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Sustainability of Concrete

Pierre-Claude Aïtcin and Sidney Mindess



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Maddalena ene maiteari

For Joanne and Katherine

Contents

<i>List of figures</i>	xiv
<i>List of tables</i>	xxii
<i>Preface</i>	xxiv
1 Sustainability	1
1.1 <i>Introduction</i>	1
1.2 <i>Steps to sustainability</i>	5
<i>References</i>	10
2 Terminology and definitions	11
2.1 <i>Introduction</i>	11
2.2 <i>Cement, cementitious material, binders, and fillers</i>	12
2.3 <i>Binary, ternary, and quaternary cements (or binders)</i>	12
2.4 <i>Cementitious material content</i>	13
2.5 <i>Specific surface area</i>	13
2.6 <i>Alite and belite</i>	13
2.7 <i>Hemihydrate</i>	13
2.8 <i>Water–cement, water–cementitious materials, and water–binder ratios</i>	13
2.9 <i>Saturated surface-dry state for an aggregate (SSD)</i>	14
2.10 <i>Water content, absorption, and moisture content of an aggregate</i>	14
2.11 <i>Mixing water</i>	15
2.12 <i>Specific gravity</i>	15
2.13 <i>Superplasticizer dosage</i>	15
<i>References</i>	15

3	The water–cement and water–binder ratios	16
3.1	<i>Introduction</i>	16
3.2	<i>Historical background</i>	17
3.3	<i>The water–cement ratio: the personal progression of P.-C. Aïtcin</i>	17
3.4	<i>The concrete industry and the w/c ratio</i>	20
3.5	<i>Water–cement or water–binder ratio</i>	20
3.6	<i>How to transform the w/b into MPa</i>	21
3.7	<i>The sustainability of low w/b ratio concretes</i>	22
3.8	<i>Conclusion</i>	25
	<i>References</i>	25
4	Durability, sustainability, and profitability	27
4.1	<i>Introduction</i>	27
4.2	<i>Durability: the leitmotif of the construction industry during the twenty-first century</i>	28
4.3	<i>Sustainability</i>	32
4.4	<i>What about profitability?</i>	42
4.5	<i>Conclusion</i>	42
	<i>Acknowledgement</i>	43
	<i>References</i>	43
5	Modern binders	44
5.1	<i>Introduction</i>	44
5.2	<i>Production of Portland cements and binders</i>	47
5.3	<i>Manufacturing modern binders from a sustainable development perspective</i>	50
5.4	<i>Non-clinker binders</i>	85
5.5	<i>Testing Portland cements and binders</i>	85
5.6	<i>Introducing cementitious materials and fillers</i>	91
5.7	<i>Concreting with blended cements</i>	93
5.8	<i>Testing concrete containing cementitious materials</i>	97
5.9	<i>Concluding remarks</i>	98
	<i>References</i>	99
6	Water	102
6.1	<i>Introduction</i>	102
6.2	<i>The crucial roles of water</i>	103
6.3	<i>Water and fresh concrete rheology</i>	104
6.4	<i>Water and hydration</i>	105
6.5	<i>Water and shrinkage</i>	106
6.6	<i>Water and alkali/aggregate reaction</i>	108
6.7	<i>Internal curing</i>	108

6.8	<i>Use of special waters</i>	108
	<i>References</i>	109
7	Superplasticizers	110
7.1	<i>Introduction</i>	110
7.2	<i>Definitions</i>	111
7.3	<i>Dispersion of cement particles</i>	113
7.4	<i>Compatibility and robustness</i>	117
7.5	<i>Utilization of superplasticizers</i>	123
7.6	<i>Commercial superplasticizers</i>	124
7.7	<i>Polysulfonates</i>	124
7.8	<i>Polycarboxylates</i>	131
7.9	<i>Practical use of superplasticizers</i>	132
7.10	<i>Concluding remarks</i>	137
	<i>References</i>	138
8	Natural aggregates	139
8.1	<i>Introduction</i>	139
8.2	<i>The SSD state: the reference state for aggregates</i>	140
8.3	<i>Influence of the mechanical properties of the coarse aggregate on the corresponding concrete properties</i>	144
8.4	<i>Partial substitution of a normal weight aggregate by a saturated lightweight aggregate</i>	154
	<i>References</i>	155
9	Aggregates derived from industrial wastes	157
9.1	<i>Introduction</i>	157
9.2	<i>Recycled concrete</i>	158
9.3	<i>Other industrial wastes</i>	162
9.4	<i>Other waste materials</i>	165
	<i>References</i>	165
10	Entrained air	168
10.1	<i>Introduction</i>	168
10.2	<i>Myths of entrained air</i>	168
10.3	<i>Beneficial action on the workability of fresh concrete</i>	170
10.4	<i>Beneficial action against damage</i>	171
10.5	<i>Beneficial action on permeability and sorptivity</i>	171
10.6	<i>Beneficial action against expansive reactions</i>	171
10.7	<i>Beneficial action on freeze-thaw durability</i>	172

10.8	<i>Entrained air and supplementary cementitious materials</i>	173
	<i>References</i>	174
11	Hydration reactions	176
11.1	<i>Introduction</i>	176
11.2	<i>The paradoxical experiment of Le Chatelier</i>	177
11.3	<i>Powers' work on hydration</i>	181
11.4	<i>Schematic representation of the hydration reaction (after Jensen and Hansen)</i>	182
11.5	<i>Composition of the cement gel</i>	189
11.6	<i>Heat of hydration</i>	196
	<i>References</i>	198
12	Shrinkage	200
12.1	<i>Introduction</i>	200
12.2	<i>Types of shrinkage</i>	201
12.3	<i>Plastic shrinkage</i>	202
12.4	<i>Autogenous shrinkage</i>	203
12.5	<i>Thermal shrinkage</i>	207
12.6	<i>Limiting the risk of cracking due to thermal gradients</i>	208
12.7	<i>Aggregates and shrinkage</i>	208
12.8	<i>Conclusion</i>	209
	<i>References</i>	209
13	Curing	212
13.1	<i>Introduction</i>	212
13.2	<i>Curing concrete as a function of its w/c ratio</i>	213
13.3	<i>Curing concrete to avoid plastic shrinkage</i>	216
13.4	<i>Curing concrete to avoid autogenous shrinkage</i>	218
13.5	<i>Curing concrete to mitigate drying shrinkage</i>	221
13.6	<i>Implementing concrete curing in the field</i>	222
13.7	<i>Conclusion</i>	223
	<i>References</i>	223
14	Specifying durable and sustainable concrete	225
14.1	<i>Introduction</i>	225
14.2	<i>Controlling the initial temperature</i>	225
14.3	<i>Entrained air or not?</i>	230
14.4	<i>External curing</i>	231
14.5	<i>Internal curing</i>	233
14.6	<i>Expansive admixtures</i>	234
14.7	<i>Shrinkage reducing admixtures</i>	234

14.8	<i>Slip-forming</i>	234
14.9	<i>Specifying testing age and testing conditions</i>	235
14.10	<i>Quality control</i>	236
	<i>Acknowledgement</i>	238
	<i>References</i>	238
15	Performance specifications	240
15.1	<i>Introduction</i>	240
15.2	<i>What is a performance specification?</i>	241
15.3	<i>How do we move from prescription to performance?</i>	242
15.4	<i>Sustainability and specifications</i>	243
15.5	<i>Establishing performance specifications</i>	246
15.6	<i>Examples of performance specifications</i>	246
	<i>References</i>	248
16	Statistical evaluation of concrete quality	249
16.1	<i>Introduction</i>	249
16.2	<i>Normal frequency curve</i>	249
16.3	<i>Controlling the quality of concrete production</i>	253
16.4	<i>Specifying concrete compressive strength</i>	261
16.5	<i>Limitations of a statistical analysis</i>	264
16.6	<i>Conclusion</i>	267
	<i>References</i>	267
17	Producing sustainable concrete with minimal environmental impact	269
17.1	<i>Introduction</i>	269
17.2	<i>Transportation of materials</i>	269
17.3	<i>Examples of modern ready-mix plants</i>	272
17.4	<i>Concluding remarks</i>	287
	<i>Index</i>	288

Figures

1.1	The holistic view of sustainability. (Adapted from The Concrete Centre, 2007)	2
1.2	Sources of greenhouse gases (Rohde, 2006). Reproduced under the terms of the GNU Free Documentation License, v1.2. (Courtesy of Wikipedia)	3
3.1	Schematic representation of two cement pastes having a w/c ratio of 0.65 and 0.25. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	18
3.2	Dale Bentz's model representing the concept of w/c. Reproduced with permission of the American Concrete Institute, 38800 Country Club Drive, Farmington Hills, MI 48331, USA.	19
3.3	Comparison of 25 MPa and 75 MPa columns	23
3.4	Confederation Bridge	24
3.5	Viaduc de Millau	24
3.6	The Burj Khalifa Tower in Dubai	25
4.1	Schematic representation of the preoccupations of the cement industry during the twentieth century	28
4.2	The Bermuda triangle of the twenty-first century	29
4.3	The $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram. (a) Composition area of co-existing $\text{C}_3\text{S-C}_2\text{S-C}_3\text{A}$. (b) Composition area of Portland cement clinker. (c) Obtaining K with a binary raw meal. (d) Obtaining K with a ternary raw meal	34
4.4	Calculation of the raw meal composition using the clay (D) or the slag (B) and limestone (C) to produce clinker K	35
4.5	Raw meal compositions to produce the slag and clay clinkers	36
4.6	Schematic representation of the composition of slag, class F and class C fly ash, anorthite, and natural clays	37
5.1	Increase in worldwide Portland cement production during the twentieth century. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	45

5.2	Correletion between the per capita consumption of cement and the per capita gross national income in 1997. Reproduced from Scheubel and Nachtwey, 1997	47
5.3	Polished surface of a clinker particle after its attack with succinic acid. (Courtesy of A. Tagnit-Hamou)	51
5.4	Portland cement clinker seen through an electron microscope. (Courtesy of A. Tagnit-Hamou)	51
5.5	Striated belite crystals. (Courtesy of A. Tagnit-Hamou)	52
5.6	Large alite crystals. (Courtesy of A. Tagnit-Hamou)	52
5.7	Deposits on alite crystals. (Courtesy of A. Tagnit-Hamou)	53
5.8	Lime cluster (free lime). (Courtesy of A. Tagnit-Hamou)	53
5.9	Belite nests. (Courtesy of A. Tagnit-Hamou)	54
5.10	Secondary belite (Bs) formed during a slow cooling of the clinker. (Courtesy of A. Tagnit-Hamou)	54
5.11	Transformation of the raw meal into clinker. (Courtesy of KHD Humboldt Wedag, 1986)	55
5.12	Formation of clinker in a short kiln equipped with a precalcinator. (Courtesy of KHD Humboldt Wedag, 1986)	56
5.13	Chemical composition of hydraulic binder components. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	64
5.14	Schematic representation of a high furnace. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	65
5.15	Position of the two eutectics having the lowest melting temperature in a $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	66
5.16	X-ray diffractogram of a hot slag after its quenching. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	67
5.17	Melilite crystals in a slag particle after quenching. This slag was a cold slag quenched below the temperature of the liquidus. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	67
5.18	Vitreous angular slag particles (in white). This slag was quenched at a high temperature because no melilite crystals are visible. Such a slag is called a hot slag. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	68
5.19	Spherical particles of fly ash. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	69

