar age where different structural materials have been used (e.g. a reinforced concrete frame with solid slabs *versus* structural brick masonry walls supporting timber pavements). Statistics from different countries exhibit this heterogeneity (compare Table 3 for Denmark with Figure 1 for Brazil).

Table 3. CDW composition in Denmark in 2003 (DEPA 2005)

Materials	%
Concrete	25
Coil and rocks	22
Asphalt	19
Roof tiles	6
Other construction waste	11
Other waste	8
Other recyclable waste	6
Non-incineratable waste	3

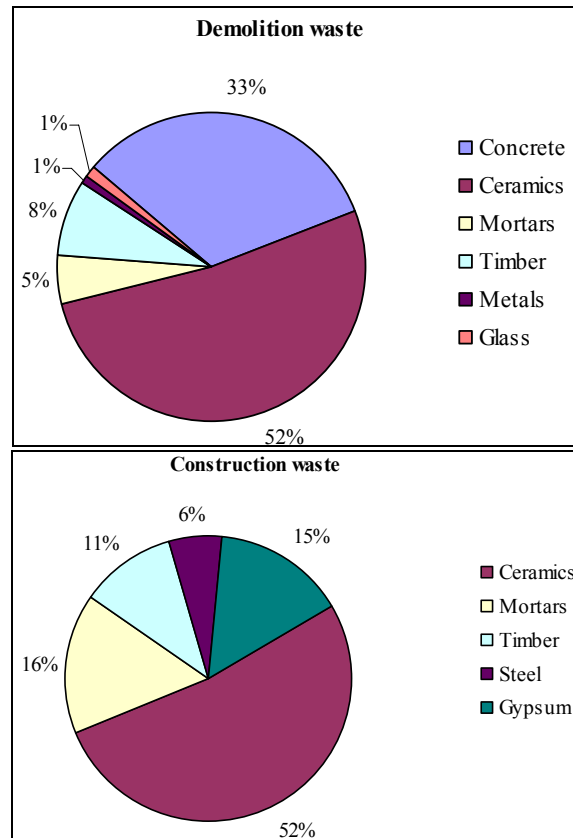


Figure 1. Composition of CDW from a demolition and a new construction site (Angulo 1998)

Production of Aggregates in Europe

In terms of aggregates, various countries have been increasing the reuse of CDW for that effect. Table 4 shows the production of aggregates by type in each country while Figures 2 and 3 indicate the relative importance of recycled aggregates (RA) production in the overall aggregates market, which covers 3 million tonnes per year (Arab 2006).

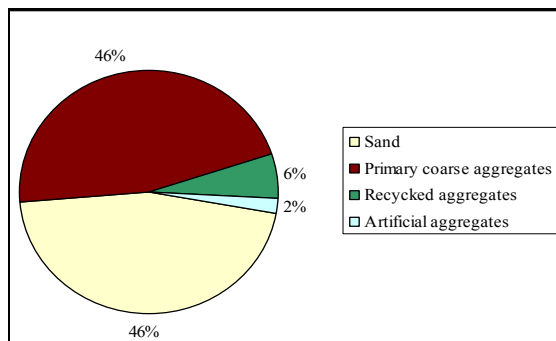
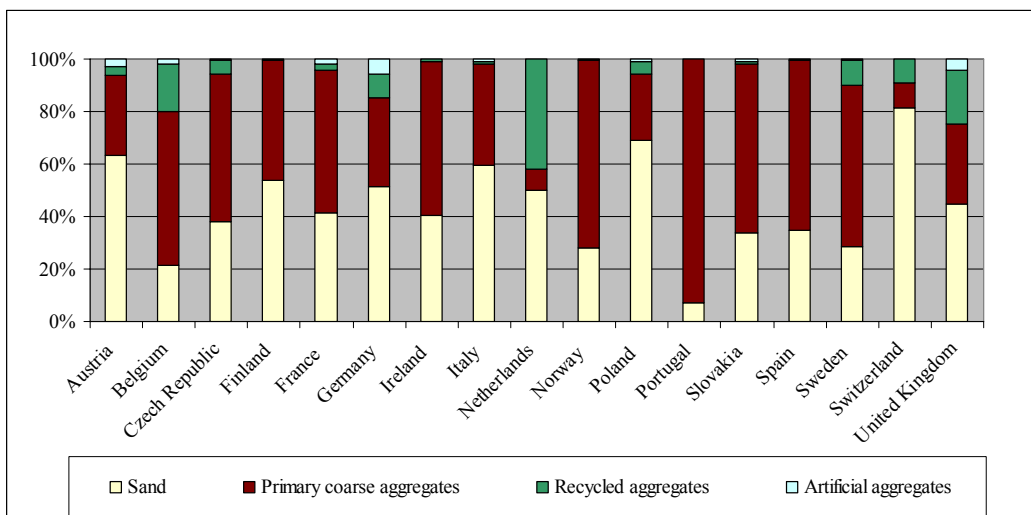


Figure 2. Aggregates produced by type in the EU in 2005 (UEPG 2006)

Table 4. Production of aggregates in the EU by country in 2005 (UEPG 2006)

Country	Aggregate production (Mt)				
	Sand	Primary coarse aggregates	Recycled aggregates	Artificial aggregates	Total
Austria	66.0	32.0	3.5	3.0	104.5
Belgium	13.9	38.0	12.0	1.2	65.1
Czech Republic	25.5	38.0	3.4	0.3	67.2
Finland	53.0	45.0	0.5	n/a	98.5
France	170.0	223.0	10.0	7.0	410.0
Germany	263.0	174.0	46.0	30.0	513.0
Ireland	54.0	79.0	1.0	0.0	134.0
Italy	225.0	145.0	4.5	3.0	377.5
Netherlands	24.0	4.0	20.2	n/a	48.2
Norway	15.0	38.0	0.2	n/a	53.2
Poland	104.3	37.7	7.2	1.6	150.8
Portugal	6.3	82.0	n/a	n/a	88.3
Slovakia	8.9	16.9	0.2	0.3	26.3
Spain	159.0	300.0	1.3	0.0	460.3
Sweden	23.0	49.0	7.9	0.2	80.1
Switzerland	46.5	5.3	5.3	n/a	57.1
United Kingdom	124.0	85.0	56.0	12.0	277.0
Total	1 381.4	1 391.9	179.2	58.6	3 011.1

**Figure 3. Aggregates produced by type and country in the EU in 2005 (UEPG 2006)**

RECYCLED AGGREGATES FROM CONSTRUCTION AND DEMOLITION WASTE

Classification of Recycled Aggregates

To refer to “recycled aggregates” (RA) without specifying their origin is as vague as mentioning “steel” or “timber” without describing their production process and class in the first case and the species and quantity of defects in the second case. As a matter of fact and taking into account the various possible uses of AR, there are fundamentally the following types rated in decreasing order of their quality (measured in terms of water absorption and density and the consequent potential of the construction materials / elements in which they are used; e.g. in concrete the quality of the aggregates is reflected in its mechanical and durability-related performance), as it is generally reported in the literature (de Brito 2005):

- (Coarse) stone aggregates recovered after washing fresh ready-mixed concrete which for some reason has not been used (this material is virtually identical to the original primary aggregates (PA) and is currently reused for new ready-mixed concrete);
- The coarse and/or fine fractions resulting from the demolition of architectural concrete elements (from buildings, special structures and the waste from the precast industry), when there is a reasonable assurance that no other materials will enter the mixture;
- The coarse and/or fine fractions resulting from the demolition of architectural concrete elements already made with RA (multiple recycling), where the RA may have several sources but it is likely that they will only be coarse recycled concrete; this type of RA is not likely to be found in large quantities until some decades from now;
- The coarse and/or fine fractions resulting from the demolition of rendered / coated concrete elements similar to the previous ones but where the resulting RA are made of a mixture of stone, mortar and possibly ceramics; this is today the most common CDW in construction sites;
- The coarse and/or fine fractions resulting directly from more or less undifferentiated CDW, where the stone, mortars and ceramic elements may be joined by small quantities of other materials such as timber, plastics, metals, glass and so on, leading to a mixture with worse characteristics and less quality control; one of the purposes of selective demolition (as an alternative to conventional demolition) is exactly to separate the materials at the building site in order to minimize this contamination;
- The coarse and/or fine fractions resulting from the ceramic industry waste or from the demolition of ceramic elements (bricks and tiles) with or without mortars, leading to mostly ceramic RA with worse characteristics for producing concrete.

This classification is generally reflected in international legislation. In his comparative study of 17 norms for the use of RA in concrete production, from 14 different countries, Gonçalves (2007) concluded that the following three main types of RA were considered with variable quantities of other materials allowed:

- RCA: recycled concrete aggregates;
- RMA: recycled (brick and/or stone) masonry aggregates;
- MRA: mixed (concrete and masonry) recycled aggregates.

In the following sections of this Chapter the main differences in terms of the properties of the concrete mixes made with the different types of AR described above will be described. To understand these characteristics, the main differences between PA and RA are presented next:

- Greater water absorption (both for the RA obtained from concrete elements and those with incorporation of ceramic elements, for the coarse fraction as well as the fine fraction), with various consequences in terms of the workability and, water / cement ratio of fresh concrete and of the mechanical and durability-related properties of hardened concrete;
- Lower compactness (especially for the ceramic RA) and consequent lower crushing resistance and modulus of elasticity, which has an impact on both the immediate and long-term deformability of the concrete elements, and to a lesser degree on its mechanical strength.

Recycled Concrete Aggregate

In the case of the RA from uncoated (or almost uncoated) concrete elements, there are two types of RA: the coarse fraction (CRA) and the fine fraction (FRA), whose differences are more qualitative than quantitative.

What distinguishes these CRA from the equivalent coarse primary aggregates (CPA) is the hardened paste (mortar) that adheres to the former original CPA. This paste is made of primary fines and cement (there is no consensus in the scientific community on whether the non-hydrated part of this cement provides the paste with pozzolanicity).

Their high water absorption and reduced density are responsible for the lower performance of these RA. In other words, the greater the proportion of hardened paste adhering to the original PA, the higher the differences in performance between the CRA and the CPA. Hansen & Narud (1983) measured the percent volume of paste adhering to the PA and concluded that it increases as the size of the CRA decreases, leading to poor expectations for concrete made with FRA.

Since CRA recovered from fresh ready-mixed concrete and washed almost straightaway have hardly any adhering paste they are practically identical to CPA.

This paste is also the reason why the crushing process of the concrete elements (in terms of crusher unit, free space between the blades and number of crushing operations) can strongly affect the characteristics of the RA thus obtained. In an experimental campaign, Matias and de Brito (2005) obtained similar preliminary results in mechanical terms from concrete mixes made with coarse RCA and CPA when the crushing process was the same for the primary and the recycled aggregates, i.e. it was the aggregate crushing process and not the type of aggregates that affected the concrete performance. In another experimental campaign, Gonçalves (2002) obtained different results when the CRA were obtained in a small laboratory unit from those when the crusher unit was on an industrial scale.

Finally, it is also to be expected that the higher the replacement ratio between CPA and CRA in the production of concrete the greater the differences in terms of the respective mixes' performance. This point was unanimous in all the literature reviewed and is proven beyond doubt in the sections which deal with the analysis of this review.

The FRA obtained from crushing concrete elements display exactly the same trends as the CRA in terms of water absorption and density, only more markedly (which is emphasized by an unavoidably greater contamination rate). In practical terms this means that theoretically a lower replacement ratio of FPA with FRA is enough to lead to the same variation in behaviour of the respective RAC as a given replacement ratio of CPA with CRA. The literature review presented later identified several instances where this is not true, in particular the research by Evangelista (2007) with concrete FRA where the results in terms of mechanical strength with replacement ratios of up to 100% were very promising, and better than for equivalent ratios CPA/CRA. One of the reasons for this trend (better than for durability-related characteristics) may have been the non-consensual pozzolanicity of the concrete fines.

A question that frequently comes up is the hypothetical influence of the original concrete grade on the performance of the resulting RA and RAC (naturally if the difference in grade of two original concrete mixes results from the characteristics of the aggregates themselves, this will certainly have an influence on the resulting RA; but that is not the issue here). In their ongoing research Santos et al (2004) concluded that this influence does exist if the gap between the grades is sufficiently wide, but its importance is greater in some properties (modulus of elasticity) of the resulting RAC than in others (compressive strength). Hansen & Narud (1983) reached similar conclusions.

Multiple (repetitive) recycling, i.e. the possibility of crushing concrete elements in whose production RA (either from concrete or ceramics) have already been used is nowadays practically an academic question. Nevertheless, Gonçalves (2002) consecutively tested three concrete mixes with concrete CRA in which the original PA were always the same with promising results in terms of compressive strength, i.e. it did not decrease after the first cycle. She also concluded that cyclic recycling progressively increased the mass of adherent paste and therefore the water absorption kept growing and the density decreasing, though not linearly. In other words, the repetition of the process helped to "worsen" the CRA characteristics, and those of the resulting RAC (recycling RCA where ceramic RA have been used would further lower the quality of the resulting second-cycle RA). This was the reason why, in the classification above, the RA resulting from the first recycling of concrete elements were considered in principle to be of a higher quality than those resulting from multiple recycling.

Recycled Ceramic Aggregate

By comparison with stone aggregates, ceramic aggregates exhibit much higher water absorption (so high that these aggregates always need to be pre-saturated before being used in concrete production) and lower density. It seems obvious that ceramic aggregates, either recycled or not, are "worse" than stone (primary or concrete) aggregates, because their unfavourable characteristics affect all their volume (unlike concrete aggregates where only the adhering paste has these characteristics). Therefore, the higher the percentage of ceramics

in the RA mix the greater the differences in terms of performance for the resulting RAC, thus explaining the rating proposed above in terms of the relative quality of the RA. The use of ceramic RA in concrete production has been studied only in terms of the coarse fraction (Rosa 2002) and the fine fraction has been limited to its use in mortars (Silva 2006).