5.20	Plerosphere containing cenospheres in a fly ash. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	69
5.21	Schematic representation of the formation of fly ash. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	70
5.22	Typical X-ray diffractogram of different types of fly ash. (a) Class F or silicoaluminous. (b) Class C or silicocalcic. (c) Sulfocalcic fly ash totally crystallized. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	71
5.23	Coarse crystallized fly ash particles. (Courtesy of I. Kelsey-Lévesque)	72
5.24	Principle of the production of silica fume. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	73
5.25	Silica fume as seen in an electron microscope. (a) Scanning electron microscopy. (b) Transmission electron microscopy. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	74
5.26	X-ray diffractogram of silica fume (a) as-produced and (b) after its reheating at 1100°C. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	75
5.27	Metakaolin particles. (Courtesy of M. Cyr)	78
5.28	(a) Rice husk ash and (b) enlarged view. (Courtesy of A. Tagnit-Hamou and I. Kelsey-Lévesque)	79
5.29	Diatomaceous earth. (Courtesy of I. Kelsey-Lévesque and A. Tagnit-Hamou)	80
5.30	(a) Perlite particle and (b) enlarged view. (Courtesy of A. Tagnit-Hamou and I. Kelsey-Lévesque)	81
5.31	Typical diffractogram of various forms of amorphous silica. (a) Silica fume. (b) Rice husk ask. (c) Diatomaceous earth. (d) Metakaolin. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	83
5.32	Testing the hardening of concrete	88
5.33	Hardening of an ideal binder	89
6.1	Schematic representation of a water molecule	104
6.2	Electrical conductivity and heat release of a blended cement containing 8% silica fume. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	106
7.1	Different uses of a dispersant	112

7.2	Notion of robustness. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	112
7.3	Flocculation of cement particles (W) in water; (L) in water + water reducer; (SUP) in water + superplasticizer. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	114
7.4	Flocs of cement particles. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	115
7.5	Crystal structure of the four principal minerals found in Portland cement clinker. Reproduced from Bensted and Barnes, 2002. (Courtesy of Taylor & Francis)	115
7.6	Electrostatic repulsion. After Jolicoeur <i>et al.</i> (1994). (Courtesy of Pierre-Claver Nkinamubanzi)	116
7.7	Steric repulsion. After Jolicoeur <i>et al.</i> (1994). (Courtesy of Pierre-Claver Nkinamubanzi)	116
7.8	The complexity of the interaction of cement, polysulfonate, and calcium sulfates. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	118
7.9	Hypothetical cement particles	119
7.10	Mini slump testing. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	120
7.11	Marsh cone test. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	121
7.12	Flow time as a function of the superplasticizer dosage. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	122
7.13	Examples of flow time at 5 and 60 minutes. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	122
7.14	Inhibition of reactive sites. After Jolicoeur <i>et al.</i> (1994). (Courtesy of Pierre-Claver Nkinamubanzi)	125
7.15	Micelle of lignosulfonate. Reproduced from Rixom and Mailvaganam, 1999. (Courtesy of Taylor & Francis)	126
7.16	Polynaphthalene sulfonate	127
7.17	Polymelamine sulfonate	128
7.18	Polycarboxylate superplasticizer	131
7.19	Effects of the configuration of polycarboxylates. From Ohta <i>et al.</i> (2000). With permission of the American Concrete Institute, 38800 Country Club Drive, Farmington Hills, MI 48331, USA	132

7.20	Schematic representation of a superplasticizer. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	134
8.1	Coarse aggregate in its SSD state. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	141
8.2	Determination of the SSD state for a sand: (a) the standardized minicone used; (b) sand having a water content below its SSD state; (c) sand in a SSD state; (d) sand having a water content above its SSD state. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	141
8.3	Schematic representation of the measurement of the absorption and SSD specific gravity of a coarse aggregate. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	142
8.4	Schematic representation of a wet aggregate. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	142
8.5	Correlation between predicted and measured values of the elastic modulus using the Baalbaki model when the characteristics of the paste and the coarse aggregate are known. (Courtesy of W. Baalbaki)	149
8.6	Nomograph for predicting the value of the elastic modulus of a concrete according to the value of the elastic modulus of the coarse aggregate and concrete compressive strength. (Courtesy of W. Baalbaki)	150
8.7	Schematic representation of the response of a rock to its loading and unloading (hysteresis curve). Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	151
8.8	Schematic stress–strain curve for rock. From Houpert 1979. (Courtesy of Taylor & Francis)	152
8.9	Typical stress–strain curve used in codes. Reproduced from <i>High Performance Concrete</i> , Aïtcin 1998. (Courtesy of Taylor & Francis)	153
8.10	Different shapes of stress–strain curves. (Courtesy of Walid Baalbaki)	153
8.11	Lightweight sand (expanded shale)	155
9.1	Cross-section through 68-mm core containing recycled concrete and rubble as coarse aggregate. Reproduced from <i>Aggregates in Concrete</i> , Alexander and Mindess 2005. (Courtesy of Taylor & Francis)	159

9.2	Expansion of mortar bars with 10% glass aggregates of different size and colour. From Jin <i>et al.</i> (2000). With permission of the American Concrete Institute, 38800 Country Club Drive, Farmington Hills, MI 48331, USA	164
11.1	Le Chatelier's experiment. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	177
11.2	Reproduction of the Le Chatelier experiment with modern cement	179
11.3	Hydration with internal curing in quasi-adiabatic conditions	180
11.4	Schematic representation of Jensen and Hansen (2001)	182
11.5	Hydration of a 0.60 w/c paste in a closed system. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	183
11.6	Hydration of a Portland cement paste having a 0.42 w/c in a closed system. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	185
11.7	Hydration of a Portland cement paste having a w/c of 0.42 in the presence of an external source of water. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	185
11.8	Hydration of a cement paste having a w/c of 0.36 in the presence of an external source of water	186
11.9	Hydration of a Portland cement paste having a w/c of 0.30 in a closed system. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	187
11.10	Calcium silicate hydrate (external product)	190
11.11	Portlandite crystals. (Courtesy of I. Kelsey-Lévesque)	190
11.12	Ettringite crystals. (Courtesy of I. Kelsey-Lévesque)	191
11.13	Monosulfoaluminate crystals. (Courtesy of I. Kelsey-Lévesque)	191
11.14	Microstructure of high w/c ratio concrete: (a) high porosity and heterogeneity of the matrix; (b) oriented crystals of Portlandite (CH); (c) CH crystals. (Courtesy of Arezky Tagnit-Hamou)	192
11.15	Microstructure of a low w/c concrete. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	193
12.1	Portland cement hydration. Reproduced from <i>Binders for Durable and Sustainable Concrete</i> , Aïtcin 2008. (Courtesy of Taylor & Francis)	204

13.1	Fogging to prevent plastic shrinkage	217
13.2	Application of a curing membrane just after concrete casting	218
13.3	Yes, they are paid to water-cure concrete and they do it diligently	223
16.1	Normal frequency distribution curve. In this representation, the y axis has been placed at the average value, a , and $f(x)$ represents the number of samples having the value x_1	250
16.2	Some properties of the bell-shaped curve. I_1 and I_2 are the inflection points of the bell-shaped curve	251
16.3	Comparison of two bell-shaped curves having the same average value but different standard deviations	252
16.4	Areas under the normal frequency curve for specific values of σ	252
16.5	When compared to the total area under the bell-shaped curve, the area $A(x)$ at the left of x_1 represents the percentage of the values having a value smaller than x_1	253
16.6	(a) Histogram and (b) histogram with a fitted distribution curve	254
16.7	Examples of histograms that cannot be fitted by a bell-shaped curve. (a) A mix of two sets of values each obeying a normal distribution curve; and (b) a skewed distribution showing that very low values have been eliminated	254
16.8	Decomposition of Figure 16.7(a) into two mixed populations	255
16.9	Average strength of the samples	261
16.10	Histogram of compressive strengths	261
16.11	Variation of the average strength	262
16.12	Variation of the standard deviation	262
16.13	Variation of the coefficient of variation	263
16.14	Variation of the range	264
16.15	Variation of the average range	264
16.16	Within-test standard deviation	265
16.17	Within-test coefficient of variation	265
16.18	Average of five consecutive tests	266
16.19	Average of the last 10 ranges	266
17.1	Aggregates delivered by barges	273
17.2	Cement barge	274
17.3	Delivery of special cements by truck	274
17.4	Cleaning a ready-mix truck	275
17.5	Recovered aggregates	276
17.6	Decantation of the charged water	276
17.7	Cleanliness inside the batching plant	277

17.8	Coarse aggregate storage	277
17.9	Cleaning a truck in the decantation pit	278
17.10	Schematic of the decantation pit	278
17.11	Schematic of the treatment unit	279
17.12	The treatment unit	279
17.13	Recovered sand and gravel	280
17.14	Charged water basin	281
17.15	Sedimentation basins	282
17.16	Ready-mix trucks	282
17.17	Crushed demolition concrete	283
17.18	Forms for making concrete blocks	283
17.19	Recovery of the aggregates from the unused fresh concrete	284
17.20	pH control of the treated water	285
17.21	Hardened sludge before its elimination	285
17.22	Washing a truck	286
17.23	Hardened sludge before its elimination	286

Tables

1.1	Annual world production of materials, 2007, in tonnes (metric tons)	2
4.1	Comparison of the CO ₂ emitted when producing a clay-clinker or a slag-clinker	36
5.1	Increase in the worldwide Portland cement production during the twentieth century	45
5.2	Per capita consumption of cement, in kg (Source: CEMBUREAU)	46
5.3	Production of different cements in 1998 in the USA	49
5.4	Average chemical and Bogue compositions of some Portland cements	57
5.5	Chemical composition of some silica fumes	74
5.6	Chemical composition of some natural pozzolans and calcined clays. From Papadakis and Venuat 1966	77
5.7	Comparison of the chemical composition of Glass Frit [®] and a slag	82
5.8	Characteristics of some cements used to make reactive powder concretes with a compressive strength of about 200 MPa	87
8.1	Maximum compressive strength as a function of the w/b	146
8.2	Mechanical properties and characteristics of the aggregates used by Baalbaki (1997)	148
9.1	Some solid wastes that have been considered as concrete aggregates	158
9.2	Maximum amounts of deleterious materials in recycled concrete aggregate	159
9.3	Compositional requirements for coarse recycled concrete aggregate in BS 8500-2: 2002	160
9.4	Properties of natural aggregate (NA) and recycled concrete aggregate (RCA) concretes	160
15.1	Some concrete properties for performance specifications	247
16.1	Factors for computing within-test standard deviation	255
16.2	Results obtained during quality control testing	257

16.3	Average strength and range	258
16.4	Average strength, standard deviation, coefficient of variation, and average of the last five strengths	259
16.5	Within-test variation	260
16.6	Standard deviation and coefficient of variation according to ACI 214 (Table 3.5)	263

Preface

One more book on concrete; as if there were already not enough of them! It is all the more peculiar because this book does not purport to revolutionize the design and production of concrete, nor does it pretend to be an encyclopaedia on concrete. Only a particular selection of topics will be tackled: those in which significant changes will have to be made to fulfill the new objective of building more durable, sustainable, and economical concrete structures with cements containing less and less Portland cement clinker.

Major changes must occur in the concrete industry in order to make concrete more sustainable. First, the use of pure Portland cement will no longer be the general rule; it will rather become the exception. Therefore, it will be necessary to learn how to properly use binary, ternary, or even quaternary binders containing many other kinds of cementitious materials. The second change will be a greater use of low water–binder (w/b) ratio concrete, not only for its high strength and elastic modulus but also for its greater durability and sustainability. It will be shown that the use of low w/b concrete results in a significant reduction of the consumption of aggregates and cement, of transportation costs, of formwork, and of the manpower required to place it in the forms. A third change will be the more frequent use of internal water curing to favour a better and longer hydration of the cementitious materials contained in blended cements, and to reduce or eradicate the effects of early autogeneous shrinkage in high-performance concrete.

Another objective of this book is to present some of the latest advances in the science of concrete. Indeed, using the most recent technological breakthroughs in observing, analysing, and modelling the properties of materials in general, a new science of concrete has been born: a new science that enables us to better understand this material, and to make it more durable, more sustainable, and more economical. Concrete has, of course, always obeyed the laws of physics, chemistry, and thermodynamics as well as the law of the marketplace, but now we are finally able to really understand how it does so. Indeed, every day it becomes more and more apparent that concrete is the fruit not only of a simple technology but also of a complex science.

Now, due to this new knowledge, it is easier to understand the behaviour of concrete from its fabrication in a mixer to its performance in service in a complex concrete structure exposed to many different kinds of loads and environments. Some practical applications have already benefited from this scientific approach. This is only the beginning of a new and challenging era for concrete.

Throughout this book, we will focus on the significance of the water–binder ratio, which for us is by far the most important parameter of concrete. It governs most of the practical properties of concrete, particularly its compressive strength, although it is not always easy to transform the w/b ratio into MPa. It has recently been shown (Bentz and Aïtcin, 2008) that this basic concept, developed first by Féret and later by Abrams about 100 years ago, is much more than a mysterious abstract number. In fact, it is an indirect way of expressing how close the binder particles in the cement paste are to each other when concrete starts the journey that transforms it from a more or less fluid mixture into an artificial rock. The lower the value of the w/b, the closer to each other are the binder particles in the cement paste and the stronger and the more durable the concrete.

However, it is not the purpose of this book merely to present the formulation and characteristics of modern concretes such as high-performance concrete, self-compacting concrete, roller-compacted concrete, or reactive powder concrete. We prefer to leave this to other, more qualified, authors. Rather, this book is intended to be more general in its scope; it has been conceived as a complement to the excellent reference books that have already elucidated the principles of making, designing, constructing, and maintaining concrete structures, when sustainability and durability were not a prime concern. We will simply reference these books as necessary in order to avoid unnecessary repetition.

The limits and the challenges on which we focus in this book, as stated by Adam Neville (2006) are: “A better understanding of concrete practice for the purpose of obtaining better concrete practice”.

*Pierre-Claude Aïtcin and Sidney Mindess
Sherbrooke and Vancouver, 2010*

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1 Sustainability

1.1 Introduction

We live in a world of finite natural resources and sources of energy. Unfortunately, we are currently using these natural resources at a rate that cannot be sustained indefinitely. Moreover, the energy that we expend in exploiting these resources, and the ways in which we use and consume them, produces pollution and a degradation of the environment. In particular, the so-called *greenhouse gas emissions* resulting from our use of resources (mainly carbon dioxide, methane, and nitrous oxide), contribute significantly to global climate change. Thus, if we wish to maintain our current standard of living, and to bring the developing world up to these same standards, we must pay much more attention to the way in which we deal with our natural environment. This leads inevitably to the concept of *sustainable development*, which is most commonly defined as:

Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

(Brundtland, 1987)

Embodied in this definition is the necessity of taking a holistic approach to sustainability, by considering not only the environmental, but also the social and economic consequences of our behaviour, as indicated schematically in Figure 1.1.

Portland cement and concrete must also be considered in the light of this concept of sustainable development. As will be discussed in much more detail throughout the rest of this book, the cement and concrete industries have a considerable effect on the environment: they use large volumes of raw materials that are quarried from the earth, their production requires a large amount of energy, and the manufacture of Portland cement emits a large amount of CO₂.

2 Sustainability

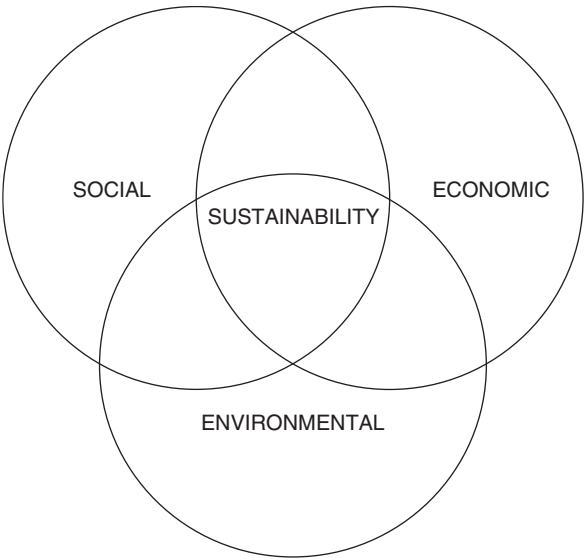


Figure 1.1 The holistic view of sustainability. (Adapted from The Concrete Centre, 2007).

Concrete is by far the most widely used construction material around the world, because of the economic and widespread availability of its constituents, its versatility, its durability, and its adaptability. It literally forms the basis of our modern society; one need only think of the concrete structures in which we live and work, the concrete roads and bridges over which we drive, or the concrete dams which store water, which is then distributed through systems of concrete waterways, conduits, and pipes to provide our drinking water, or is used to generate electricity. Concrete is also, next to water, by far the most widely used material in the world (Table 1.1), with over 5 billion cubic metres of concrete produced annually.

Portland cement is produced by first pyroprocessing the raw materials (mostly limestone and clay or shale) at temperatures from 1400°C to

Table 1.1 Annual world production of materials, 2007, in tonnes (metric tons)

Concrete	~ 13 billion
Portland cement	2.36 billion
Steel	1.34 billion
Coal	6.5 billion
Crude oil	~ 3.8 billion
Wheat	606.4 million
Salt	200 million
Sugar	162 million

1500°C, and then grinding the resulting clinker. This requires an energy input of about 4900 MJ/tonne of cement, which translates to about 900 MJ/tonne of concrete. For comparison, one barrel of oil is equivalent to 6100 MJ. This means that the energy required to produce Portland cement is equivalent to that available from about 26 days of crude oil production, or 7% of the energy generated by oil.

Perhaps of greater concern, in the production of Portland cement a considerable amount of carbon dioxide (CO₂) is liberated; on average, about 1 tonne of CO₂ is liberated per tonne of cement produced. (For any particular plant, the amount of CO₂ may be somewhat more or less than this, depending on the plant efficiency, quality of the raw materials, proximity of the plant to the raw materials, and so on.) This amounts to about 7% of the world's CO₂ emissions. While this is less than the amounts produced by the generation of electric energy from coal-fired power plants, or the amount used in transportation (Figure 1.2), it is still significant, and so efforts must be made to reduce the amount of CO₂ associated with the cement and concrete industries.

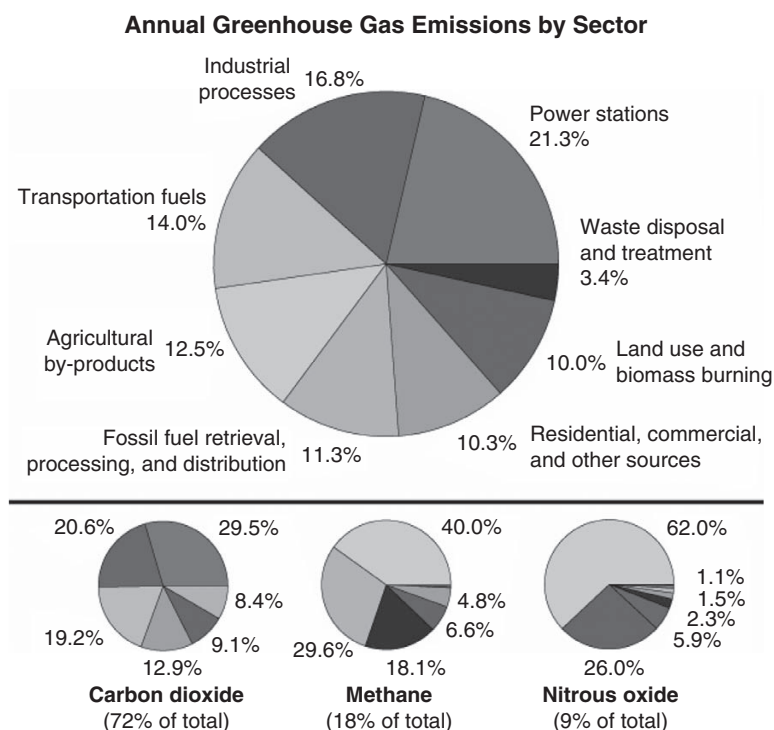


Figure 1.2 Sources of greenhouse gases (Rohde, 2006). Reproduced under the terms of the GNU Free Documentation License, v1.2. (Courtesy of Wikipedia.).

4 Sustainability

Of course, in addition to Portland cement, the concrete industry uses vast quantities of two other materials: about 10 billion tonnes of sand, gravel, and crushed rock, and over 1 trillion litres of fresh water per year go into the production of concrete. This too may have considerable ecological effects.

The use of concrete will undoubtedly grow considerably over the next few decades, as at least a number of the less developed countries in Asia, Africa, and parts of South America begin to industrialize on a large scale. Thus, the problems of resource depletion and greenhouse gas emissions are likely to become increasingly severe. It is therefore imperative that we begin now to make the concrete industry much more sustainable. Fortunately, with the knowledge that we already possess, this is an achievable goal.

Since sustainability is becoming a key factor in the design of concrete structures, it is important to focus on the changes that the cement, the concrete, and the construction industries will have to implement in order to make concrete structures more sustainable. Even in the world's richest countries, it is beyond question that it is extremely wasteful to have to rebuild our civil infrastructures every 35 to 50 years because they were poorly constructed and have achieved the end of their service life. It is too costly, it represents social costs that are too high, it is wasteful of materials, and it contributes to the accelerated degradation of not only our environment, but also the environment that our children and grandchildren will inherit.

For the foreseeable future, concrete will be the material of choice to build the infrastructure that satisfies a large part of our socio-economic needs, not only in developed countries but also in the countries that are now undergoing, or soon will undergo, rapid industrial development. Moreover, most people will live in large cities, where concrete will be exposed to increasingly aggressive environments due to urban pollution. If nothing is done soon to improve concrete durability, our concrete infrastructure will rapidly be eaten away by carbonation, sulfate attack, de-icing salts, and even bacteria (*Bacillus ferroxidans* and many others).