Expected Trends in Recycled Aggregate Concrete

Any estimation of the future performance of an RAC is impossible without knowing the origin and size distribution of the RA and their relative weight in the aggregate mixture. In other words, each RA composition has unique characteristics that will affect the performance of the concrete mix made with it. Based on the considerations set forth earlier, the following general trends are to be expected (the results of the literature review presented further on corroborate most of them) (de Brito 2005):

- Similar or worse performance of every RAC relative to the corresponding RC (reference concrete, with exactly the same characteristics as the RAC except for the use of RA, i.e. 100% PA);
- A greater replacement ratio of PA with RA (either fine or coarse, recycled concrete or ceramic) implies a similar or worse performance of the RAC;
- Worse performance of RAC made with FRA and CRA when compared with that of RAC whose RA are only CRA (this trend may depend on the class strength intended for the RAC and its dependence on the aggregates themselves, i.e. compressive strength of low grade concretes is less dependent on the coarse aggregates than on the cement and fines paste);
- Similar or worse performance of RAC with multiply recycled RA compared with RAC whose RA are being recycled for the first time (with the same replacement ratio);
- Similar or worse performance of RAC with RMA than of RAC with RCA only (with the same replacement ratio).

TECHNICAL BARRIERS TO THE USE OF RA IN GENERAL AND IN RAC PRODUCTION

There are various technical barriers to the use of RA from CDW. They are going to be presented in two parts: those that limit the use of RA in general (regardless of their application) and those that specifically concern RAC production. As a matter of fact, even in the countries that maximize the reuse of CDW and minimize CDW dumping (e.g. the Netherlands and Denmark), the production of RAC is residual and that question needs to be addressed.

Most applications of CDW as RA (in roads, streets and buildings' floors, in landscaping of worked-out mining infrastructures, or as drainage layers of landfills), in many cases using crushed concrete, can be classified as *downcycling* (as defined above), since the materials' characteristics are not fully profited from in these generally less-demanding applications.

Even though this concept is not consensual among researchers and authorities, it is the Author's opinion that only the use of RCA (especially recycled concrete) as RA in concrete production configures a *cycling* operation without a loss of potential of the material, i.e. sustainable.

General Barriers to the Use of CDW RA

The main barriers are related to the general management of CDW production and disposal. Depending on each country's legislative system, this problem is efficiently taken care of (e.g. in the Netherlands, Denmark, the United Kingdom, Germany), incipiently considered because the market has not yet risen to the opportunities presented by new legislation (e.g. in Portugal, Spain, Italy) or almost totally ignored (e.g. most countries from Eastern Europe).

These issues are addressed in the following ways:

- Classification of CDW, in particular addressing the problem of contamination with impurities and toxic waste;
- Reliable estimations of the CDW volume and average composition within each district to gain a global perspective of the needs for recycling plants and dependant post-processing industries;
- Appropriate legislation addressing the problems of compulsory selective demolition (without which CDW recycling is neither technically nor economically viable), environmental taxes and landscaping demands at CDW dumping sites and at stone quarries, state / municipal supervision of illegal dumping and CDW production ("environmental police"), fines for failing to comply with the legislation, among others; the price issue is fundamental, especially in regions where PA are particularly cheap and CDW RA thus become less competitive;
- Development of appropriate technical procedures (contract specifications) for selective demolition to minimize the economic gap relative to conventional demolition (always less expensive and time-consuming) and maximize the environmental impact advantages (in terms of safety, disturbance, air, water and soil impact, and - especially - reuse ratio); some of these techniques must also be used for new construction and rehabilitation sites; the waste from certain industries (e.g. precast concrete, ceramic artefacts) must also be governed by adequate processing specifications to maximize their potential for reuse;
- Tax (or other) incentives for the creation and adequate location of dedicated CDW dumping / sorting sites (recycling plants) and of firms specializing in reusing materials and components from CDW; failing to take care of this part of the problem leads inevitably to laws being broken because the CDW producers are too far from the recycling plants or pay too much for CDW disposal and the plants have no market to sell the processed materials;
- Technical specifications (quality control) for the reuse of CDW materials as raw materials for all the possible future applications, as well as for the specialized equipment (e.g. crushers, magnetic units, air blowers) and procedures adequate for

recycling plants and related industries; in various regions this and the other problems have been addressed in various pilot plants / projects.

Barriers to the Use of CDW RA in RAC Production

As noted above, the use of CDW RA in concrete production faces additional barriers that have so far prevented their widespread use, especially in structural applications. All other things being equal, PA are always preferred to RA by all the agents involved: quarry owners because of their profit; concrete manufacturers because they lack confidence in RA and the characteristics of conventional concrete tend to be better than those of RAC; structural designers because they have a deep-seated but mistaken notion that conventional concrete is less prone to execution errors than RAC and because their calculations would have to be adapted to the RA's actual characteristics and incorporation rate; contractors because there is an additional step in the process (screening and disposing of CDW), and building owners because they do not see any advantage in having to worry about and pay for selective demolition. The lack of technical specifications and of incentives to recycle CDW in concrete production is another major problem.

These issues are addressed thus:

- Each RA composition and PA/RA replacement ratio leads to the resulting concrete mix having different long-term properties; even though the first part of this problem also applies to conventional concrete, its impact is much greater in RAC, making it hard to devise specifications for structural RAC; other critical factors in terms of the performance of RAC are: target strength class of the RAC, water / cement used, cement content and type used in the RAC, size distribution and shape of the RA, percentage of cement and sand adhering to the PA for RC, compacting and curing methods used, type and quantity of plasticizers and fillers;
- In various norms (e.g. German DIN 4226-100, Hong Kong WBTC No. 12/2002, British BS 8500-2:2002, Portuguese LNEC E 471, Dutch CUR-VB-1994, and Swiss Ot 70085), the problem is solved by imposing limits on the PA/RA replacement ratio and the type of the RA used which, when complied with, lead to RAC with a performance sufficiently similar to that of conventional concrete to be considered for practical purposes as equivalent; the problem with this approach is that this strongly limits the incorporation of RA in RAC production due to the low values of the limit replacement ratios imposed and the high demands in terms of the quality control and source of the CDW; quite often only the coarse fraction of RA is accepted in structural concrete;
- Other norms (e.g. Brazilian NBR 15.116, RILEM TC 121-DRG, Belgian PTV 406) allow corrective factors to be applied to the properties of conventional concrete and thus obtain the properties of RAC; these coefficients are made to depend upon the use of pre-determined maximum replacement ratios and on the classification of the RA used; this is a generalization of the first approach where, by allowing the RAC's performance to be different (worse) than that of the equivalent conventional concrete, the use of CDW as RA is clearly enhanced; however, there are still stringent

limitations on this use, notably the need to use pre-determined types of RA which, since most CDW obtained from real situations and with undetermined origin, do not comply with; both these approaches may also include limitations in terms of the maximum strength class of RAC or other restrictions in terms of the field of application;

- The many properties that define fresh and hardened concrete performance (workability, density, compressive and tensile strength, modulus of elasticity, abrasion resistance, shrinkage, creep, water absorption, carbonation and chloride penetration) have evolve differently in RAC and conventional concrete (a very promising step forward is the study by Xiao et al (2006), where constitutive laws are provided for RAC); since most of the norms mentioned above only deal with compressive strength, they may deviate significantly from RAC's expected performance, especially in terms of durability; other properties such as the thermal, hydro-thermal and acoustic behaviour further complicate the possibility of viable predictions of the performance of RAC;
- The best approach, if possible, would be to make these predictions depend on easily obtained early results (such as characterization tests of the aggregate mixture used, including of the PA and/or RA or of concrete at early age) and to use corrective factors of the most important properties of a reference concrete to find the corresponding properties of RAC, without having to know the origin of the CDW or having to classify the resulting RA in standard classes; the next section of this Chapter presents a methodology that renders such an approach viable.

PREDICTION OF RAC'S LONG-TERM PROPERTIES

The methodology presented here, the subject of the Portuguese patent PT 103756 (2007), is based on the concept that trends that are found in conventional concrete also occur in RAC, specifically a strong dependency (and consequent correlation) of the former long-term performance on two characteristics of the aggregates (density and water absorption) and one characteristic of young concrete (7-day compressive strength).

“Aggregates” here is the mixture of fine and coarse aggregates in the composition of the RAC produced, i.e. taking into account the relative weight / replacement ratio that the RA represent in the mixture. In other words, if the replacement ratio PA/RA is small, the difference between the density and water absorption of the mixture of aggregates in the corresponding RAC is also small in comparison with those of the equivalent RC. Therefore, both the origin of the RA (through their intrinsic characteristics - density and water absorption) and the replacement ratio are simultaneously taken into account.

Methodology Proposed

This weighed value of the density of the mixture of all aggregates in the RAC composition is calculated using the density of each individual aggregate (RA and PA, fine

and coarse) and the composition of each concrete mix. The following equation is used to obtain the weighed density value (density of the mixture of aggregates):

$$D_{mix} = \frac{FA}{100} \times \left[\frac{subst_{FRA} \times D_{FRA} + (100 - subst_{FRA}) \times D_{FNA}}{100} \right] + \frac{(100 - FA)}{100} \times \left[\frac{subst_{CRA} \times D_{CRA} + (100 - subst_{CRA}) \times D_{CNA}}{100} \right] \quad (1)$$

where: D_{mix} - weighed density of the mixture of aggregates in the concrete mix;

FA - percentage of fine aggregates used in the mix;

$subst_{FRA}$ - replacement ratio of FRA by FPA;

$subst_{CRA}$ - replacement ratio of CRA by CPA;

D_{FRA} - density of the FRA;

D_{FNA} - density of the FPA;

D_{CRA} - density of the CRA;

D_{CNA} - density of the CPA.

The weighed value of the water absorption of the mixture of aggregates (wa_{mix}) used in the mix is calculated using a similar equation where the density values are replaced with the water absorption values for each of the different aggregates used.

In each experimental campaign, the values of D_{mix} and wa_{mix} can be determined for each RAC composition and for the RC using the replacement ratios FPA/FRA and CPA/CRA and the individual values of the density and water absorption of each type of aggregate (RA and PA). When available, the value of the 7-day compressive strength of hardened concrete (f_{c7}) for each RAC composition and for the RC can also be taken into account. By dividing the values of these parameters for each RAC by the corresponding values of the RC, non-dimensional factors are obtained that allow the comparison between different experimental results regardless of the source of the RA and the replacement ratios used.

For each property of hardened concrete determined within an experimental campaign, graphs can be prepared where the abscissas contain the non-dimensional values described above (one at a time) and the ordinates contain the ratio between the value of the property for each RAC mix and the value of the same property for the corresponding RC. By gathering the results of various campaigns it is possible to have a statistically significant number of results and to determine a linear regression trend-line that is valid for any RAC, no matter what the origin of the RA used and their replacement ratio.

In the data collection (international and Portuguese literature review) described next, the establishment of these linear correlations between the concrete mixes' properties and the aggregate mixture's density and water absorption, as well as the compressive strength of concrete at the age of 7 days, a graphic analysis methodology was created. It involved the following steps:

- Analysis and organization of available data from each experimental campaign, including information on the test results for the properties of the aggregates used to make concrete;

- Calculation of the exact value of the density and water absorption of the mixture of aggregates used in the mix, through the mix proportions of the concretes (with primary aggregates PA only and with recycled aggregates RA) and the individual density and water absorption of the aggregates (natural and recycled);
- Graphical analysis of the relationship between the replacement ratio of PA by RA and each property of concrete;
- Graphical analysis of the variation of the ratio between the properties of the concrete with RA (RAC) and the one with PA only (conventional reference concrete RC) and the replacement ratio of NA by RA;
- Graphical analysis of the variation of the ratio between the properties of the RAC and the RC and the ratio between the weighed value of the density of the mixture of aggregates (D_{mix}) in the RAC and the RC;
- Graphical analysis of the variation of the ratio between the properties of the RAC and the RC and the ratio between the weighed value of the water absorption of the mixture of aggregates (wa_{mix}) in the RAC and the RC;
- Graphical analysis of the variation of the ratio between the properties of the RAC and the RC and the ratio between the compressive strength at 7 days (f_{c7}) of the RAC and the RC;
- Superposition of the graphical results of each concrete property for the various campaigns analyzed and determination of the linear regression lines with the respective correlation coefficient;
- Correction of the linear regression lines obtained, so that they represent the physical behaviour under analysis, forcing them to pass through the point that corresponds to the RC, with the nuisance of lowering the respective correlation coefficient;
- Compilation of the data in a table, including the slope of the linear regression line and the respective correlation coefficient.

In order to analyse this graphical summary for each property, qualitative criteria were established so that it would be possible to classify the corresponding correlation value. This classification is presented in Table 5.

Table 5. Qualitative classification of the correlation values obtained in the graphical analysis of the experimental campaign literature review (Robles 2007) (Alves 2007)

Classification	Values range
Very good	$R^2 \geq 0.95$
Good	$0.80 [R^2 < 0.95$
Acceptable	$0.65 [R^2 < 0.80$
Not acceptable	$R^2 < 0.65$

Literature Reviews

To implement the methodology described above, two literature reviews were conducted, each resulting in a Masters Thesis:

- An international review by Robles (2007);
- A Portuguese review by Alves (2007).

These reviews were guided by the criteria below:

- Availability of the tests results performed on RA and PA, especially in terms of water absorption and density;
- Availability of the experimental values relative to the greatest possible number of concrete properties in the fresh and hardened states (mechanical and durability-related), especially the 7-day compressive strength;
- The greatest possible PA/RA replacement ratio options;
- The greatest possible number of fixed parameters (e.g. water / cement ratio, grading curve, workability, curing method) during the experimental production of RAC;
- Existence of a reference concrete, without which the corresponding campaign was eliminated from the survey.

The criterion related to the fixed parameters is of paramount importance. As a matter of fact, since the whole purpose of this research is to isolate the impact of the direct replacement of PA with RA, it is essential that all other factors that may disturb the understanding of this influence are eliminated. The following factors are the most important (but not the only) ones since, when they change, almost every concrete property can be affected thus masking the influence of the replacement PA/RA and jeopardizing the objectives of the study:

- Effective water / cement ratio (differentiating the total amount of water introduced into the mix from that which effectively contributes to the hydration of the cement and the workability of fresh concrete); this property has a strong influence on the concrete's mechanical performance, but even more on its durability;
- Workability (this property must be maintained by using plasticizers or increasing the total amount of water without increasing the effective water / cement ratio, for example, by pre-saturating the recycled aggregates); for practical purposes, concrete mixes with different workability levels may not have the same range of applications and therefore should not be directly compared;
- Grading curve (size distribution) of the aggregates (when replacing PA with RA this curve should be kept exactly constant because any change leads to uncontrolled shifts in almost every relevant property of concrete);
- In the case of RA from recycled concrete, the origin / nature of the original PA should not differ drastically from that of the PA used in to make the RAC and RC.

Surprisingly, since the number and quality of the references accessed was much greater than for the Portuguese literature review, it was more difficult to find international literature references that complied with these criteria. The main reasons for this were (Robles 2007):

- Significant differences at the level of procedures and of organization / presentation of the results;
- Unavailability of data due to existing information being excluded from the test

description or because relevant data were simply not determined (absence of data on the aggregates' properties, both RA and PA, or on the composition of the concrete mixes tested, lack of specification on whether the water / cement ratio specified was the global or the effective w/c ratio);

- Variability of individual factors of each campaign.

Since most of the campaigns on RAC in Portugal took place at the same location (IST - Instituto Superior Técnico in Lisbon) and under the same supervision, the criteria used in the tests and in the presentation of the results were basically the same, which was crucial to the outcome of the literature review.

In both cases, a database (much too large to be presented here) was prepared where all the information collected was organized so as to facilitate perception of the main points analyzed in each experimental campaign. The main points recorded in the database were (Robles 2007):

- The origin of the RA: concrete, ceramic, the two types, and undifferentiated;
- The grading of the aggregates replaced: coarse, fine or both;
- The fixed parameters, i.e. those that remained constant in the production of the various families of concrete mixes (e.g. water / cement ratio, grading curve, compressive strength, mass or volume proportions, workability, cement content);
- The parameters that varied, i.e. the criteria that defined the various RAC families produced that were correlated with the variation of the concrete properties in the fresh and hardened states (e.g. replacement ratio of PA with RA, water / cement ratio, added flying ash or synthetic fibre content, type of curing used, RA density, RA age at crushing, type of cement, surface treatment of the RA, age at testing);
- The tests performed on aggregates (e.g. density, water absorption, abrasion resistance, retained water content, grading curve, fineness module, crushing resistance, bulk density, frost resistance, shape coefficient);
- The tests performed on fresh concrete (e.g. workability, density, bleeding, and air content); the test standard is also provided when known;
- The tests performed on hardened concrete (e.g. compressive strength, flexural and splitting tensile strength, creep, shrinkage, abrasion resistance, chloride and carbonation penetration resistance, water absorption, density, porosity, permeability); the test standard is also provided when known.

Short Description of the Experimental Campaigns Selected

Given the difficulties mentioned above, only a relatively small number of experimental campaigns were selected for analysis in each literature review. Their results are analyzed in the next section and the resulting conclusions presented for each property of hardened concrete.

The following experimental campaigns that complied with the criteria defined above were analysed in the international literature review:

- Leite (2001), at the Federal University of Rio Grande do Sul (UFRGS), tested replacement ratios of 0, 11.5, 50, 88.5 and 100% of coarse and fine natural aggregates with coarse and fine concrete and ceramic aggregates to determine the compressive and tensile strength and modulus of elasticity of hardened concrete;
- Soberón (2002), at the Technical University of Catalonia (UTC), tested replacement ratios of 0, 15, 30, 60 and 100% of coarse natural aggregates with coarse concrete aggregates to determine the porosity, density, permeability, compressive and tensile strength, modulus of elasticity, shrinkage, creep and water absorption of hardened concrete;
- Katz (2003), at the Israel Institute of Technology (IIT), tested replacement ratios of 0 and 100% of coarse and fine natural aggregates with coarse and fine concrete aggregates to determine the compressive and tensile strength, modulus of elasticity, shrinkage, water absorption and carbonation penetration of hardened concrete;
- Kou et al (2004), at the Hong Kong Polytechnic University (HKPU), tested replacement ratios of 0, 20, 50 and 100% of coarse natural aggregates with coarse undifferentiated aggregates to determine the compressive strength, modulus of elasticity, shrinkage and chloride penetration of hardened concrete;
- Carrijo (2005), at the São Paulo University (USP), tested replacement ratios of 0 and 100% of coarse basaltic aggregates with coarse concrete and ceramic aggregates to determine the compressive strength, water absorption by immersion and modulus of elasticity of hardened concrete;
- Cervantes et al (2007), at the University of Illinois (UI), tested replacement ratios of 0, 50 and 100% of coarse natural aggregates with coarse concrete aggregates to determine the compressive and tensile strength, shrinkage and modulus of elasticity of hardened concrete.

The following experimental campaigns that complied with the criteria defined above were analysed in the Portuguese literature review:

- Rosa (2002), at the Technical University of Lisbon (IST), tested replacement rates of 1/3, 2/3 and 3/3 of coarse limestone aggregates with coarse recycled ceramic aggregates to determine the compressive and tensile strength, abrasion resistance, water absorption by capillarity and immersion of hardened concrete;
- Rocha and Resende (2004), at the University of Aveiro (UA), tested replacement rates of 50 and 100% of coarse granite aggregates with coarse recycled concrete aggregates to determine the density, compressive and tensile strength and modulus of elasticity of hardened concrete;
- Figueiredo (2005), at the Faculty of Engineering of Porto University (FEUP), tested replacement rates of 50 and 100% of coarse granite aggregates with coarse recycled concrete and white ceramic aggregates to determine the compressive and tensile strength, modulus of elasticity, abrasion resistance, shrinkage, water absorption by capillarity and immersion, carbonation and chloride penetration of hardened concrete;
- Matias and de Brito (2005), at IST, tested replacement rates of 25, 50 and 100% of fine limestone aggregates with fine recycled concrete aggregates (with a focus on the

use of super-plasticizers) to determine the compressive and tensile strength, abrasion resistance, shrinkage, water absorption by capillarity and immersion, carbonation and chloride penetration of hardened concrete;

- Evangelista (2007), at IST, tested replacement rates of 10, 20, 30, 50 and 100% of fine limestone aggregates with fine recycled concrete aggregates to determine the compressive and tensile strength, modulus of elasticity, abrasion resistance, shrinkage, water absorption by capillarity and immersion, carbonation and chloride penetration of hardened concrete;
- Gomes (2007), at IST, tested various combinations of replacement rates of coarse limestone aggregates with coarse recycled concrete, ceramic and mortar aggregates to determine the compressive and tensile strength, modulus of elasticity, shrinkage, water absorption by capillarity and immersion, carbonation and chloride penetration of hardened concrete;
- Ferreira (2007), at IST and Polytechnic University of Barcelona (UPC), tested replacement rates of 20, 50 and 100% of coarse limestone aggregates with coarse recycled concrete aggregates (with a focus on the pre-saturation of recycled aggregates) to determine the density, compressive strength, modulus of elasticity, shrinkage and water absorption by capillarity and immersion of hardened concrete.

RESULTS AND DISCUSSION

General Remarks

The methodology proposed above made it possible to compare directly results from different experimental campaigns with different test procedures and norms, different origins and sizes of RA, and various other factors that led to the dispersion of results (e.g. curing method, addition of flying ash or synthetic fibres, different strength classes, different w/c ratios, different crushing ages of recycled concrete aggregates).

Therefore, the linearity (measured by the correlation factor R^2) exhibited by each individual experimental campaign for each property naturally decreased when other experimental campaigns' results were juxtaposed in the same graph. There was a further reduction of the correlation factors obtained when the linear regression lines in each graph were corrected to pass through the point that corresponds to the RC, to make them representative of the physical behaviour under analysis.

As a consequence of these two situations the correlation factors obtained for each of the properties of hardened concrete with the three parameters selected (density and water absorption of the mixture of aggregates used in the concrete mix and 7-day compressive strength of the concrete mix) were not always high enough to prove the accuracy of the methodology beyond doubt. However, it must be stated that similar rates of dispersion of the results would be obtained for conventional concrete (i.e. without recycled aggregates) and that RAC therefore does not exhibit higher scatter than conventional concrete.

In the following points all the more relevant properties of hardened concrete (from a mechanical and a durability point of view) are analyzed using the methodology proposed, and the results are described and explained based on the intrinsic properties of RA and their

effects on hardened concrete. These properties include density, compressive strength, modulus of elasticity, splitting and flexural tensile strength, abrasion resistance, shrinkage, creep, water absorption by capillarity and immersion, carbonation and chloride penetration resistance.

Most of these properties showed a poorer performance for RAC than for the corresponding RC, as expected and in agreement with the international and Portuguese studies cited above, and others mentioned in the references.

Density

Only the Portuguese literature review collected results on RAC's density.

Figures 4, 5 and 6 show the relationship of the ratio between the hardened concrete densities and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of the concrete, respectively. The correlation coefficients determined (see Table 5) are respectively good, acceptable and not acceptable.

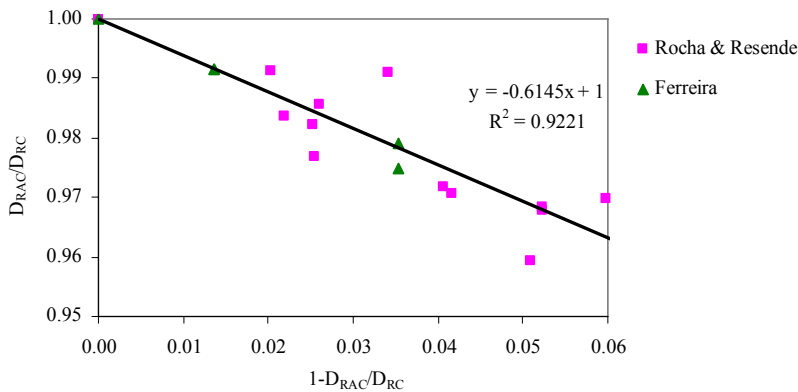


Figure 4. Ratio between hardened concrete densities *versus* the ratio between the densities of the mixture of aggregates (Alves 2007)

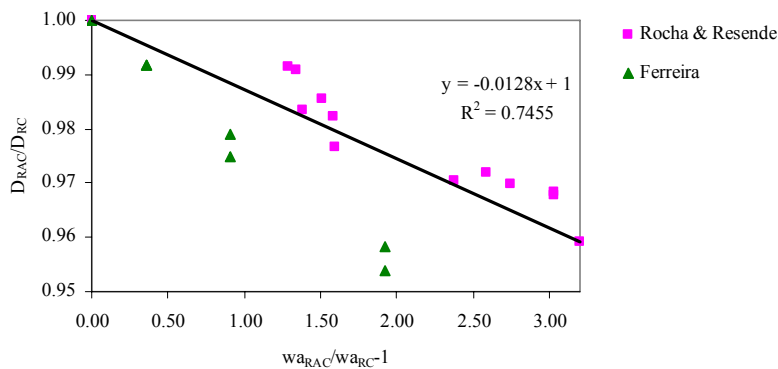


Figure 5. Ratio between hardened concrete densities *versus* the ratio between the water absorptions of the mixture of aggregates (Alves 2007)

For every parameter used as an indicator, the concrete density decreases with the replacement ratio. This is because of the lower density of the recycled aggregates, due to their lower intrinsic porosity (in ceramic and mortar aggregates) or the mortar adhering to the original aggregates (in recycled concrete aggregates).

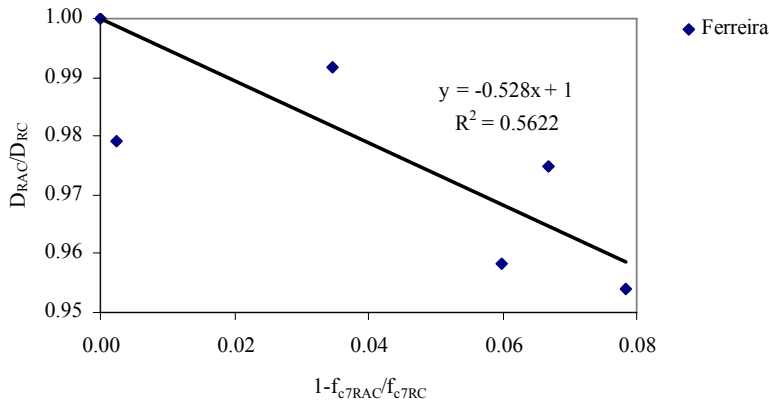


Figure 6. Ratio between hardened concrete densities *versus* the ratio between the concrete's 7-day compressive strengths (Alves 2007)

Compressive Strength

The international and the Portuguese literature reviews both contain many results on RAC's compressive strength, since it is the most defining property of hardened concrete. Other references analyzed but not included in the graphs are: Angulo (1998), Angulo (2005), Azzouz et al (1998), Barra and Vázquez (1998), Buttler (2003), Buyle-Bodin and Hadjieva-Zaharieva (2002), Chen et al (2003), Corinaldesi (2003), Etxeberria et al (2004), Etxeberria et al (2006), Fraaij et al (2002), Juan and Gutiérrez (2004), Larrañaga (2004), Latterza and Machado (2003), Levy (2001), Levy and Helene (2004), Limbachiya et al (2000), Lin et al (2004), Khatib (2004), Kimura et al (2004), Knights (1998), Mendes et al (2004), Merlet and Pimienta (1993), Muller (2004), Oliveira et al (2004), Roos (1998), Sagoe-Crentsil (2001), Sugiyama (2004), Tsujino et al (2007), Vieira et al (2004), and Wainwright et al (1994).

Figures 7, 8 and 9 respectively show the relationship of the ratio between the compressive strengths of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively good, not acceptable and not acceptable.

Even though the correlation coefficients were disappointingly low in two of the cases (due to the large number and variety of studies juxtaposed in the same graph), it is still possible to identify a clear trend towards a decrease in compressive strength as the replacement ratio increases, explained by the lower mechanical characteristics of the ceramics and of the mortar adhering to the natural aggregates (in recycled concrete).