When we look at concrete from the perspective of sustainability, many errors were made (and are still being made) in the developed countries; it would be a pity to repeat the same errors in developing countries. Recently, concrete science has made significant progress. It is now time to exploit this progress to its full potential so that developing countries may take advantage of it, and build their necessary infrastructure in a more sustainable way than did the developed countries.

It is no longer possible simply to shovel our environmental problems into our neighbour's yard, or into some faraway undeveloped country, because these problems will quickly fall back upon us. This is a rare instance in which both rich and poor people and countries are stuck together, because this is a global problem that transcends artificial human frontiers. It is imperative to decrease the environmental impact of concrete structures: it is time to make them more sustainable. What, then, must we do?

1.2 Steps to sustainability

There are a number of approaches to making concrete more sustainable, including:

- the use of higher strength concretes
- making concrete much more durable
- replacing up to half of the Portland cement with supplementary cementing materials (SCMs)
- using fillers
- manufacturing Portland cement more efficiently
- using waste materials as fuels
- using recycled concrete, and other industrial wastes, as aggregate sources
- finding ways to capture and store or sequester CO₂ emissions
- using cement kiln dust in some applications
- using less water
- improving structural design and building codes.

Of course, some of these approaches will be more effective than others, but taking them all together can lead to enormous efficiencies, from both an environmental *and* an economic perspective, in the concrete industry. Many of these issues will be dealt with in considerable detail later on in this book. However, it is worth summarizing them all here, to provide an overview of the approaches that can be taken.

1.2.1 *Manufacturing Portland cement more efficiently*

On average today, it requires about 4.9 GJ of energy to produce 1 tonne of cement; this includes the energy not only for the pyroprocessing in the kiln, but also that used to extract and transport the raw materials, to crush and grind them, and finally to grind and transport the cement itself. This represents a considerable decrease in the required energy over the last 20 years, as the industry has moved from wet process to dry process kilns, with efficient preheaters and precalciners. Cement kilns have also become shorter, but with greater diameters, which also increases their efficiency. It should be noted that the theoretical fuel requirement to produce 1 tonne of clinker is only about 1.7 GJ. There is thus still room to improve kiln efficiency, saving fuel, but this would have relatively little effect on the greenhouse gas emissions.

1.2.2 *Use of alternative fuels*

As fuel costs have increased in recent years, there has been a move to use materials other than the traditional coal, gas, and oil to heat the kilns.

These other materials now include spent solvents, waste oil, used automobile tires, and other organic materials, depending on local availability. While this has no particular effect on either the energy required to produce cement, or on greenhouse gas emissions, it does provide a means of utilizing and disposing of what would otherwise be waste materials, and it does save on the use of fossil fuels.

1.2.3 Use of supplementary cementing materials (SCMs)

Probably the most effective means of decreasing both energy consumption and the production of greenhouse gases is to substitute what are referred to as *supplementary cementing materials* (SCMs) for a portion of the Portland cement; each kilogram of substitution reduces by about 1 kg the emission of CO₂, and saves the energy required to produce 1 kg of cement. There are a number of SCMs available, several of which are already used extensively in the industry; they may be interground or blended with the cement at the cement plant, or substituted for cement at the batch plant. They are all *pozzolanic* materials; that is, fine siliceous materials that react at room temperature with the lime released during the hydration of dicalcium silicate and tricalcium silicate, to form what is referred to as secondary C–S–H. They may substitute for the Portland cement at levels up to about 50% (and even more for slag). These materials are primarily by-products (or wastes) of other industrial processes, and include:

- *Fly ash* is the fine powder retrieved from the dust-control systems of electric power plants burning coal or lignite. It is the most widely used SCM, commonly at substitution levels of about 10% to 15% in North American concrete practice, though it could be used at much higher substitution rates in many applications. For instance, it has been shown that, with the w/c held to ≤ 0.30 , up to 60% of the Portland cement can be replaced with fly ash, resulting in a concrete with excellent strength and durability properties (Malhotra, 1994). Fly ash tends to slow down somewhat the rate of strength development at early ages, but over time (a few months) will lead to stronger and more durable concretes.
- *Ground granulated blast furnace slag* (or simply slag) is a by-product of the production of pig iron. It consists primarily of silica, alumina, and lime, with a composition close to that of Portland cement. It can be substituted for Portland cement at proportions varying from about 25% to 85%. It is more commonly used in Europe than in North America.
- *Silica fume* is the by-product of the silicon and ferrosilicon industries. It is about 100 times finer than Portland cement, and is the most reactive by far of the pozzolanic materials. Its use is essential in the production of high strength concretes having compressive strengths greater than 100 MPa. Because of its high cost, and because high substitution rates

may lead to workability problems, it is generally used at substitution rates of between 5% and 10%.

- *Metakaolin and calcined clay.* Kaolin, the clay used to make fine china, is a hydrated aluminosilicate. When it is heated to about 750°C to 850°C, the water is driven off, and the material is then called metakaolin. Metakaolin is a very reactive pozzolan, though not as effective in this regard as silica fume. It is not yet in common use, but several natural deposits of this mineral are now being exploited for use in cement and concrete. Ordinary clays can also be dehydrated at about the same temperature as kaolin, and they then also become pozzolanic. Indeed, calcined clays were the original pozzolanic materials to be used, first by the Phoenicians, and later by the Romans.
- *Natural pozzolans.* The Greeks, and later the Romans, found that certain volcanic ashes (rich in vitreous silica) could be used to improve the durability of lime mortars. The Romans used a volcanic ash found around the Bay of Naples, which was generally called *pozzolana* because the best variety was found near the village of Pozzuoli, near Mount Vesuvius. Natural pozzolans tend to react quite slowly at room temperature, and are thus not used at addition rates greater than about 15%.
- *Rice husk ash.* Rice husks have a siliceous skeleton representing about 20% of their mass. When they are burned at about 750°C, the resulting ash is essentially composed of vitreous silica, and is highly pozzolanic.
- *Other pozzolans.* There are also a number of other materials that have good pozzolanic properties, but which are not commonly used. These will be described briefly in Chapter 5.

1.2.4 Fillers

Fillers are materials which do not react chemically with Portland cement, but whose presence may nonetheless be beneficial through physical action. The most common such materials are finely divided limestone (which is, of course, readily available at a cement plant) and finely divided silica. Current North American codes permit up to 5% substitution of limestone, though recent research has shown that up to about 12% can be added without deleterious effects on the cement (Hooton *et al.*, 2007; Bentz *et al.*, 2009; Thomas *et al.*, 2010).

1.2.5 Cement kiln dust

Cement kiln dust is the fine material carried by the hot gases in a cement kiln and collected by a filter system. It differs from cement clinker in that it has not been completely burnt. It is, however, produced in substantial amounts: about 9 tonnes per 100 tonnes of cement clinker. Currently, it is often treated as a waste by-product, but it can replace Portland cement in a number of

applications, such as in soil stabilization, or in the production of controlled low strength materials (Lachemi *et al.*, 2007; Lachemi *et al.*, 2009).

1.2.6 Making more durable concrete

Currently, most concrete mixtures are designed on the basis of their 28-day compressive strength, with durability a secondary concern. This has, unfortunately, led to many concrete structures failing prematurely. However, probably the most effective way of making concrete truly sustainable is to increase its effective service life. By an appropriate use of admixtures, and a considerable decrease in the w/c ratio, it would be relatively easy to at least double the service life of concrete, with a consequent saving in energy and greenhouse gas emissions (or the ability to make twice as much concrete as we do now with the same carbon footprint, calculated over the entire life cycle of the structure).

1.2.7 Use higher strength concretes

It can be shown that high strength concrete (more properly called high performance concrete, or HPC) is much more sustainable than normal strength concrete. For instance, when constructing a concrete column with a 75 MPa concrete rather than a 25 MPa concrete, only one-third the amount of aggregate, and one-half the amount of cement are required to carry the same load (see Chapter 2). Even in flexure, the material savings would be of the order of 25% to 30%.

1.2.8 Recycled concrete aggregate

Concrete reclaimed from the demolition of old concrete structures or pavements may be processed to produce aggregates suitable for use in new concrete. The processing is similar to that used with many natural aggregates: crushing, removal of contaminant materials, and washing. In general, the use of recycled concrete aggregate results in concretes that are somewhat weaker and less durable than concretes made with natural aggregates at the same w/c ratio. Recycled concrete aggregates are most commonly used as coarse aggregate; some specifications recommend that fine recycled aggregate not be used at all, or be limited to no more than 30% of the total fine aggregate. Nonetheless, there are many applications in which recycled concrete aggregate can be used safely and economically.

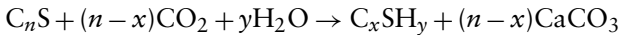
1.2.9 Capture and storage or sequestration of CO₂ emissions

One way of lessening the impact of cement manufacture on greenhouse gas emissions is to capture and then sequester or store the CO₂ that is produced, and there is a currently a great deal of research in this area. The technology

already exists, though on a smaller scale, to capture CO₂ from the flue gases in a cement plant. The CO₂ could then, it is hoped, be permanently stored in underground geological formations, or injected at great depths into the ocean, where it would then dissolve.

A more interesting possibility, however, is to use the CO₂ in the curing of concrete blocks and other precast elements (Shao and Shi, 2006; Shi and Wu, 2009). This may be referred to as one form of CO₂ *sequestration*. The reactions of CO₂ with cement are shown below:

- Early carbonation mechanism (Young *et al.*, 1974):



- CO₂ uptake (Steinour, 1959):



These are, indeed, the reactions that take place during carbonation of concrete when exposed to the atmosphere. The advantages of curing concrete in a CO₂-rich atmosphere include accelerated hydration and early strength gain, elimination of the Ca(OH)₂ that results from the cement hydration reactions, reduced efflorescence, and decreased permeability. The economic feasibility of employing this technology on an industrial scale is currently under active consideration.

1.2.10 Using less water

As stated earlier, over 1 trillion litres of fresh water are used annually in the production of concrete. Typically, w/c ratios are about 0.5, and often much higher. A reduction in the w/c ratio to ≤ 0.4 would result in not only stronger and more durable concrete, but also in a significant saving in fresh water.

1.2.11 Improving structural design and building codes

Currently, concrete is specified primarily on the basis of its 28-day compressive strength, using mix design procedures that are highly prescriptive; durability and other performance characteristics are all too often seen as only secondary considerations. This is generally wasteful: it leads to the use of higher than necessary cement contents, and tends to stifle innovation on the part of the concrete producers. It would be much more rational to move from *prescriptive* to *performance* specifications. This would provide an incentive to the producer to make efficient use of all of the available resources to produce concretes satisfying the requirements of any specific project.

Of course, it may not be possible to follow all of the above suggestions for a particular project, because of limitations on material availability, special project requirements, and so on. However, the engineers and specifiers should at least be aware of the many possible ways in which the concrete can be made more sustainable.

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2 Terminology and definitions

2.1 Introduction

Those who have already read the book *High Performance Concrete* (Aïtcin, 1998) will think that it is madness for us to start this book as well with a chapter devoted to terminology and definitions. In 1998, Aïtcin wrote:

Discussions on terminology are tricky and can be endless but it must be admitted that often the quality of the information in a technical book is diminished by the lack of consensus on the exact meaning of the terms used. The author makes no claim for the superiority of the terminology he uses; he wants only to make clear the exact meaning of the terms he employs. The reader is free to disagree with the pertinence and the validity of the proposed terminology but, by accepting it momentarily, he will better understand the concepts and values expressed in this book. The acceptance of these definitions is essential to make the most of reading this book. As stated by A.M. Neville “The choice of one term over another is purely a personal preference and does not imply a greater accuracy of definition”.