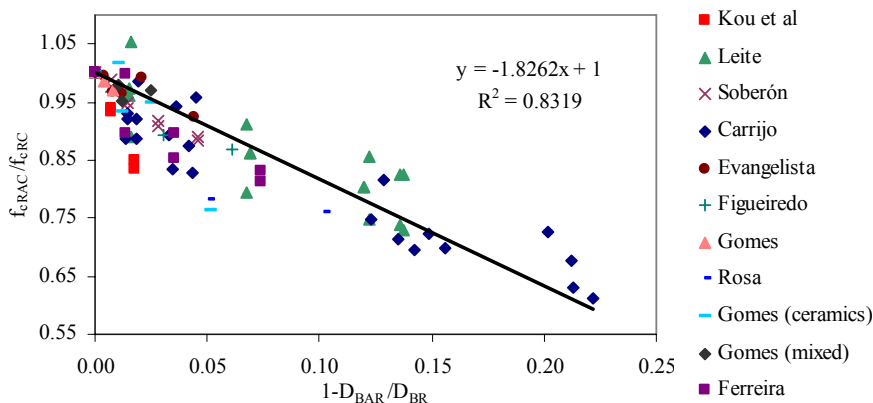


Figure 7. Ratio between concrete compressive strengths *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

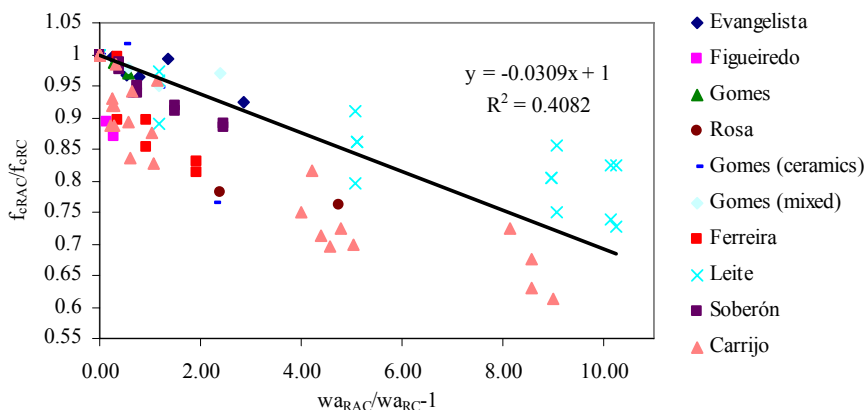


Figure 8. Ratio between concrete compressive strengths *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

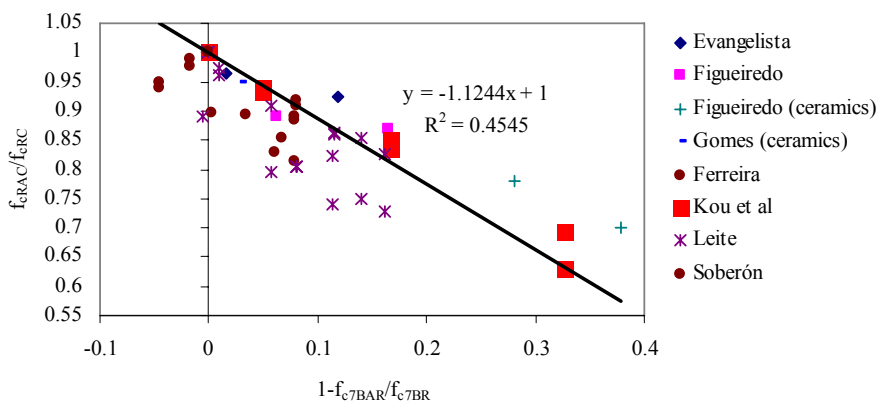


Figure 9. Ratio between concrete compressive strengths *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

Modulus of Elasticity

Both the international and the Portuguese literature reviews contain many results on RAC's modulus of elasticity, another of the most defining properties of hardened concrete. Other references analyzed but not included in the graphs are: Angulo (2005), Azzouz et al (1998), Barra and Vázquez (1998), Buttler (2003), Chen et al (2003), Etxeberria et al (2004), Etxeberria et al (2006), Juan and Gutiérrez (2004), Larrañaga (2004), Latterza and Machado (2003), Levy (2001), Khatib (2004), Mendes et al (2004), Merlet and Pimienta (1993), Oliveira et al (2004), Roos (1998), Sugiyama (2004), and Tsujino et al (2007).

Figures 10, 11 and 12 display the relationship of the ratio between the modules of elasticity of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively acceptable, acceptable and not acceptable.

Again there is a clear trend towards a fall in the mechanical property of hardened concrete (in this case the modulus of elasticity) as the replacement ratio increases. The reason is the same as for the compressive strength, even though this time it is related to the lower stiffness of the recycled aggregates. A very interesting conclusion is that the slope of the correlation lines is higher for the modulus of elasticity than for the compressive strength in every parameter, confirming a trend of higher loss of stiffness of RAC reported in the literature review undertaken within the study.

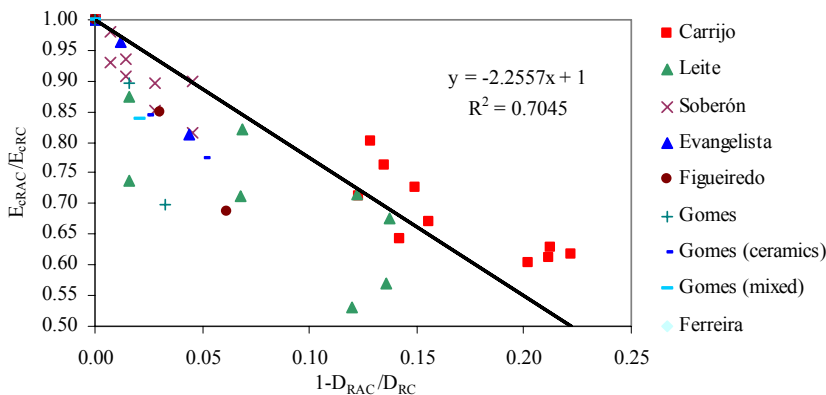


Figure 10. Ratio between concrete modules of elasticity *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

Splitting Tensile Strength

Both the international and the Portuguese literature reviews contain results on RAC's splitting tensile strength. Other references analyzed but not included in the graphs are: Angulo (1998), Buttler (2003), Corinaldesi (2003), Etxeberria et al (2004), Juan and Gutiérrez (2004), Larrañaga (2004), Latterza and Machado (2003), Merlet and Pimienta (1993), Sagoe-Crentsil (2001), and Tsujino et al (2007).

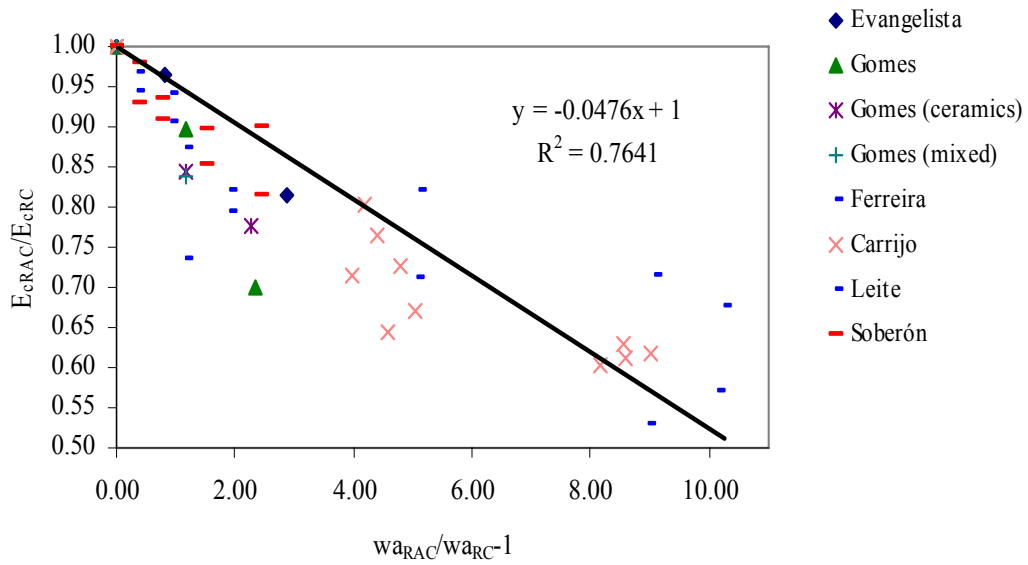


Figure 11. Ratio between concrete modules of elasticity *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

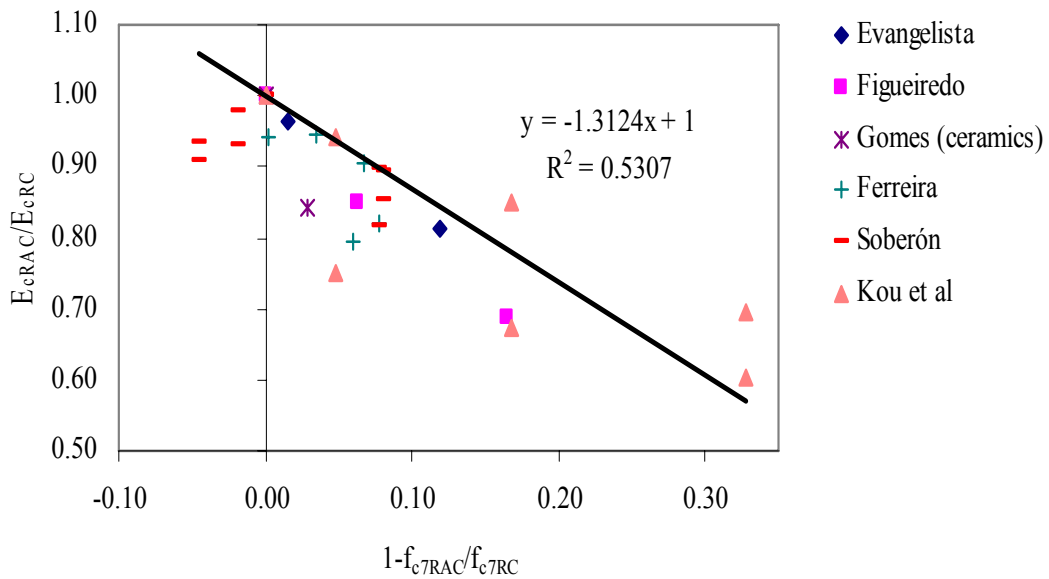


Figure 12. Ratio between concrete modules of elasticity *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

Figures 13, 14 and 15 display the relationship of the ratio between the splitting tensile strengths of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively acceptable, not acceptable and not acceptable.

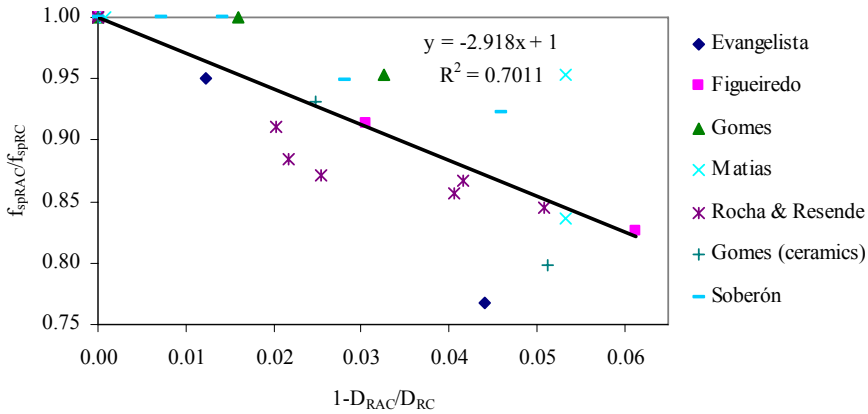


Figure 13. Ratio between concrete splitting tensile strengths *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

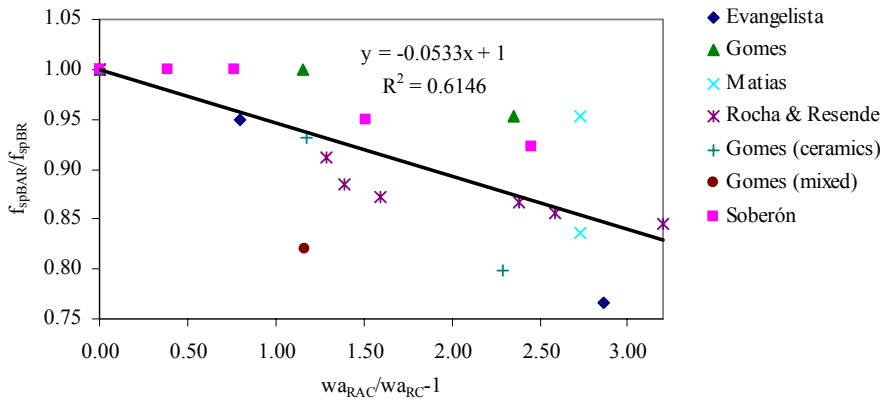


Figure 14. Ratio between concrete splitting tensile strengths *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

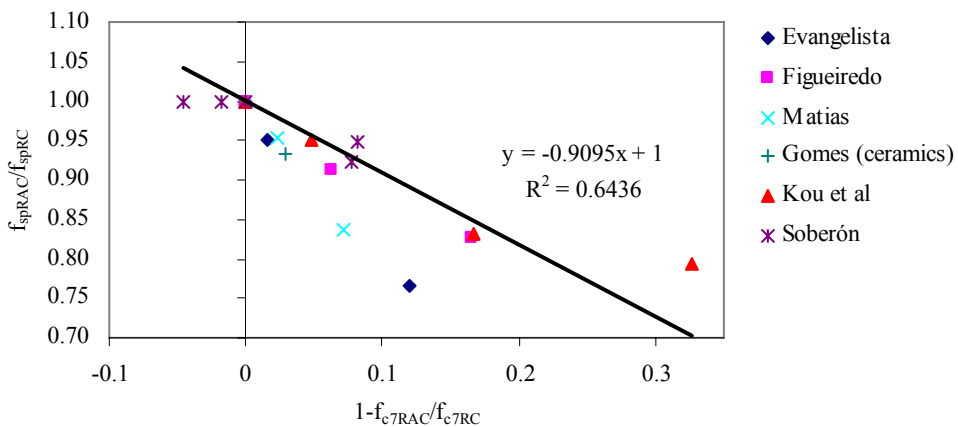


Figure 15. Ratio between concrete splitting tensile strengths *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

Once again, the lower mechanical properties of RA when compared with PA lead to a decrease in the splitting tensile strength of the former as the replacement ratio increases. Notwithstanding the relatively low values of the correlation factors, the slope of the correlation lines is generally higher than for the compressive strength and even for the modulus of elasticity (except for the correlation with the 7-day compressive strength of concrete). This contradicts existing literature that states that the RAC is slightly less sensitive to the inclusion of these aggregates for tensile strength than for compressive strength and even more than for the modulus of elasticity. A possible explanation for this is the well known scatter that is usually registered in the results for the splitting tensile strength of concrete, both RAC and conventional.