(Neville, 1996)

Now, more than 10 years later, in 2010, we remain convinced of the necessity to do this again.

As our professional careers have been spent in North America, we have become used to the American Concrete Institute (ACI) cement and concrete terminology. This is the terminology that we will essentially adopt in this book, though with some divergence from time to time. The chairman of ACI committee ACI 116-90 on cement and concrete terminology was, for a long time, Bryant Mather, and we are certain that those who knew Bryant are convinced of the value of these definitions arrived at through the long discussions of the committee. Of course, with Bryant Mather as chairman, these discussions were never endless; they always ended in an acceptable compromise (reflecting naturally his strong opinion on any subject!).

2.2 Cement, cementitious materials, binders, and fillers

ACI Standard 116 R contains 41 entries starting with the word “cement” to define some of the cements used in the concrete and asphalt industries, plus five additional entries containing the expression “Portland cement” (with an upper case P). There are no entries for *supplementary* cementitious materials, only for cementitious (having cementing properties) materials.

In accordance with the recommendation of ACI Committee 116, we will use the expression “blended cement” to refer to all of the various types of (hydraulic) powders currently used by the concrete industry. Of course, this “dilution” of Portland cement clinker is closely related to the necessity of decreasing the environmental impact of concrete at the level of CO₂ emissions. However, we will continue to add a personal touch to this ACI terminology by also using the word “binder” in reference to blended cements when speaking of the finely divided materials that react with water that are now used in concrete mixtures. Personally, we prefer the expression “blended cement” because it is simple: it clearly indicates that the final product is a mixture of fine materials; the ACI 116 definition is too long, too descriptive, and too limiting. We also like to use the rather imprecise word “binder” because its imprecision better reflects the diversity of the blends that are now being used, and the even greater diversity that will be used in the future to make concrete more sustainable by minimizing the amount of Portland cement clinker in the concrete.

We will use the word “clinker” rather than the phrase “Portland cement clinker” because, for us, the word “clinker” automatically implies Portland cement. “A clinker is a partially fused product of a kiln which is ground to make cement ... consisting primarily of hydraulic calcium silicates”.

In this book, the word “filler” will be used in a more restrictive way than that proposed by the ACI Committee definition. Filler will refer to any finely divided (more or less) inert material such as pulverized limestone or silica added to the Portland cement material. Fillers are already used in binders to improve the sustainability and often other properties of concrete. In particular, they lead to a decrease in the CO₂ content of the binder.

The expression “CO₂ content of a binder” represents the amount of CO₂ that was emitted by the materials and the processes used during the manufacture of the binder. For example, to produce 1 tonne of clinker in a modern cement plant, it is necessary to emit about 1 tonne of CO₂, half coming from the decarbonation of the limestone and most of the rest from the fuel necessary to reach partial fusion during the production of the clinker.

2.3 Binary, ternary, and quaternary cements (or binders)

These expressions will be used to define certain blended cements. They indicate how many cementitious materials or fillers are included in the

blend without indicating their nature or content. For example, a ternary cement can be composed of Portland cement clinker, slag, and silica fume, or Portland cement clinker, fly ash, and silica fume, or Portland cement clinker, slag, and fly ash, and so on.

2.4 Cementitious material content

When a blended cement is composed of several cementitious materials, the content of each in the blend will be always calculated as a percentage of the total mass of the blended cement. Therefore, for example, a quaternary cement might be composed of: 67% clinker, 15% slag, 10% fly ash, 3% silica fume, and 5% gypsum.

2.5 Specific surface area

Specific surface area refers to the total surface area of all the particles contained in a unit mass of a material. As the specific surface area is always obtained through an indirect measurement, it is essential to specify by which method it has been determined, for example Blaine or B.E.T. (nitrogen). It is usually expressed in units of m^2/kg with no more than 2 significant digits. For example, the Blaine specific surface area of a typical Portland cement is $350 \text{ m}^2/\text{kg}$; the nitrogen (B.E.T.) specific surface area of a typical silica fume is $18\,000 \text{ m}^2/\text{kg}$.

2.6 Alite and belite

Alite and belite will be used to refer to the impure forms of tricalcium silicate (C_3S) and dicalcium silicate (C_2S), as suggested by Thornborn in 1897 (Bogue, 1952).

2.7 Hemihydrate

We will use the abbreviated expression “hemihydrate” to designate calcium sulfate hemihydrate.

2.8 Water–cement, water–cementitious materials, and water–binder ratios

We will use the ACI definition for the water–cement ratio, using a “–” and not a “/” to separate the word “water” from the word “cement”. In its abbreviated form, this ratio will be expressed as w/c (using the lower case w and c) but this now with a slash, with w and c representing the masses of water and cement, respectively. (The use of the upper case W and C will be reserved to express the volumetric water–cement ratio.)

14 Terminology and definitions

The water–cement ratio is the ratio of the amount of water exclusive only of that absorbed by the aggregates to the amount of cement in a concrete, mortar, grout, or cement paste mixture, preferably stated as a decimal by mass and abbreviated as w/c.

The definition of the water–cementitious material ratio and water–binder ratio are obtained by substituting in the preceding definition the words cementitious material and binder for the word cement. Consequently, we will use the abbreviated form w/b and occasionally w/cm to represent the water–binder and water–cementitious material ratios. However, we will *not* use the expression “net w/c” that is used by the ACI Committee in the definition of batch(ed) water. We do not see the necessity of adding the qualifier “net” because there are no such expressions as “gross” w/c or “net” w/c: w/c is a unique number.

2.9 Saturated surface-dry state for an aggregate (SSD)

This is an important concept for the design of concrete mixtures as well as for internal curing. In Chapter 8, it will be treated in greater detail. Here it simply refers to the condition of an aggregate particle or other porous solid when the permeable voids are filled with water, but no water is on the exposed surfaces. In its abbreviated form, the notation SSD will be used. The SSD state represents the reference state of an aggregate when calculating or expressing the composition of concrete mixtures.

2.10 Water content, absorption, and moisture content of an aggregate

In the book *High Performance Concrete* (Aïtcin, 1998), the ACI definitions were not used. Here again, we continue to persist in not following the recommendation of ACI Committee 116.

- *Moisture content of aggregate* is the ratio, expressed as a percentage, of the mass of water in a given granulate mass to the dry weight of the mass. We will instead use the expression “(total) water content”.
- *Absorbed moisture* is the moisture that has entered a solid by absorption and has physical properties not substantially different from ordinary water at the same temperature and pressure. We will instead use the expression “absorption of an aggregate”.
- *Free moisture* is the moisture having essentially the properties of pure water in bulk ; moisture not absorbed by aggregate. We will instead use the expression “moisture content of an aggregate”.

2.11 Mixing water

- *Mixing water* is the water in freshly mixed concrete exclusive of any previously absorbed by the aggregate (i.e. the water considered in the computation of the water–cement ratio).
- *Batched water or batch water* is the mixing water added by a batcher to a cementitious mixture either before or during the initial stage of mixing.

2.12 Specific gravity

Here we will (more or less) follow the ACI terminology. The *specific gravity* is the ratio of the mass of a volume of a material at a stated temperature to the mass of the same volume of distilled water at a stated temperature. This is a relative number given always with no more than two digits after the decimal point. Here, we will use the expression “SSD specific gravity” for an aggregate and not the recommended “bulk specific gravity” because the term “bulk” does not bring to mind the SSD state of the aggregate.

The specific gravity of a powder is used instead of “absolute specific gravity” because we are uncomfortable in using the qualifier “absolute” before a relative number. Moreover, for us, the theoretical specific gravity of Portland cement is not 3.15 or 3.16; it is instead 3.14. (The first author does not like to clutter his memory with too many numbers, as he is slightly dyslexic!)

2.13 Superplasticizer dosage

We will continue to express the superplasticizer dosage as the percentage of active solids contained in the commercial solution used relative to the mass of the binder used in a mixture. In some cases, we will indicate the number of litres of the commercial solution used to reach this percentage.

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3 The water–cement and water–binder ratios

3.1 Introduction

This chapter is one of the shortest in this book but, in our opinion, it is the most important. When sustainability becomes the key design factor, the most important characteristic of concrete will no longer be its 28-day compressive strength, but rather its w/c or w/b. In fact, throughout this book, it will be shown that this number determines the conditions of hydration upon which the properties of both fresh and hardened concrete depend.

About 100 years ago, Féret (1892) and then Abrams (1918) stated that, all other things being equal, the compressive strength of a paste (Féret) or of a concrete, f'_c (Abrams) is a function of the w/c (Aïtcin and Neville, 2003). Later, the importance of the water–cement ratio on many other properties of hardened concrete was established, particularly when durability was a concern. Unfortunately, however, w/c never received as much attention as f'_c , which to structural engineers still remains the key factor when designing concrete structures.

In most building codes, the w/c is taken into consideration primarily when the concrete is expected to face specific severe environmental conditions. But, in our opinion, the critical values found in these codes were (and still are) not severe enough because, in the absence of efficient dispersing agents (water reducers, superplasticizers) it was impossible to lower the w/c value below about 0.45 when making a 100 mm slump concrete. This technical limitation, and the laxity reigning in the industry, has had serious drawbacks for the durability of concretes exposed to severe environments. At present, we are learning this the hard way every time it becomes necessary to demolish a concrete structure after a life cycle as short as 35 to 50 years, because it was unable to face the severe environment to which it was exposed. There is no country in the world rich enough to afford such an economic waste; moreover, this waste is also unacceptable from a sustainability point of view. The premature reconstruction of our infrastructures corresponds to an unacceptable waste of materials, energy, and work and an unnecessary emission of greenhouse gases.

In order to lengthen the life cycle of concrete structures to 100 years or more there is no choice other than to lower the w/c or w/b of the concrete, and to cure it properly. Therefore, it is now more necessary than ever to learn how properly to make, place, and cure low w/b concretes made with blended cements containing less and less Portland cement clinker; this is the challenge that faces the concrete industry. The principal objective of this book is to point out the necessary changes in our attitudes and ways of treating concrete in the field, in order to be able to fulfill the goal of building concrete structures that are durable, sustainable, and economical. This new vision of concrete will be the key factor for the long-term competitiveness, prosperity, and indeed survival of our industry.

3.2 Historical background

In the paper “How the water–cement ratio affects concrete strength” (Aïtcin and Neville, 2003), it was shown how Féret and Abrams were able to link cement paste and concrete compressive strengths not to the amount of cement used in a concrete mixture, but rather to the ratio of the mass of the water to the mass of cement used. This apparently very simple and important concept was initially developed when concrete technology was in its infancy. The expression “water/cement” was then absolutely clear: concrete was made using solely Portland cement, aggregate, and water. But, in order to make concrete structures more sustainable, modern binders contain more and more cementitious materials or fillers different from Portland cement and so it is legitimate to question the validity of the old concept (Barton, 1989; Kosmatka, 1991). Can the water–cement ratio be simply transformed into the water–binder ratio calculated as the ratio of the mass of water to the mass of all of the cementitious materials composing the blended cement? Might it be useful also to calculate separately the water–cement ratio when using a blended cement? (In this case, this water–cement ratio would be calculated by dividing the mass of water by the mass of the Portland cement present in the blended cement.) Before trying to find an answer to these questions, let us go back to the simple water–cement ratio of the “good old days”.