Flexural Tensile Strength

Both the international and the Portuguese literature reviews contain results on RAC's splitting tensile strength, though very few (no correlations between this property and the 7-day compressive strength of concrete were found in the Portuguese literature review). Other references analyzed but not included in the graphs are: Chen et al (2003), Etxeberria et al (2006), and Latterza and Machado (2003).

Figures 16, 17 and 18 show the relationship of the ratio between the flexural tensile strengths of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively acceptable, good and good.

Conclusions are the same as for splitting tensile strength, except that this property seems to be less sensitive to the inclusion of recycled aggregates (the exception is the correlation with the 7-day compressive strength of concrete). However, these conclusions are only provisional due to the small number of valid results obtained and experimental campaigns analysed.

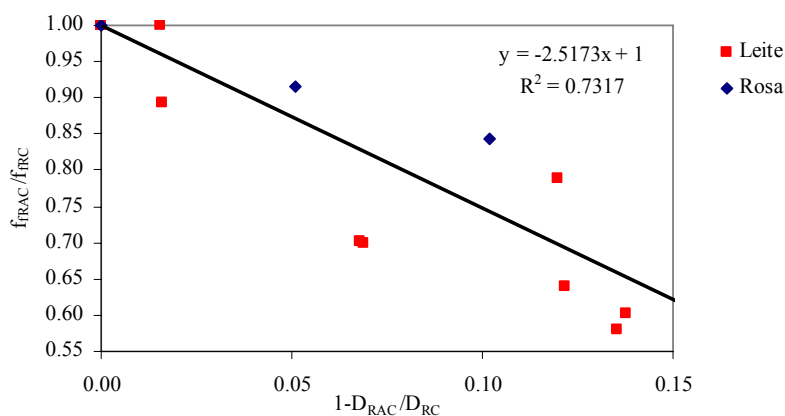


Figure 16. Ratio between concrete flexural tensile strengths *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

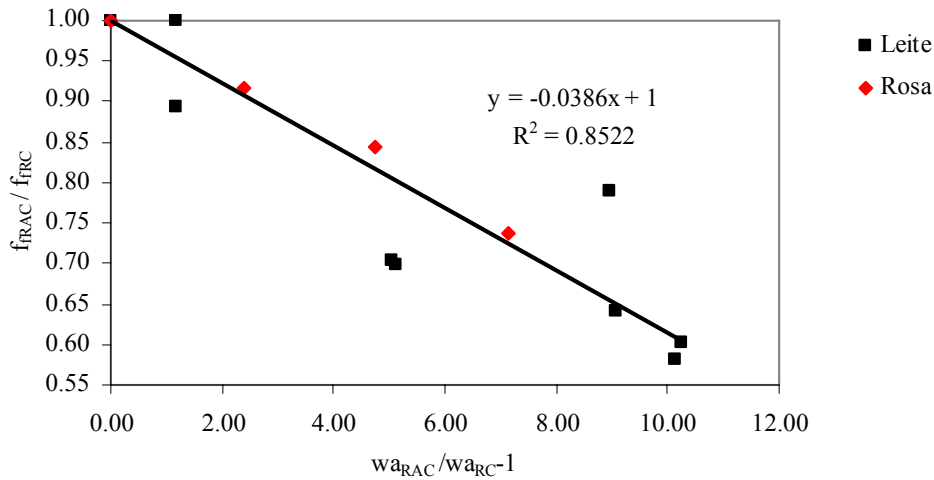


Figure 17. Ratio between concrete flexural tensile strengths *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

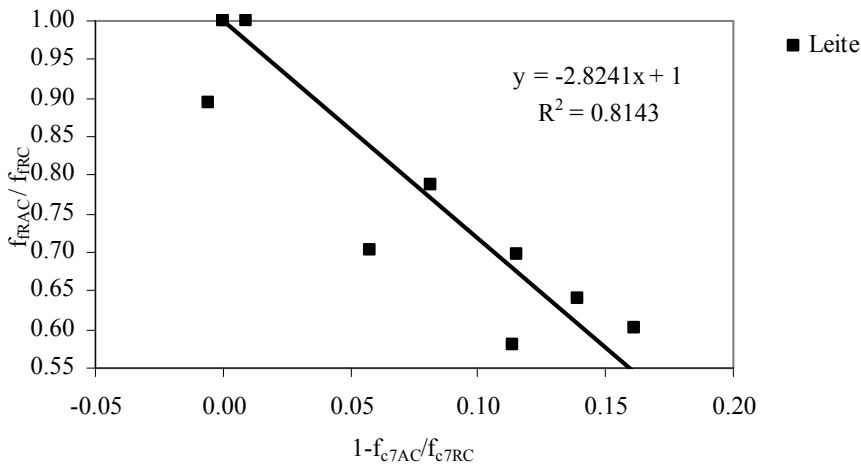


Figure 18. Ratio between concrete flexural tensile strengths *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007)

Abrasion Resistance

Only the Portuguese literature review contains results on RAC's abrasion resistance, a relatively unimportant property in terms of concrete's most common applications. Other references analyzed but not included in the graphs are: Latterza and Machado (2003), Limbachiya et al (2000), and Sagoe-Crentsil (2001).

Figures 19, 20 and 21 display the relationship of the ratio between the abrasion resistances (inversely proportional to the loss of mass) of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively good, good and not acceptable.

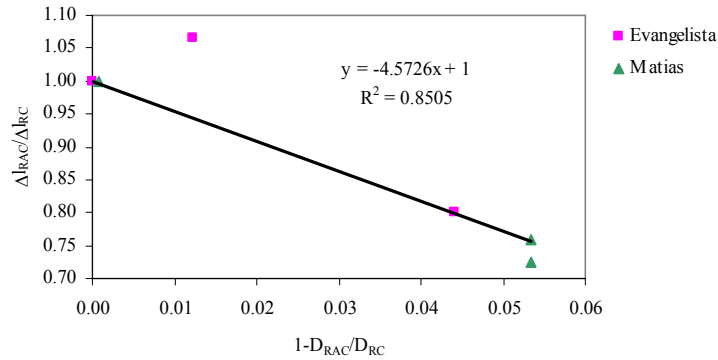


Figure 19. Ratio between concrete abrasion mass losses *versus* the ratio between the densities of the mixture of aggregates (Alves 2007)

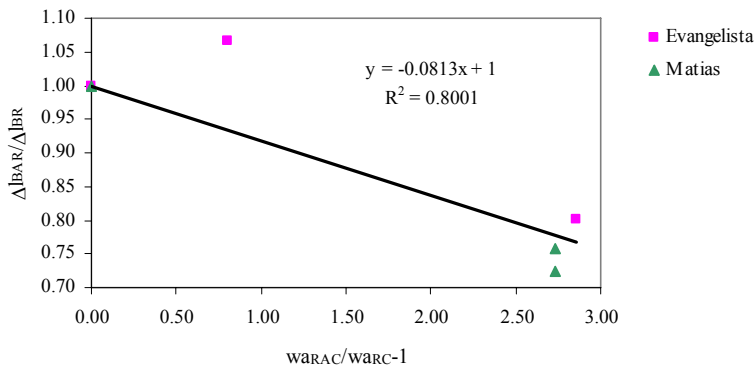


Figure 20. Ratio between concrete abrasion mass losses *versus* the ratio between the water absorptions of the mixture of aggregates (Alves 2007)

The abrasion resistance of RAC tends to increase (less loss of mass) as the replacement ratio increases, which is explained in the meagre existing literature by greater adherence between particles provided by the more porous surface of recycled aggregates. This is the only property analysed where RAC performs markedly better than conventional concrete.

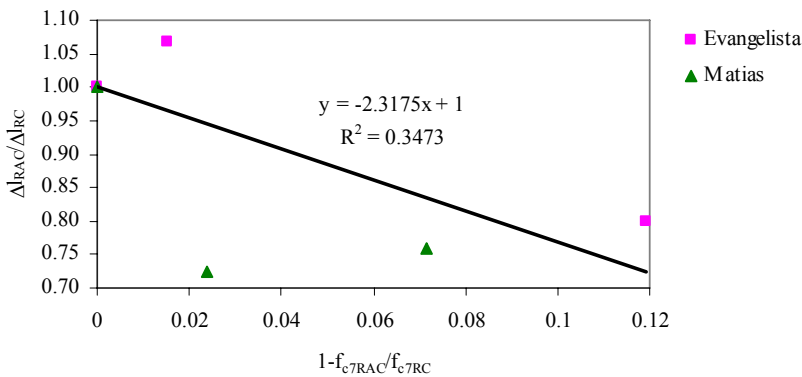


Figure 21. Ratio between concrete abrasion mass losses *versus* the ratio between the concrete 7-day compressive strengths (Alves 2007)

Shrinkage

Both the international and the Portuguese literature reviews contain results on RAC's shrinkage, a particularly defining characteristic of hardened concrete. Other references analyzed but not included in the graphs are: Azzouz et al (1998), Buyle-Bodin and Hadjieva-Zaharieva (2002), Corinaldesi (2003), Fraaij et al (2002), Juan and Gutiérrez (2004), Limbachiya et al (2000), Khatib (2004), Kimura et al (2004), Merlet and Pimienta (1993), Roos (1998), and Sagoe-Crentsil (2001).

Figures 22, 23 and 24 show the relationship of the ratio between the shrinkages of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. All the correlation coefficients are considered not acceptable, which may be explained by the great influence that curing conditions have on shrinkage results and by the fact that it could not be known in detail which curing conditions were used in each experimental campaign.

Shrinkage of hardened concrete is greatly affected by the porosity of the aggregates and their stiffness and, regardless of the poor correlation factors determined, shows a clear trend towards increasing with the PA/RA replacement ratio. This was expected, based on the relative properties of the RA and on the literature review. Another common conclusion in the literature is that shrinkage is the most sensitive property in terms of the inclusion of recycled aggregates, and this is confirmed in the present study by the considerably higher slopes of the correlation lines, even higher than those for the modulus of elasticity.

Creep

Creep is one of the least studied properties of concrete because testing is both costly and time-consuming. Therefore, only the international literature review contains results on RAC's creep. Other references analyzed but not included in the graphs are: Fraaij et al (2002), Limbachiya et al (2000), Kimura et al (2004), Mendes et al (2004), and Roos (1998).

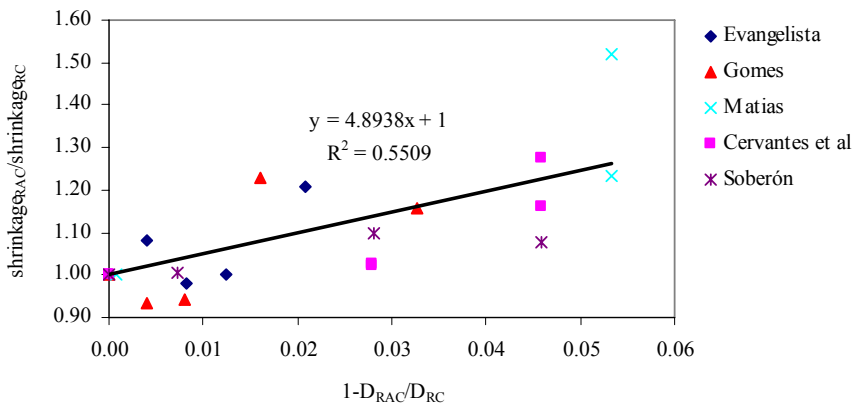


Figure 22. Ratio between concrete shrinkages *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

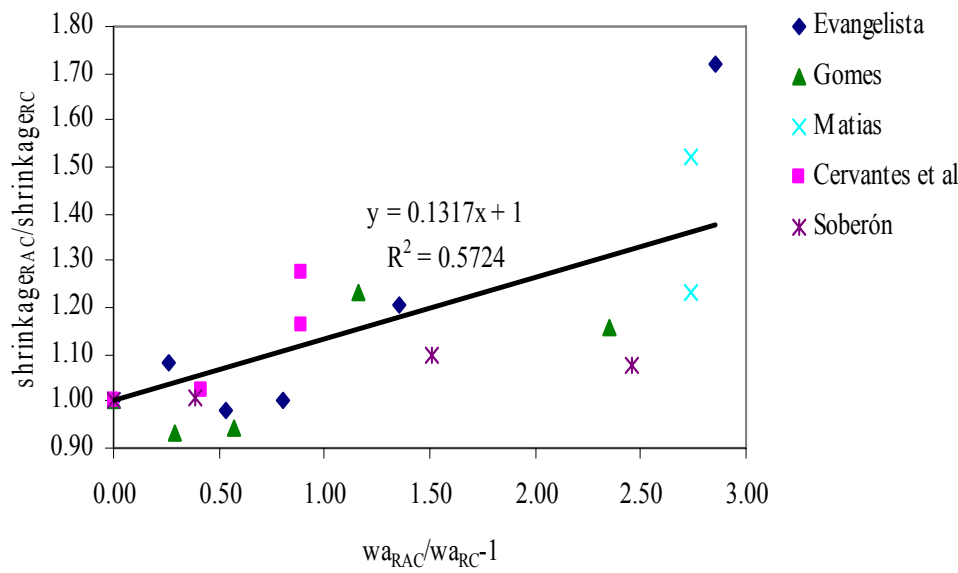


Figure 23. Ratio between concrete shrinkages *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

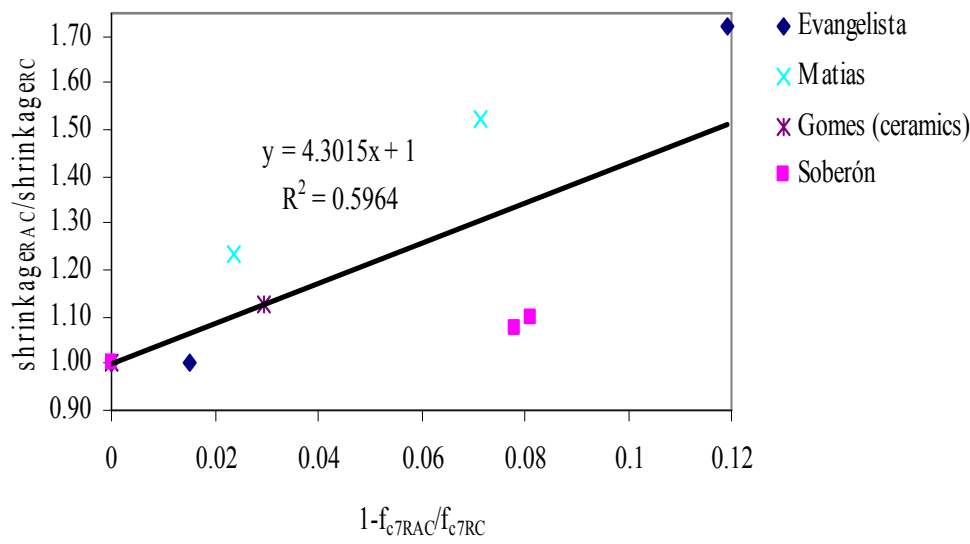


Figure 24. Ratio between concrete shrinkages *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

Figures 25, 26 and 27 display the relationship of the ratio between the creep of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. All the correlation coefficients are considered very good, which is mostly due to the fact that only one experimental campaign (Soberón 2002) was used for the graphs.

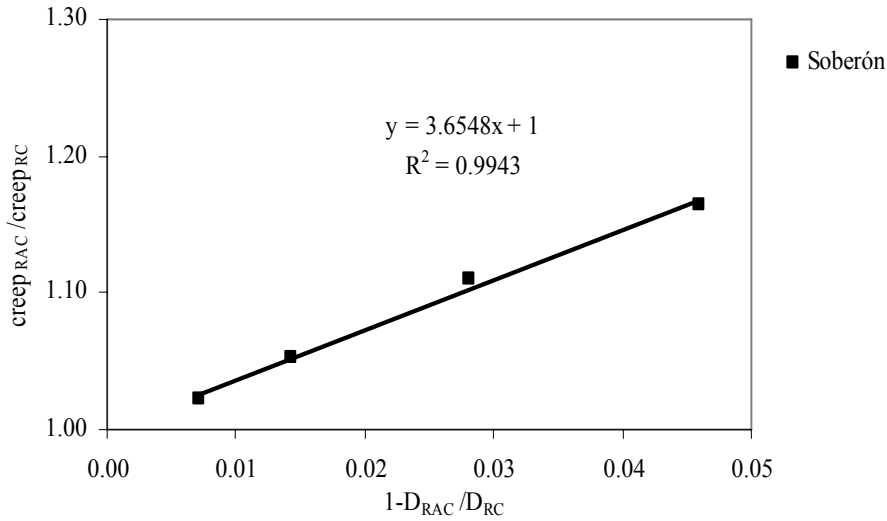


Figure 25. Ratio between concrete creep *versus* the ratio between the densities of the mixture of aggregates (Robles 2007)

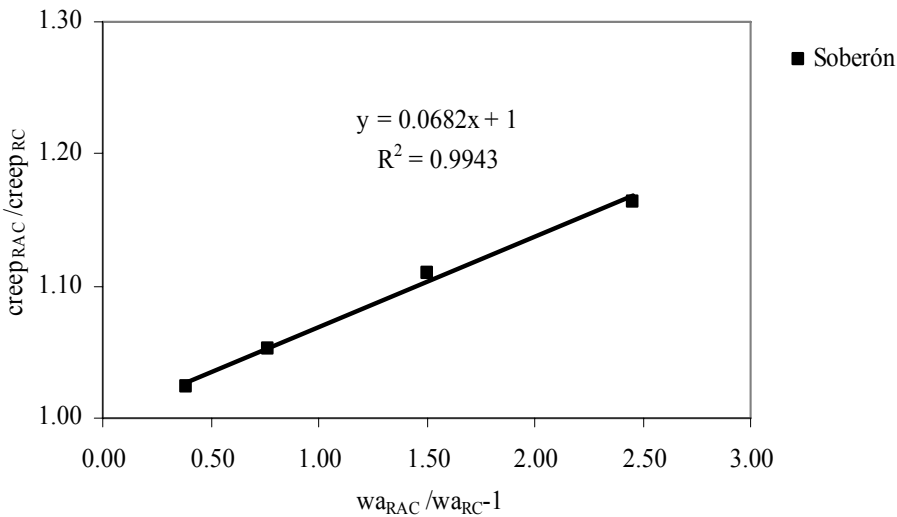


Figure 26. Ratio between concrete creep *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007)

The lower stiffness of RA when compared with PA contributes to higher creep with increasing replacement ratio of PA with RA, as seen in Figures 25 to 27. Also, a hypothetical increment of the w/c ratio, to balance the higher water absorption of RA compared with PA, can contribute to higher values of creep in the concrete made with RA. The few studies listed above on creep in RCA suggest a slightly better behaviour than for shrinkage. However, the slopes of the correlation lines obtained from the Soberón study (2002) are slightly higher than those in Figures 25 and 26 (the exception is Figure 27, in relation to the 7-day compressive strength of concrete). The small number of valid results in terms of both shrinkage and creep does not allow definitive quantitative conclusions.

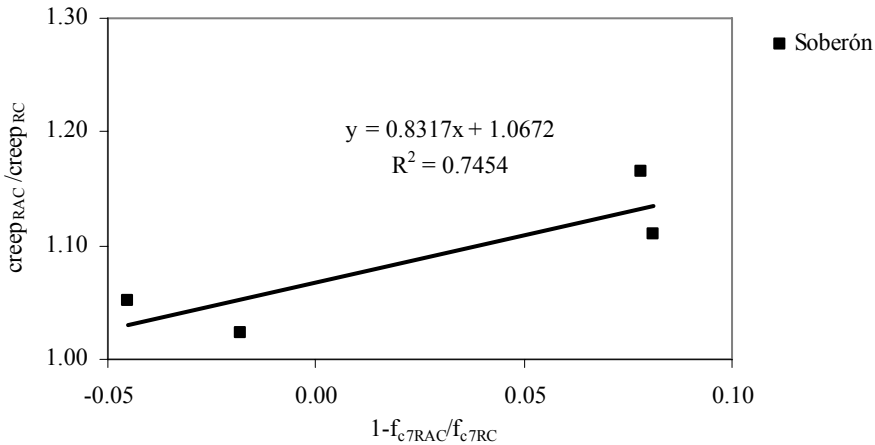


Figure 27. Ratio between concrete creep *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007)

Water Absorption by Capillarity

Only the Portuguese literature review contains results on RAC's water absorption by capillarity. Only one international reference was found for this property in RCA (Limbachiya et al 2000), but was not used to build the graphs.

Figures 28, 29 and 30 display the relationship of the ratio between the capillary water absorptions of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. All the correlation coefficients are considered not acceptable and are very low, which may be an indication that for this particular property the methodology proposed is not appropriate for quantitative estimations.

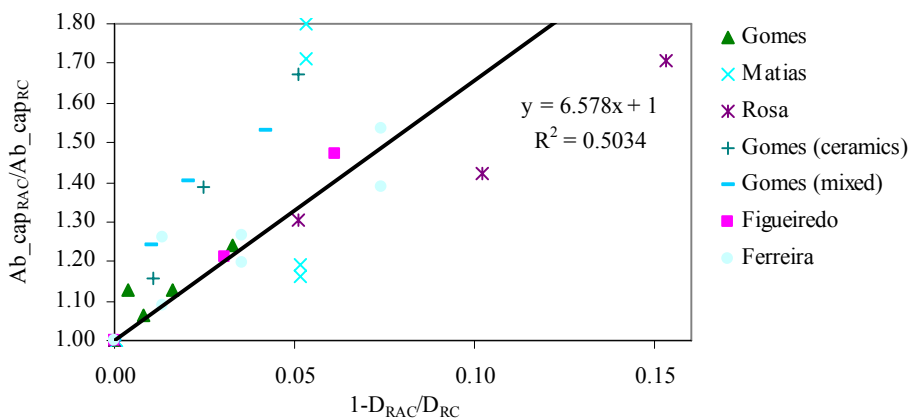


Figure 28. Ratio between concrete capillary water absorptions *versus* the ratio between the densities of the mixture of aggregates (Alves 2007)

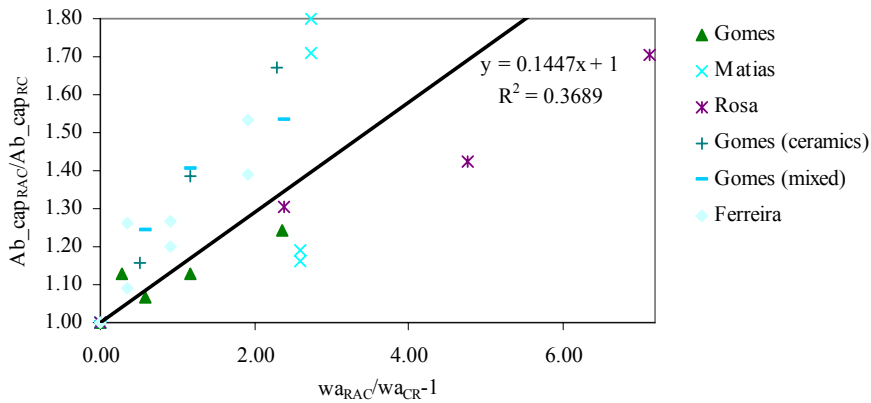


Figure 29. Ratio between concrete capillary water absorptions *versus* the ratio between the water absorptions of the mixture of aggregates (Alves 2007)

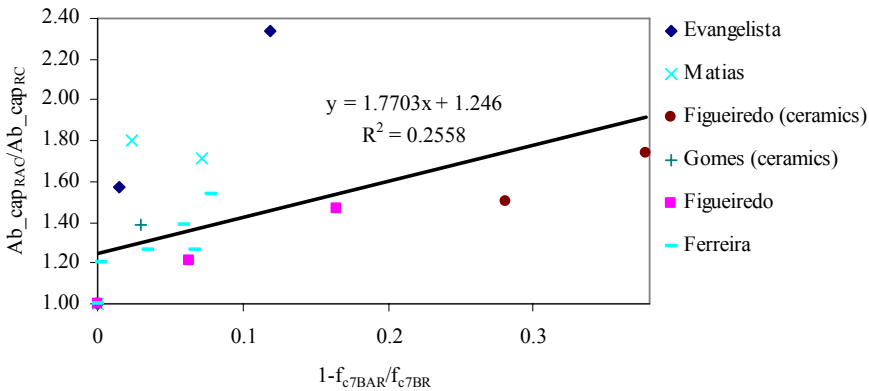


Figure 30. Ratio between concrete capillary water absorptions *versus* the ratio between the concrete 7-day compressive strengths (Alves 2007)

Even though the correlation obtained is poor, the trend is very clear for all the parameters and it shows the strong impact of the higher porosity of the RA on the water absorption by capillarity, an impact that is even greater than that found for shrinkage and creep (except for the correlation found between shrinkage and the 7-day compressive strength of concrete). Again, this confirms the literature, which singles out durability, along with volume stability, as the performance aspects of RCA exhibiting the greatest losses.

Water Absorption by Immersion

Both the international and the Portuguese literature reviews contain results on RAC's water absorption by immersion. Other references analyzed but not included in the graphs are: Angulo (2005), Azzouz et al (1998), Barra and Vázquez (1998), Buttler (2003), Buyle-Bodin and Hadjieva-Zaharieva (2002), Levy (2001), Levy and Helene (2004), Knights (1998), Merlet and Pimienta (1993), Oliveira et al (2004), Olorunsogo and Padayachee (2001), Sagoe-Crentsil (2001), and Wirquin et al (2000).

Figures 31, 32 and 33 show the relationship of the ratio between the water absorptions by immersion of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively not acceptable, acceptable and good.

The conclusions are similar to those for water absorption by capillarity, with similar slopes (higher in two cases) in terms of correlation lines, proving once again the great susceptibility of concrete made with RA to absorb water.