3.3 The water–cement ratio: the personal progression of P.-C. Aïtcin

During my career as a university professor, year after year, I tried to inculcate in my students the fundamental importance of the water–cement ratio, because it influences most concrete properties, from strength to durability. I must admit that with the years, I realized that I was not very convincing and successful: I was not exactly preaching in the desert, but not far from it. (The experience of the second author was not dissimilar.) I tried various

different approaches but apparently without much better results. One day I asked a good student: “What is the problem with the w/c ?” His answer was very simple and straightforward: first, it is an abstract number without any particular meaning except that it is the ratio of two masses; second, it is an inverse relationship with strength and I don’t like inverse relationships, I prefer direct ones.

Since that day I knew what I would have to do to be more convincing about the importance of the w/c , but it took me some time to develop a more sensible approach and to find a physical meaning for the water–cement ratio. I remember that the first significant step forward was made when I tried to explain to my graduate students that in high-performance concrete the water–cement ratio was decreased not only because more cement was introduced into the mixer, but also, and above all, because less water was used due to the very efficient dispersing properties of superplasticizers. To illustrate this point I asked my computer technician to represent in two dimensions two cement pastes having a w/c equal to 0.25 and 0.65. In this primitive model, the ratio of the surface of the grey particles representing the cement particles to the white part of a unit volume representing the water was equal to the (mass) water–cement ratio (Figure 3.1).

This very primitive model clearly showed that in a unit volume of paste there were many more cement particles when the w/c was 0.25 rather than 0.65. The cement particles were also closer to each other, made possible by the reduction of the mixing water due to the use of a superplasticizer. From a pedagogical point of view I was pretty satisfied and I used this “model” not only with my students but also in all kinds of situations and in some of my presentations, where I was able to improve it by colouring the water in my slides blue. However, from a scientific point of view, I realized how primitive this model was.

It was only recently, in Puerto Rico at the ACI Fall Convention in 2007, that I asked Dale Bentz if, using the sophisticated models he was juggling with, he could calculate the average distance between cement particles in a

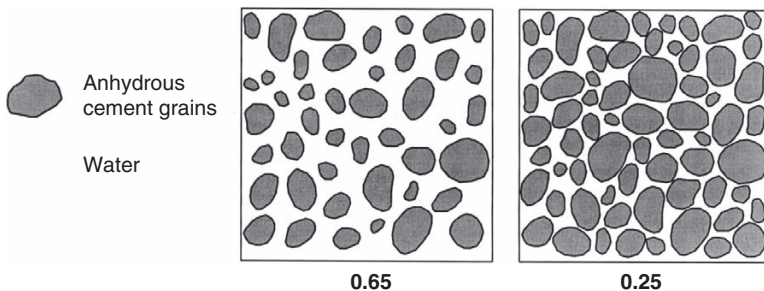


Figure 3.1 Schematic representation of two cement pastes having a w/c ratio of 0.65 and 0.25. Reproduced from *High Performance Concrete*, Aitcin 1998. (Courtesy of Taylor & Francis).

cement paste as a function of the water–cement ratio. In a fraction of second, I saw his face light up, and 2 weeks later I had my answer with a proposal for a co-authored paper on the hidden meaning of the w/c (Bentz and Aïtcin, 2008). With his model, Bentz was able to show the influence of the grain size distribution of the cement particles and their specific surface area on the average distance between cement particles in a cement paste. He was also able to show that the Blaine specific surface area does not permit a proper evaluation of the microstructure of a cement paste.

We have incorporated the two-dimensional representation of Bentz's model in this book (Figure 3.2). Using this model, it is possible to show **quantitatively rather than qualitatively** that the w/c ratio is an indirect way of evaluating the average distance between the cement particles in a cement paste. This, then is the hidden meaning of the w/c: *the smaller the w/c the smaller the distance between cement particles*; this is the direct relationship that I was looking for to demythologize the w/c concept. The w/c then becomes a number with a simple physical meaning.

From this direct relationship, it is easy to understand that the smaller the spacing between cement particles, the faster the cement hydrates fill in the gaps between cement particles, and the stronger the links created by these hydrates; most importantly, the stronger the concrete. Additionally, the smaller this spacing, the greater the effect of the interaction between cement particles on the rheology of the fresh concrete, the smaller the size of the pores created by self-desiccation, and when there is no extra source of external or internal water, the smaller the menisci that develop in these pores and the larger the stresses generated by autogenous shrinkage.

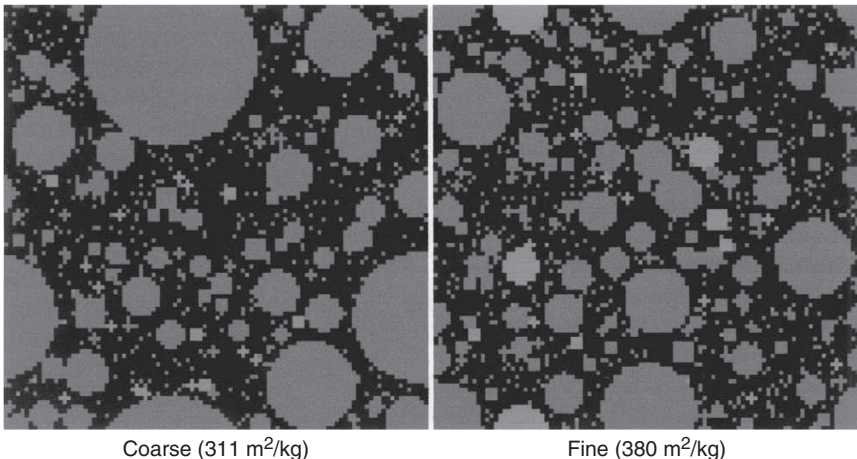


Figure 3.2 Dale Bentz's model representing the concept of w/c. Reproduced with permission of the American Concrete Institute, 38800 Country Club Drive, Farmington Hills, MI 48331, USA.

3.4 The concrete industry and the w/c ratio

The penetration of the w/c concept into the industry has been even poorer than its penetration into the brains of our students. This is essentially due to the fact that, in general, the concrete industry is an industry that is fully satisfied with its “low tech” level and does not see the necessity to “fly with the eagles”. Hopefully, there are some exceptions; John Albinger (Albinger and Moreno, 1991) was one when, in the late 1960s, he began to propose 60 MPa concretes for the columns of sky-scrapers in the Chicago area.

The concrete industry has been always reluctant to focus on the w/c because it is not easy to determine it exactly. It is difficult and troublesome to track precisely the “hidden” water of the aggregates and the water left by the truck drivers at the bottom of their mixers after they wash out. It is so much easier to monitor it indirectly by measuring the slump and the 28-day compressive strength of the batched concrete. Moreover, in the “good old days”, when a barrel of oil was only \$2.00, Portland cement was not so expensive (fuel expenses represent 30% to 35% of the cost of production of Portland cement clinker); therefore, it was much easier to add a few extra kilograms of cement into the mixer rather than to bother with tracking all the forms of “hidden” water.

This “comfortable” situation started to change when the market for high-performance concrete emerged (Aitcin, 1998). The full control and knowledge of the water present in the mixer in its different forms is a must in order to make economical and satisfactory high-performance concrete. At present, both the price of a barrel of oil and sustainability have become major parameters when designing and building concrete structures. The concrete industry has no other choice than to control the w/c ratio of **all** of its concrete mixtures. It is no longer simply a troublesome operation; it has become a necessity for survival.

3.5 Water–cement or water–binder ratio

As stated in the Preface, modern binders will increasingly contain less and less Portland cement clinker and more and more cementitious materials of a different nature: slag, fly ash, silica fume, metakaolin, calcined clay, rice husk ash, diatomaceous earth, natural and artificial pozzolans, limestone filler, silica filler, powdered glass, and even 0% clinker (Gebauer *et al.*, 2005; Cross *et al.*, 2010). Therefore, the very simple w/c concept is “passé” but the questions remain: Do we simply throw it out? Do we replace it and, if so, by what? These questions have been abundantly debated in the technical literature and it is not our intention here to embark on a discussion of the various opinions. We would rather state our personal opinion on the subject, based on what we believe is a scientific approach to the real meaning of the w/c ratio: the distance between binder particles within the binder paste.

Throughout this book, we will speak of the w/b of a concrete mixture, the w/b ratio being obtained by dividing the mass of effective water by the mass of the binder. We only replace the word “cement” by “binder” in the original definition of the water–cement ratio. However, as most of the cementitious materials and fillers blended with Portland cement clinker are much less reactive than Portland cement during setting and early hardening, it is still important to calculate the actual value of the water–cement ratio because the early strength and impermeability of the hardening concrete are almost entirely a function of the bonds created by the early hydration of the Portland cement portion of the binder. Therefore, the water–cement ratio is not entirely “passé”; it is still a very important characteristic of modern concretes made with blended cement.

It is not always easy to calculate the exact water–cement ratio because the exact composition of the blended cement is not always known, with some standards specifying only a range of potential compositions and not a precise composition. A phone call to the cement producer should solve this lack of certainty.

It would, however, be simplistic and erroneous to think that the early properties of concrete depend exclusively on the w/c while the long term ones depends on the w/b. In fact the early properties of the fresh concrete depend not only on the w/c and on the *reactivity* of the Portland cement, but also on its content. The shape and the reactivity of the other cementitious materials introduced in the blended cement also influence the properties of the fresh concrete, but usually to a lesser extent.

On the other hand, the early autogenous shrinkage developed in a concrete depends on the w/b rather than the w/c because it is the spatial distribution of the particles of the binder in the cement paste that determines the pore size distribution of the solid skeleton, the size of the menisci, the stresses generated in these menisci, and finally the intensity of autogenous shrinkage. Thus, it will be necessary to consider both ratios, the w/c and w/b, as equally important when dealing with modern concretes.

3.6 How to transform the w/b into MPa

Before ending this chapter, we will not consider how to lower the w/b; this topic will be developed in Chapter 7 devoted to superplasticizers. Rather, we will see how, from a practical point of view, it is possible to link the w/b to concrete strength. As building codes are based on f'_c , it is of great importance for designers to pass from the w/b to concrete compressive strength.

In his paper “In defence of the water–cement ratio” Kosmatka (1991) reproduced Abrams’ original curve, showing the relationship between 28-day strength and water–cement ratio. In “Design and Control of Concrete Mixtures”, Kosmatka and his co-authors (2002) present the relationships linking the water–cement ratio and concrete compressive strength recommended by the Portland Cement Association for concretes made

exclusively with Portland cement. However, with modern concretes being made with so many types of blended cements, the only thing that remains valid in these relationships is the general shape of the curves. As the cementitious nature of modern binders is extremely diverse, it is no longer possible to provide any general relationship linking the compressive strength of a concrete with its w/b; only trial batches, made preferably with the equipment that will be used to make the concrete, can give the appropriate relationships.