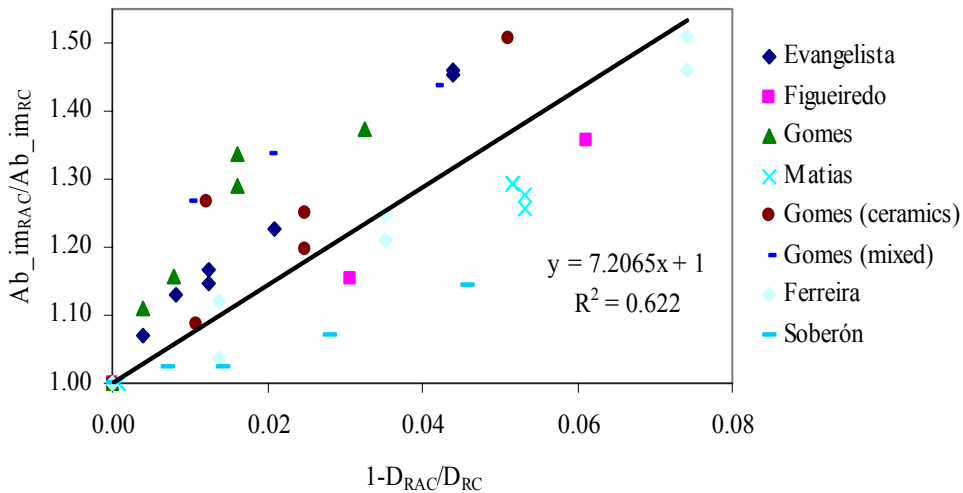


Figure 31. Ratio between concrete water absorptions by immersion *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

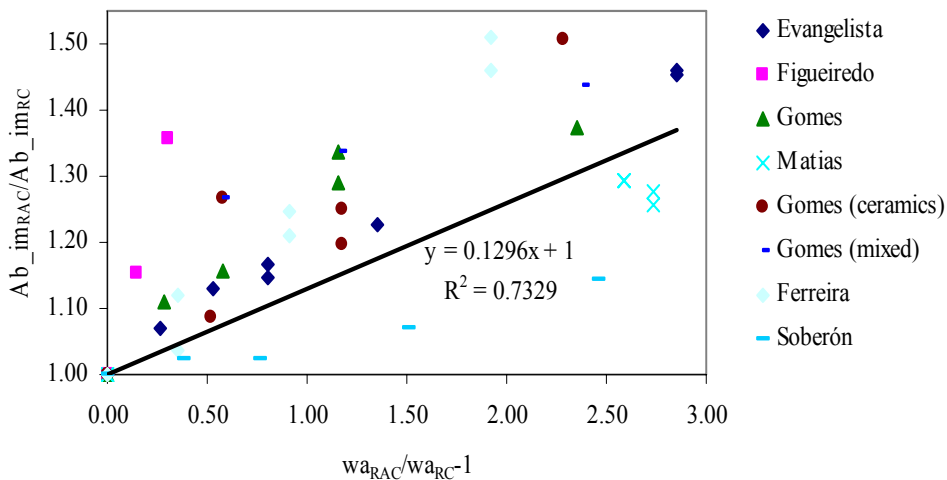


Figure 32. Ratio between concrete water absorptions by immersion *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

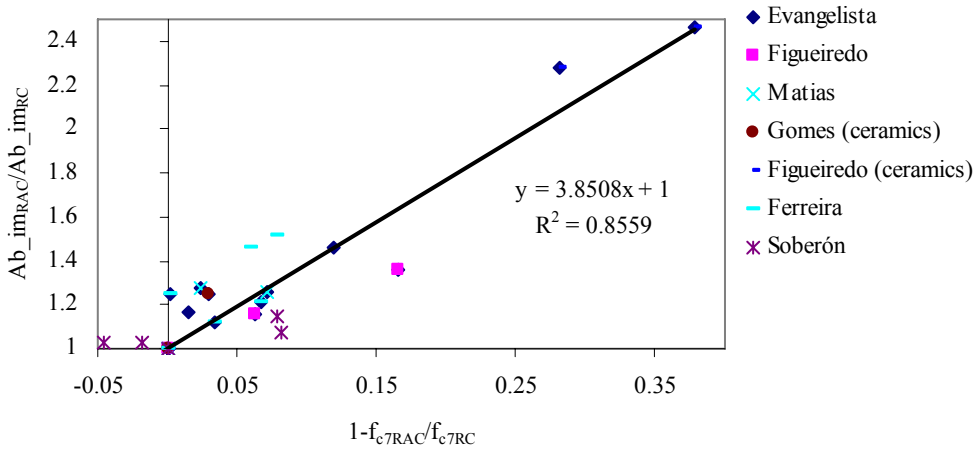


Figure 33. Ratio between concrete water absorptions by immersion *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

Carbonation Resistance

Both the international and the Portuguese literature reviews contain results on RAC's carbonation resistance, a vital characteristic in terms of reinforcement corrosion. Other references analyzed but not included in the graphs are: Buyle-Bodin and Hadjieva-Zaharieva (2002), Corinaldesi (2003), Levy (2001), Levy and Helene (2004), Kimura et al (2004), Merlet and Pimienta (1993), and Sagoe-Crentsil (2001).

Figures 34, 35 and 36 show the relationship of the ratio between the carbonation depths of hardened concrete and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively acceptable, acceptable and not acceptable.

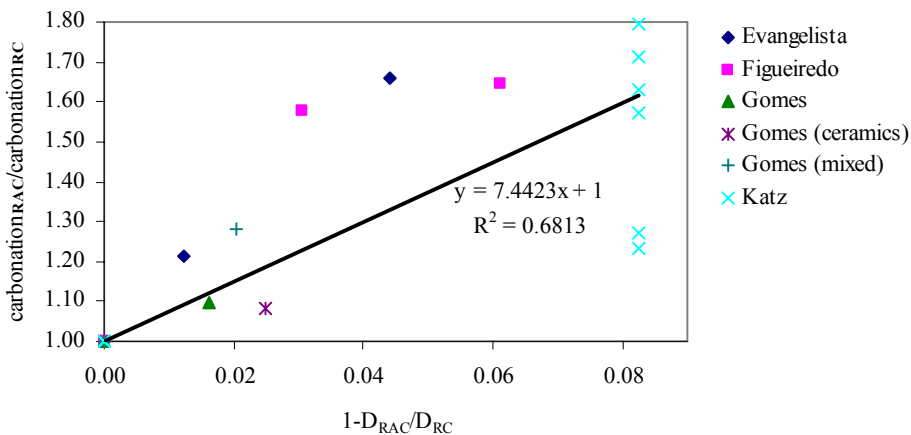


Figure 34. Ratio between concrete carbonation depths *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

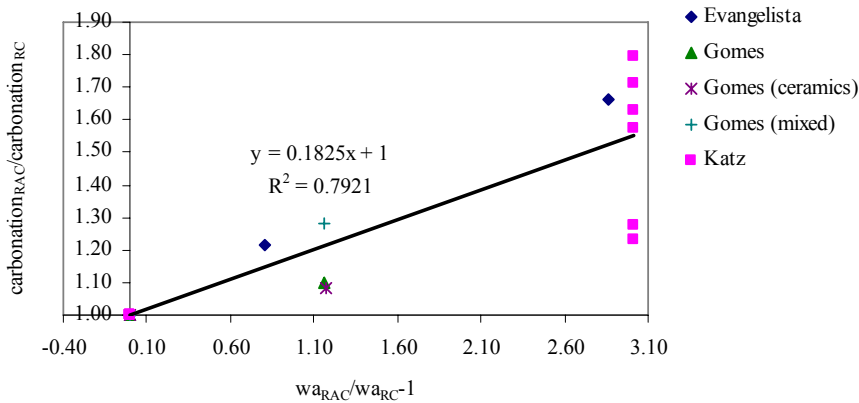


Figure 35. Ratio between concrete carbonation depths *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

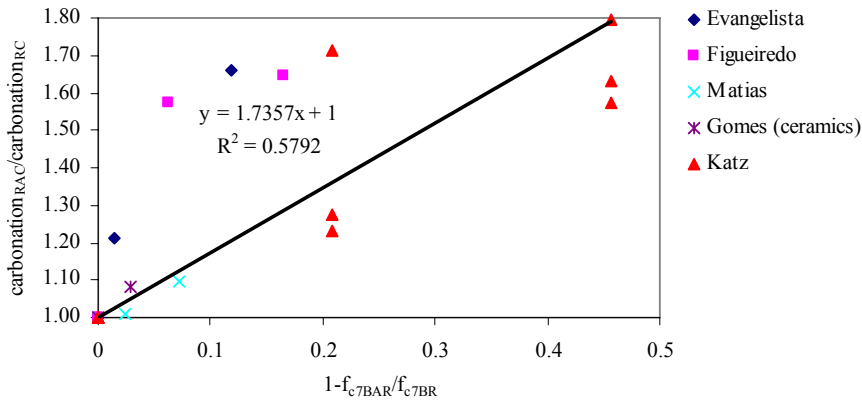


Figure 36. Ratio between concrete carbonation depths *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

The graphs exhibit a very strong influence of the replacement ratio on the depth the carbonation front reaches within concrete, stronger than for any other characteristic so far (except for the correlation with the 7-day compressive strength of concrete, which exhibits stronger trends for some other properties). This has been identified in the literature review as one of the most vulnerable aspects of the inclusion of RA in concrete production and is explained, as for the other durability-related characteristics (e.g. water absorption) by the greater porosity of these aggregates compared with that of PA.

Chloride Penetration Resistance

Both the international and the Portuguese literature reviews contain results on RAC's chloride penetration resistance, a defining characteristic for concrete's durability in coastal areas. Other references analyzed but not included in the graphs are: Corinaldesi (2003), Fraaij et al (2002), Levy (2001), Limbachiya et al (2000), and Olorunsogo and Padayachee (2001).

Figures 37, 38 and 39 display the relationship of the ratio between the chloride penetration of hardened concrete resistance (in terms of the diffusion coefficients or electric charge measured) and the ratio between the densities and the water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete, respectively. The correlation coefficients are considered respectively good, not acceptable and acceptable.

The slope of the correlation lines is similar to that for carbonation (in one case slightly higher and in the other two lower) and therefore the trend of increasing vulnerability to chloride penetration arising from the inclusion of RA is also very clear. The reasons for this phenomenon remain the same (i.e. greater porosity of the RA).

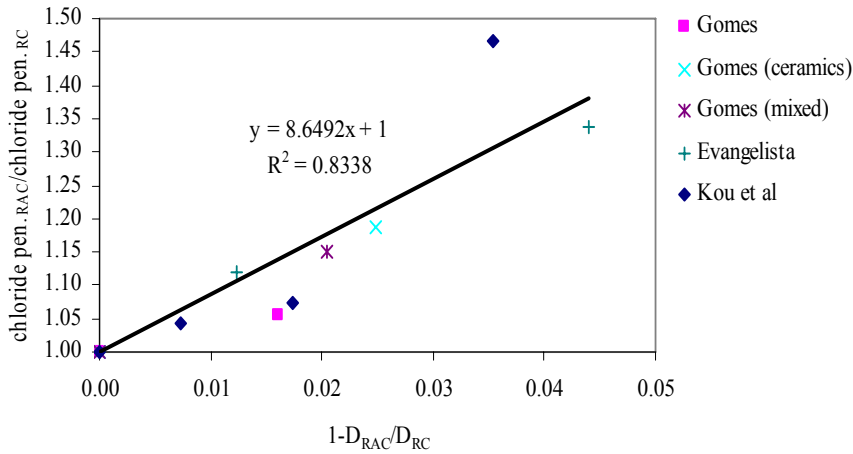


Figure 37. Ratio between concrete chloride penetration depths *versus* the ratio between the densities of the mixture of aggregates (Robles 2007) (Alves 2007)

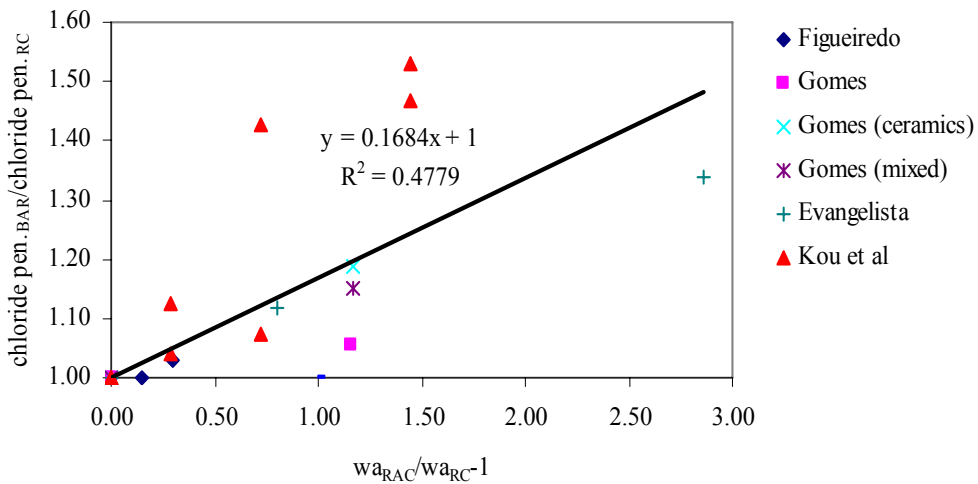


Figure 38. Ratio between concrete chloride penetration depths *versus* the ratio between the water absorptions of the mixture of aggregates (Robles 2007) (Alves 2007)

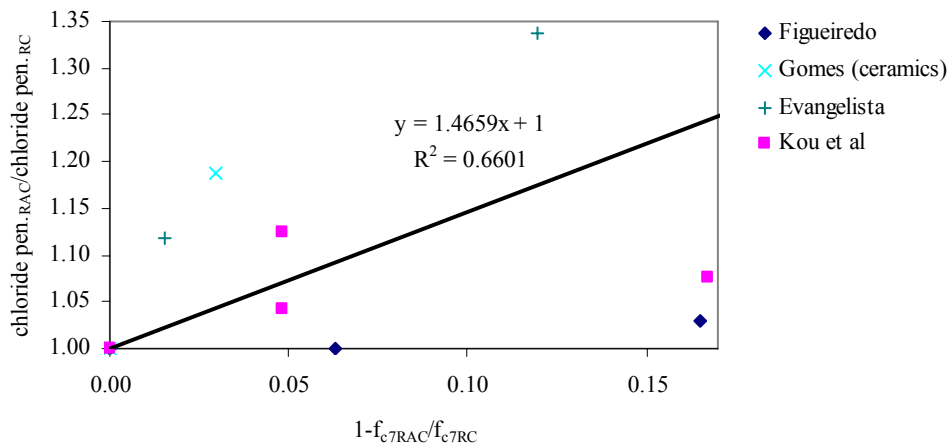


Figure 39. Ratio between concrete chloride penetration depths *versus* the ratio between the concrete 7-day compressive strengths (Robles 2007) (Alves 2007)

Summary of the Results

Table 6 summarizes the correlation coefficients for the relationship of each hardened concrete property with the weighed densities and water absorptions of the mixture of aggregates and the 7-day compressive strengths of concrete. The regression lines' slopes are also presented.

The correlation coefficient classification is indicated by different colours.