Using the same principle as an artillery officer zeroing in on a target, to establish such a relationship we suggest using an approach derived from the adjustment of artillery firing. It consists of making three experimental concretes having w/b ratios that cover the design compressive strength, one being low, one high, and one supposedly adjusted to the target strength. In this approach, it is very important that the low design be really low and the high one really high. Then, it is only a matter of interpolation to find the characteristics of the mixture to obtain the desired compressive strength. Usually, for high-performance concrete, we use w/b values of 0.30, 0.35, and 0.40; for normal strength concrete w/b values of 0.40, 0.50, and 0.60. Generally, the intended compressive strength is obtained with the fourth trial batch.

This method allows the integration of the diversity of the materials used to make concrete as well as the diversity of the equipment used. Even for concrete having strength slightly outside the studied ranges, it is legitimate to make extrapolations. Concrete producers should make available to designers the relationships they have developed within a certain predictive range, taking into account the variability inherent in their production.

3.7 The sustainability of low w/b ratio concretes

Here, a very simple example will be used to show how high-performance concrete having a low w/b ratio is more sustainable than a normal strength concrete. Let us consider two unreinforced concrete columns built with 25 and 75 MPa concretes supporting the same load L (Figure 3.3). If A is the cross-sectional area of the column made with the 75 MPa concrete, the cross-sectional area of the 25 MPa concrete will be $3A$ since $L = A \times 75 = 3A \times 25$.

In Figure 3.3, the 25 MPa column will be three times larger in cross-section than the 75 MPa column. Let us now consider the volume of materials necessary to build these two columns. The volume of coarse aggregate in 1 m^3 of these two concretes can be considered the same without making a large error: it is about 1000 to 1100 kg/m^3 . Of course, the amount of sand used to make 1 m^3 of 75 MPa concrete will be slightly lower than that necessary to make the 25 MPa concrete, about 650 kg/m^3 rather than 850 kg/m^3 . Let us suppose that to make a normal strength concrete having a design strength of 25 MPa, nine times out of 10, it is necessary to use roughly 300 kg/m^3 of blended cement without any admixture. Some might

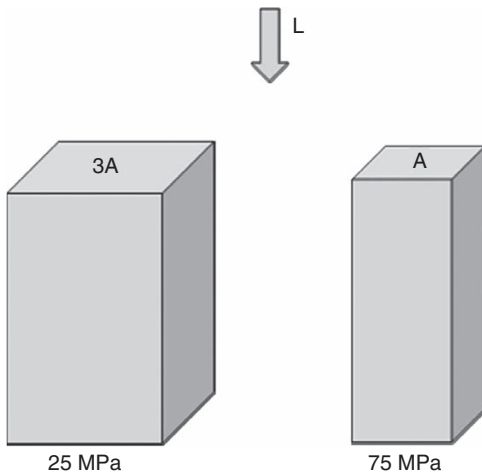


Figure 3.3 Comparison of 25 MPa and 75 MPa columns.

consider this amount of cement somewhat too large but for the purpose of this demonstration, it is easier to work with a round number. Let us suppose that to make the 75 MPa concrete, it is necessary to use 450 kg/m^3 of the same blended cement with, of course, about 5 l/m^3 of a good superplasticizer that is compatible and robust. Consequently, to get a 75 MPa concrete, it is only necessary to use 1.5 times more cement than in the case of the 25 MPa concrete, which means that only half as much cement will be used for the 75 MPa column.

If, in this rough analysis, we neglect the difference in the volume of sand and superplasticizer needed to make these two concretes, it can be said that when using a 75 MPa concrete instead of a 25 MPa one to build an unreinforced concrete column supporting the same design load L , it is necessary to use only half as much cement and one-third as much aggregate.

Of course, the savings in cement and aggregates are less impressive for concrete elements working in flexure, but Denis Mitchell at McGill University (private communication) has estimated them to be (conservatively) of the order of 20% to 25%.

The consideration of sustainability when designing concrete structures unquestionably involves the use of low w/b concrete rather than normal strength concrete. Designing with low w/b concrete whenever possible will be the great contribution of designers in the search to improve as much as possible the sustainability of concrete structures. In order to eliminate buckling and improve the stability of the structure, it may be necessary to design hollow columns. Architects should be happy with such a move because they will then have a very safe place for all of the unaesthetic wiring that is invading modern buildings. The use of hollow piles is already quite



Figure 3.4 Confederation Bridge.



Figure 3.5 Viaduc de Millau.



Figure 3.6 The Burj Khalifa Tower in Dubai.

common when building large bridges, such as the Confederation Bridge in Canada or the Viaduc de Millau in France (Figures 3.4 and 3.5). The Burj Khalifa Tower was also built with a low w/b concrete (Figure 3.6).

3.8 Conclusion

As will be seen throughout this book, if durable and sustainable concrete structures are to be built, it is imperative to lower the w/b of modern concretes, and to control as precisely as possible the w/b of the concretes that will be used to build them. There is no other choice. Those who are not convinced that the water–binder ratio is the most fundamental concept on which the durability, the sustainability, the profitability, and the survival of our industry depends should close this book now and continue to wander in the wilderness.

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26 *The water–cement and water–binder ratios*

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4 Durability, sustainability, and profitability

4.1 Introduction

The cement industry is known as an industry that changes very slowly, but during the twentieth century it succeeded in going from a modest industry producing, annually, only 10 million tonnes of Portland cement at the beginning of the century to a global industry producing about 2.5 billion tonnes, annually, at the end of the century. In reality, the consumption of cement started to increase significantly only after the end of the Second World War (Aitcin, 2007a).

From a theoretical point of view the manufacture of Portland cement clinker has always been simple. It consists of burning at about 1450°C a well-proportioned mixture of limestone, clay, and iron oxide and then grinding the resulting clinker finely after mixing it with about 5% gypsum. What is not so simple is to manufacture, economically, millions of tonnes of cement in a plant costing US\$200 to \$300 million that cannot produce anything other than Portland cement (Dumez and Jeûnemaitre, 2000). It took two petroleum shocks that drastically raised the cost of the fuel that represents more than 30% of the production cost of Portland cement clinker to get the cement companies moving along the path of change in their process. Over a period of 15 to 25 years the wet production process has almost disappeared. Decarbonation is now carried out in towers outside the kiln, so that only a few kilocalories are lost during the process. The length of the kilns has decreased significantly, their diameter has increased, and their output has increased enormously. In the early 1970s, an up-to-date kiln could only produce around 2000 tonnes per day, while presently there are kilns producing about 10 000 tonnes per day.

It took the pressure of both environmentalists and governments for the cement plants to reduce their solid emissions as well as their SO_3 and NO_x emissions. Technically, it was not too complicated, and financially not too expensive to achieve this, but some plants had to face a new problem; what to do with the large amounts of cement kiln dust (CKD) that could not be reintroduced into the cement as limestone filler. Such CKDs also cannot be stockpiled as such in quarries because they can contaminate surface water or the water table.

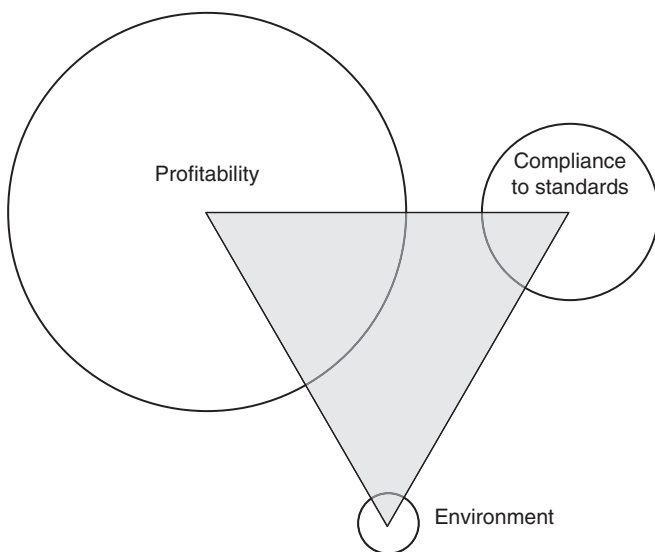


Figure 4.1 Schematic representation of the preoccupations of the cement industry during the twentieth century.

Figure 4.1 represents, schematically, the essential preoccupations of the cement industry until quite recently. It was a comfortable situation permitting a slow rate of change in the face of relatively mild constraints, and an increase in profits.

Currently, a new effort to improve the process is being asked of the cement industry as sustainability has become the *leitmotif* of the development of our societies (Figure 4.2), but this time it requires more than simply reducing the CO₂ emissions associated with the production of Portland cement clinker; it also requires improving the durability and sustainability of concrete structures in order to preserve our natural resources. For the first time, a simultaneous effort is being asked of both the cement and concrete industries, two industries that, surprisingly, did not collaborate much in the past.

In this chapter, it will be shown that it should not be too difficult or too costly to face these new challenges. It will only be necessary to put into practice technologies already well known. The real challenge will be to change the old bad habits of a not very highly educated industry.

4.2 Durability: the *leitmotif* of the construction industry during the twenty-first century

We cannot continue to rebuild our infrastructure every 30 years or so just because it was initially poorly built by using the wrong Portland cement,

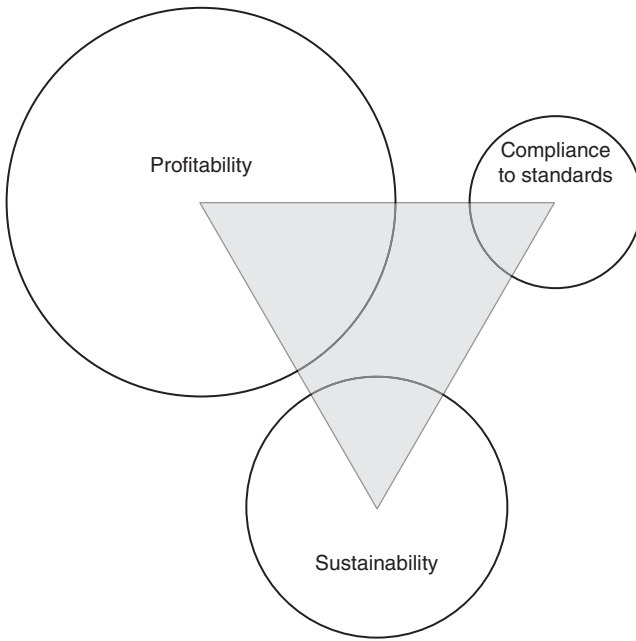


Figure 4.2 The Bermuda triangle of the twenty-first century.

ignoring environmental conditions, forgetting the importance of the w/c “law”, and skimping on placing and curing procedures. No country in the world is rich enough to continue to do so, and it is the duty of the cement companies to promote and to teach the necessity of building a durable infrastructure. Cement companies are the only link in the construction industry that are global and rich enough to do so. Such a promotional and educational effort should finally improve the competitiveness and profitability of the cement industry. It is particularly urgent to develop these efforts in emerging countries where the consumption of cement will increase drastically. They should profit from the Swiss and the Japanese experiences in building durable structures.

We sincerely hope that CO₂ emissions will soon be taxed. This will create new business opportunities. The companies that move the fastest in the reduction of CO₂ emission per MPa will be the ones that will profit the most rapidly from this. It is easy to demonstrate that within the same global CO₂ quota, at least twice as much durable concrete (>100-year life cycle) can be produced with the present technology and without any major financial investment. The only investment will be to put into practice present technologies and to educate the industry to change their bad habits.