Based on the thirteen experimental campaigns on RAC chosen (six international and seven Portuguese), it was possible to analyze twelve different properties of hardened concrete. The relationship between these properties and the density and water absorption of the mixture of aggregates and the 7-day compressive strength of concrete allowed the following conclusions to be drawn (according to Table 6):

- With very few exceptions, it is possible to establish a linear relationship for the variation of the ratio between the concrete properties and the ratio of the three parameters mentioned;
- Generally, the density of the mixture of aggregates showed higher correlation coefficients with the hardened concrete properties, in the graphical analysis;
- The 7-day compressive strength of concrete seems to be the least adequate parameter to estimate the long-term concrete properties, since the lowest correlation coefficients were, in general, obtained for this property; this behaviour may be due to the influence of the variation of mixture procedures from one campaign to another and to the higher scatter of results for young concrete; an additional reason is the relative rate of growth of compressive strength for RCA *versus* RC (in some of the Portuguese campaigns, it was faster and in other others it was slower, and therefore it needs further research);

Table 6. Summary of the correlation trend lines between the different concrete properties and the density and water absorption of the mixture of aggregates and the 7-day compressive strength of concrete (Robles 2007) (Alves 2007)

Property	Experimental studies	Aggregates' density		Aggregates' water absorption		Concrete's 7-day compressive strength	
		R ²	Slope	R ²	Slope	R ²	Slope
Density	Rocha and Resende/ Ferreira	0.9221 (0.9225)	- 0.6145	0.7455 (0.7555)	-0.0128	-	-
	Ferreira					0.5622 (0.6208)	-0.528
Compressive strength	Evangelista/ Figueiredo/ Gomes/ Rosa/ Ferreira/ Carrijo/ Kou/ Leite/ Soberón	0.8319 (0.8490)	- 1.8262	-	-	-	-
	Evangelista/ Figueiredo/ Gomes/ Rosa/ Ferreira/ Carrijo/ Leite/ Soberón	-	-	0.4082 (0.5484)	-0.0309	-	-
	Evangelista/ Figueiredo/ Gomes/ Ferreira/ Kou/ Leite/ Soberón	-	-	-	-	0.4545 (0.6254)	-0.8568
Modulus of elasticity	Evangelista/ Figueiredo/ Gomes/ Ferreira/ Carrijo/ Leite/ Soberón	0.7045 (0.7641)	- 2.2557	-	-		
	Evangelista/ Gomes/ Ferreira/ Carrijo/ Leite/ Soberón	-	-	0.7641 (0.8166)	-0.0476	-	-
	Evangelista/ Figueiredo/ Ferreira/ Kou/ Leite/ Soberón	-	-	-	-	0.5307 (0.7022)	-1.3124
Splitting tensile strength	Evangelista/ Figueiredo/ Gomes/ Matias/ Rocha and Resende	0.7011 (0.7012)	-2.918	-	-	-	-
	Evangelista/ Gomes/ Matias/ Rocha and Resende/ Soberón	-	-	0.6146 (0.6149)	-0.0533	-	-
	Evangelista/ Figueiredo/ Gomes/ Matias/ Kou/ Soberón	-	-	-	-	0.6436 (0.7211)	-0.9095
Flexural tensile strength	Rosa/ Leite	0.7317 (0.7388)	- 2.5173	0.8522 (0.8556)	-0.0386	-	-
	Leite	-	-	-	-	0.8143 (0.8477)	-2.8241
Abrasion resistance	Evangelista/ Matias	0.8505 (0.8856)	- 4.5726	0.8001 (0.8313)	-0.0813	0.3473 (0.3855)	-2.3175
Shrinkage	Evangelista/ Gomes/ Matias/ Cervantes/ Soberón	0.5509 (0.5606)	4.8938	0.5724 (0.5819)	0.1317	-	-
	Evangelista/ Gomes/ Matias/ Soberón	-	-	-	-	0.5964 (0.5972)	4.3015
Creep	Soberón	0.9943 (0.9943)	3.6548	0.9943 (0.9943)	0.0682	(0.7454)	0.8317
Water absorption by capillarity	Figueiredo/ Gomes/ Matias/ Rosa/ Ferreira	0.5034 (0.5769)	6.578	-	-	-	-
	Gomes/ Matias/ Rosa/ Ferreira	-	-	0.3689 (0.5052)	0.1447	-	-
	Evangelista/ Figueiredo/ Gomes/ Matias/ Ferreira	-	-	-	-	(0.2558)	1.7703

Table 6. Summary of the correlation trend lines between the different concrete properties and the density and water absorption of the mixture of aggregates and the 7-day compressive strength of concrete (Robles 2007) (Alves 2007)

Property	Experimental studies	Aggregates' density		Aggregates' water absorption		Concrete's 7-day compressive strength	
		R ²	Slope	R ²	Slope	R ²	Slope
Water absorption by immersion	Evangelista/ Figueiredo/ Gomes/ Matias/ Ferreira /Soberón	0.622 (0.6657)	7.2065	0.7329 (0.7332)	0.1296	0.8559 (0.8656)	3.8508
Carbonation resistance	Evangelista/ Figueiredo/ Gomes/ Matias/ Katz	-	-	-	-	0.5792 (0.6276)	1.7357
	Evangelista/ Figueiredo/ Gomes/ Katz	0.6813 (0.6919)	7.4423	-	-	-	-
	Evangelista / Gomes/ Katz	-	-	0.7921 (0.7923)	0.1825	-	-
Chloride penetration resistance	Evangelista/ Figueiredo/ Matias/ Gomes/ Kou	-	-	-	-	0.5792 (0.6276)	1.7357
	Evangelista/ Gomes/ Kou	0.8338 (0.8398)	8.6492	-	-		
	Evangelista/ Figueiredo/ Gomes/ Kou	-	-	0.4779 (0.4953)	0.1684	-	-
		correlation coefficient acceptable ($0.65 \leq R^2 < 0.80$)					
		correlation coefficient good ($0.80 \leq R^2 < 0.95$)					
		correlation coefficient very good ($R^2 \geq 0.95$)					

Note: the values of R2 between parentheses correspond to the correlation lines that do not pass through the point corresponding to the RC.

- The lowest results were obtained for water absorption (especially by capillarity), which can be justified by the greater variability of this property compared with compressive strength, for example (a trend shared with conventional concrete);
- For every property of hardened concrete analyzed, except abrasion resistance, the performance of RCA is worse than that of the corresponding RC and the difference increases with the value of the replacement ratio;
- Based on the slope of the correlation lines for either of three reference parameters - density and water absorption of the mixture of aggregates and 7-day compressive strength of concrete - the vulnerability of RCA with the inclusion of RA instead of PA grows from mechanical properties (compressive strength, splitting and flexural tensile strength and modulus of elasticity) to those related to its rheologic behaviour (shrinkage and creep) and from these to the durability-related properties (water absorption, carbonation and chloride penetration).

An Application of the Methodology

In order to illustrate the potential of the methodology, a theoretical example of its application is now described. Even though this is not a real situation, all the values suggested are feasible and in agreement with past experience in experimental campaigns on RAC.

Let us suppose that the following types of aggregates are available: coarse primary (limestone) aggregates - CPA, fine primary (river sand) aggregates - FPA, coarse recycled concrete aggregates - CRA(RCA), coarse brick masonry aggregates - CRA(RMA), and fine recycled (concrete) aggregates - FRA. Their main characteristics (oven-dry density and water absorption) are provided in Table 7.

Table 7. Density and water absorption of the aggregates

	CPA	FPA	CRA(RCA)	CRA(RMA)	FRA
Oven-dry density (kg/m ³)	2650	2550	2350	2050	1950
Water absorption (%)	1.0	1.0	6.0	12.0	13.0

The composition of a C30/37 reference concrete (RC) was determined using the Faury method (leading to 35% of fine and 65% of coarse aggregates). Four types of RAC are being examined (Table 8). RAC1 is a composition which, according to various norms for RAC, is equivalent to a conventional concrete. The other three RAC compositions are more or less within the pragmatic limits for the maximization of the application of CRA(RCA), FPA and CRA(RMA) without unacceptable loss of performance. For every RAC composition, the following factors are expected to remain the same as for the RC: aggregates (fine and coarse fractions) grading curve, effective water / cement ratio, and slump value. Several specimens of each RAC and of the RC were tested for 7-day compressive strength and the corresponding results are given in Table 8, together with the weighed values for density (in accordance with equation (1) presented above) and water absorption of the mixture of aggregates used in each concrete mix.

Table 9 presents the corrective factors for the hardened concrete properties of all the RAC mixes, according to the correlation lines determined in the research described, as summarized in Table 6. These factors were obtained as an average of the factors provided by each of the parameters: D_{RAC}/D_{RC} ; w_{aRAC}/w_{aRC} ; f_{c7RAC}/f_{c7RC} .

This study shows that RAC1 in fact performs very much like the RC: practically the same density, losses of mechanical performance limited to 3% (with a 5% gain in abrasion resistance), increased deformability limited to 6%, and losses in durability-related aspects limited to 8% (not negligible, but

small). Therefore, it shows that small percentages of coarse recycled concrete aggregates can in fact be used to make structural concrete without affecting its properties.

Table 8. PA/RA replacement ratios and reference parameters for all concrete mixes

Replacement ratios (%)			D_{mix} (kg/m ³)	$w_{a,mix}$ (%)	f_{c7} (MPa)	D_{RAC}/D_{RC}	$w_{a,RAC}/w_{a,RC}$	$f_{c7,RAC}/f_{c7,RC}$
CPA/ CRA(RCA)	CPA/ CRA(RMA)	FPA/ FRA						
RC 20	0	0	2576.0	1.65	26.8	0.9851	1.65	0.9926
RAC1 100	0	0	2420.0	4.25	26.0	0.9254	4.25	0.9630
RAC2 0	0	25	2562.5	2.05	26.5	0.9799	2.05	0.9815
RAC3 0	25	0	2356.3	2.79	26.0	0.9011	2.7875	0.9630
RAC4 0	0	0	2615.0	1.00	27.0	-	-	-

Contradicting most norms that bar the use of FRA, the RAC3 composition (25% replacement) is the one with the next best performance: practically the same density as the RC, losses of mechanical performance limited to 5% (with a 7% gain in abrasion resistance), increases in deformability limited to 11% (not negligible, but small), and losses in durability-related aspects limited to 13% (not negligible, but small). This is good news for the environment since in some countries (e.g. Portugal) the greatest impact from aggregate production is related to the fine fraction (obtained from river beds, estuaries and sandy beaches).

Table 9. Corrective factors for the hardened concrete properties of all RAC mixes

	RAC1	RAC2	RAC3	RAC4
D_{RAC}/D_{RC}	0.99	0.96	0.99	0.97
$f_{c,RAC}/f_{c,RC}$	0.98	0.91	0.97	0.91
$E_{c,RAC}/E_{c,RC}$	0.98	0.88	0.96	0.88
$f_{sp,RAC}/f_{sp,RC}$	0.99	0.93	0.98	0.93
f_{IRAC}/f_{IRC}	0.97	0.86	0.95	0.86
$\Delta i_{RAC}/\Delta i_{RC}$	0.95	0.77	0.93	0.77
$\Delta \epsilon_{RAC}/\Delta \epsilon_{RC}$	1.06	1.32	1.11	1.29
ϕ_{RAC}/ϕ_{RC}	1.03	1.17	1.05	1.17
$Ab_{cap,RAC}/Ab_{cap,RC}$	1.07	1.34	1.11	1.33
$Ab_{im,RAC}/Ab_{im,RC}$	1.07	1.37	1.12	1.36
$carb_{.RAC}/carb_{.RC}$	1.08	1.40	1.12	1.13
$chlo_{.RAC}/chlo_{.RC}$	1.08	1.42	1.13	1.41

Legend: D_{RAC}/D_{RC} - concrete density; $f_{c,RAC}/f_{c,RC}$ - compressive strength; $E_{c,RAC}/E_{c,RC}$ - modulus of elasticity; $f_{sp,RAC}/f_{sp,RC}$ - splitting tensile strength; f_{IRAC}/f_{IRC} - flexural tensile strength; $\Delta i_{RAC}/\Delta i_{RC}$ - loss of mass due to abrasion; $\Delta \epsilon_{RAC}/\Delta \epsilon_{RC}$ - extension due to shrinkage; ϕ_{RAC}/ϕ_{RC} - creep coefficient; $Ab_{cap,RAC}/Ab_{cap,RC}$ - water absorption by capillarity; $Ab_{im,RAC}/Ab_{im,RC}$ - water absorption by immersion; $carb_{.RAC}/carb_{.RC}$ - carbonation depth; $chlo_{.RAC}/chlo_{.RC}$ - chloride diffusion coefficient.

The RAC2 and RAC4 compositions have similar levels of performance: practically the same density as the RC, losses of mechanical performance limited to 12% (with a 23% gain in abrasion resistance), increases in deformability up to 32% (liable to create problems in service), but, especially, losses in durability-related aspects up to 42% (which may have to be countered by increasing the reinforcement cover, in this case around 20%). These are not excellent results but they are acceptable in contexts where the importance of recycling large amounts of CDW outweighs the needs for exceptional concrete performances.

GENERAL CONCLUSIONS

The search for international experimental results for this study revealed great differences in the test procedures and organization of the published information. Most of the campaigns accepted the variation of more than one parameter, including the w/c ratio, making the analysis of the effect of the replacement ratio impracticable. These obstacles excluded a great number of campaigns from the graphical analysis undertaken.

The Portuguese literature review, even though it had a much shorter campaign domain, did not suffer the same difficulties, largely thanks to the scientific supervision, which was common to most of the works.

Notwithstanding the variability of factors introduced by each researcher in the experimental procedures, it was still possible to validate this methodology for the estimation of the properties of the concrete with recycled aggregates. Again, it must be pointed out that the scatter found in the relationships between the various properties of hardened RAC and the reference parameters is no greater than that found in similar relationships concerning conventional concrete, i.e. RAC are no less trustworthy in this aspect than conventional concrete.

The major advantage of this procedure is related to its low cost and the short time needed to obtain the results required to estimate the long-term properties of hardened concrete. The generalization of this methodology can, in the future, allow construction developers to decide, in an economic and fast way, cheaply and quickly about the use of RA in the building of new concrete structures.

Structural designers may also use acceptable estimations of the expected RAC properties in their designs, based on data provided by the contractor, the aggregates supplier or the CDW recycling plant. They can also provide the contractors with limits of application of RA in terms of the three parameters proposed here: D_{RAC}/D_{RC} (ratio between weighed values of the density of the mixture of aggregates used in the concrete mix); $w_{RAC}/w_{RC} D_{RC}$ (ratio between weighed values of the water absorption of the mixture of aggregates used in the concrete mix); f_{c7RAC}/f_{c7RC} (ratio between 7-day compressive strengths). As long as the contractors comply with the limits established by the structural designer the latter's calculations are valid.

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