4.2.1 Durability and profitability

Like any other industry the cement industry must be profitable. In fact, it is already very profitable. One of its great achievement during the second part of the twentieth century was to succeed in marketing an inexpensive commodity material (remarkably inexpensive in spite of the usual complaints of concrete producers), while reaching a high degree of profitability. This profitability is the result of constant improvements in the process that resulted in a high degree of automation. However, what has been missing is the concomitant teaching of the proper use of Portland cement when making concrete. Presently, by ignorance or by error, large amounts of concrete (and consequently of cement) are wasted because:

- water reducers are neither systematically used when making concrete nor introduced systematically at the cement plant during the final grinding;
- designers focus only on strength without taking into account environmental conditions;
- placing and curing specifications are poorly written;
- contractors do not place and cure concrete properly, because they are not specifically paid to do so.

Too often all of these basic mistakes, and many others, decrease the durability of concrete structures, which results in early repairs, in expensive rehabilitation programmes, or in even more expensive demolition and reconstruction projects. It is always difficult and costly to repair, rehabilitate, or demolish bad concrete. This type of work generates high labour costs but few material expenses, and there are also always high social costs associated with them (detours, traffic jams, accidents, etc.). As a result, on a long-term basis, this is not a profitable proposition for the cement and concrete industries, or for all of us taxpayers.

The cost of the cement itself represents only 2% to 4% of the cost of a new structure, depending on the degree of sophistication of the formwork system and reinforcement, while in repair or reconstruction work the cement can represent as little as 0.1% of the cost. Let us consider the case of the rehabilitation of a concrete wharf at Bora-Bora Island. This wharf required a serious rehabilitation programme because the piles supporting the deck were in very bad shape due to their poor performance in the marine environment. In the year 2000, the cost of the repair was US\$850 000, apart from the engineering costs. Only 32 m³ of concrete were used. Most of the expenses were labour costs (divers, carpenters, steel workers, extra time) and travel and transportation expenses. The cost of each cubic metre of concrete used in this rehabilitation work was US\$26 500. These must be amongst the most expensive cubic metres of concrete ever placed! If we assume that the cement content of the concrete used to rehabilitate the wharf was 365 kg per m³,

this represents a cement consumption of $32 \times 365 = 11\,680$ kg, that is slightly less than 12 tonnes of cement. If these US\$850 000 had been used in Bora-Bora to build a new structure the cost of the cement would have represented about US\$17 000 to 34 000, which is much more than the cost of 12 tonnes of cement.

From a business point of view, finally, the worst competitor of concrete is not steel, wood, aluminium, glass, or bricks, it is bad concrete. As long as the cement and concrete industries remain inactive in the field of teaching good concreting practices and durability, they decrease their long-term profitability, because building durable structures requires the use of more cement initially, but less repair work, less rehabilitation, and less demolition. The cement and concrete industries must promote durability to increase their profitability!

4.2.2 *Durability and sustainability*

It is not too difficult to understand why any increase in the durability of concrete structures increases the sustainability of the construction industry. A structure built with durable concrete will necessitate less repair work, will delay and decrease significantly any rehabilitation work, and will lengthen the life cycle of the structure. As stated earlier, no single country is rich enough to rebuild its infrastructures every 30 years, as we are doing now. As a consequence of this huge rehabilitation or reconstruction programme, there is not enough “fresh” money to build new infrastructure. Contractors do not care because they charge mostly for labour expenses rather than material expenses, but the cement and concrete industries are hurt by this. More repair work means less new construction and a decrease in the cement consumption. It is not surprising that the consumption of cement per capita remains at high levels in Japan and Switzerland as compared to other countries with a high per capita income: the Swiss and Japanese build primarily durable structures, initially rich in cement but with a low w/c, which do not need as much repair.

It is actually very simple to make a durable structure. It necessitates the use of appropriate cements and aggregates which are able to face successfully the specific environmental conditions, the use of a concrete having a w/c between 0.35 and 0.40 that keeps its fluidity for about $1\frac{1}{2}$ hours, placing it correctly and curing it appropriately with water. The durability of a concrete always depends on its weakest link.

Designers must focus on environmental conditions more than on MPa's. Why use sophisticated finite element programs to calculate the stresses and the strains in a structure while ignoring whether the concrete will be able to maintain its 28-day f'_c and E'_c during the life cycle of the structure? **Cement producers** will have to optimize the characteristics of their cement, not to increase the cube strength of the cement, but rather to maintain the initial rheology of the cement paste for $1\frac{1}{2}$ hours with the aid of chemical

admixtures (Aïtcin, 2007b). *Specifiers* will have to learn how to write appropriate specification for placing and curing concrete. *Contractors* will have to be paid specifically to cure concrete properly. Then it will be easy and not too costly to build durable structures. It is a win-win solution for all of the sectors of the construction industry, for the owners, and for the taxpayers.

4.3 Sustainability

For the cement, the concrete, and the construction industries, sustainability means simply more durable kN's with less CO₂ emissions. In other words, it means:

- more clinker made with less limestone and less fuel,
- more cement with less clinker,
- more concrete with less cement,
- more kN's with less cement and less aggregate,
- more durable structures with a longer life cycle.

It is our view that this is not too difficult a challenge because we have now already mastered all of the technologies to achieve such goals separately. The true challenge is to oppose the inertia to change that characterizes our industry. Innovation is not the driving force of our industry; it is, rather, experience and tradition. But there is some hope: experience teaches us that conviction, education, and patience allow us to progress and move forward slowly. Political pressure can also force our industry to change its habits a little bit faster.

How many years did it take to put into practice the findings of Féret and Abrams? How many years did it take to realize the potential of Freysinnet's work on post-tensioning? How many years did it take to see the concrete industry realize the technical potential of silica fume? How many years will it take to impose durability as the most important design criterion?

We are not in a mass production industry, but rather in a commodity industry, rarely building two identical structures except occasionally, and in a competitive industry where up to now the winners are the **lowest** bidders and not the **best** bidders. Let us examine point by point how, by tomorrow morning, we could start to improve the sustainability of our industry.

4.3.1 *Making more clinker with less limestone and less fuel*

Presently, in a modern cement plant, the production of 1 tonne of clinker implies the extraction of 1.15 tonnes of limestone and the emission of 0.8 to 1.2 tonnes of CO₂ (to simplify let us assume 1 tonne). Roughly,

0.5 tonnes come from the decarbonation of limestone and 0.5 tonnes from the combustion of the fuel. Do these last two numbers constitute impassable technological barriers or can we decrease them significantly?

4.3.1.1 *Making more clinker with less limestone*

Until recently, for cement company managers the easiest and most profitable way to make Portland cement clinker was to find limestone and clay quarries close to each other and to a market area. Later, with the progress in water transportation, the proximity of a harbour, river, or canal became a serious economic advantage to facilitate the export or import of clinker during the lows and the highs of the cycles of the construction industry, as well as to take advantage of the decrease in the transportation cost of the fuel. However, up to now, the limestone quarry has always been the heart of a cement plant.

From a theoretical point of view the use of limestone as a source of lime (CaO) is not an essential prerequisite for making Portland cement clinker. The chemistry of Portland cement clinker tells us that the raw meal must contain well-known proportions of CaO , SiO_2 , Al_2O_3 , and Fe_2O_3 to be able to end up as Portland cement clinker. If we look at the ternary phase diagram $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ represented in Figure 4.3, we can see, for example, that a combination of anorthite and quartz or gehlenite and quartz in combination with limestone could be used to make Portland cement. We seriously doubt that cement companies will dispatch their geologists in the field to find these new sources of raw materials, but we are pretty sure that in the near future the existence of a source of blast furnace slag (it does not matter whether it is crystalline or vitreous) or of a class C fly ash rich in lime will be considered when deciding where to build a new cement plant (Figure 4.4). Even if CO_2 emissions are limited and taxed, the transportation of slag or class C fly ash to the limestone quarry could become a profitable operation.

It is easy to show that the replacement of clay by a blast furnace slag already containing 40% of CaO corresponds to a 22% decrease in CO_2 emissions when producing Portland cement clinker (Figure 4.5 and Table 4.1) (Aïtcin, 2007c); or within the same CO_2 emission quota, an increase in the production of clinker by 28%. Of course, when using a class C fly ash that contains less CaO than a slag these figures are less impressive. Moreover, as will be seen in the next section, if 30% of Portland cement clinker is replaced by 30% of vitreous slag (this time it is important that the slag be vitreous) it is possible to make 100% more cement within the same CO_2 quota. And if modern concrete technology is put into application this means that at least three times more concrete can be made within the same CO_2 quota. There is enough hope to dream that this will happen soon!

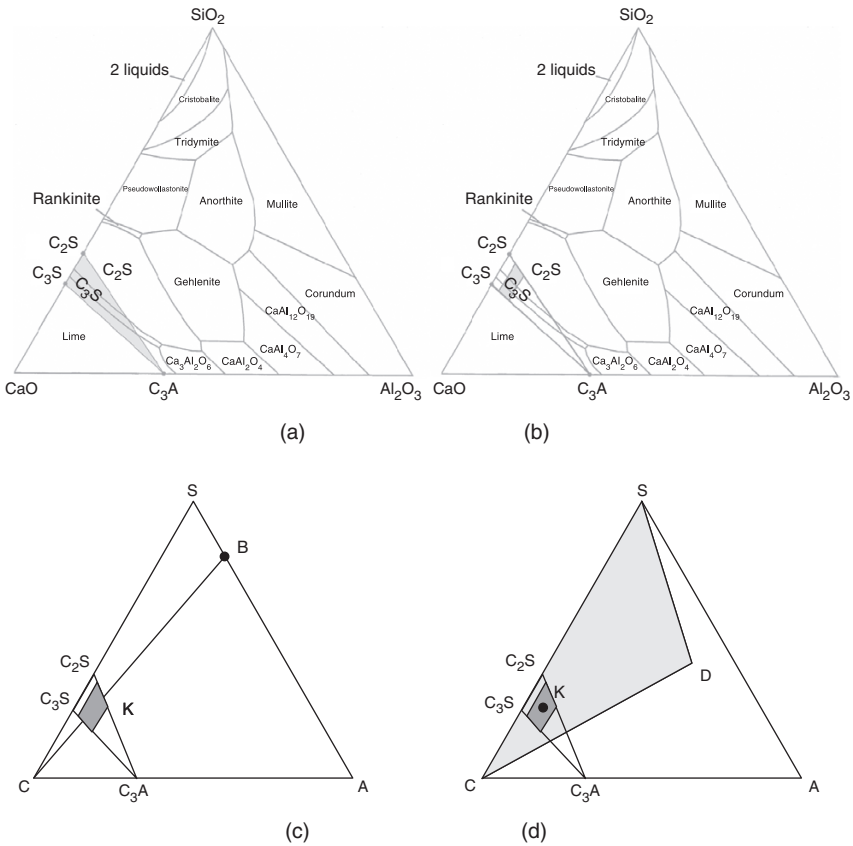


Figure 4.3 The $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram. (a) Composition area of co-existing $\text{C}_3\text{S-C}_2\text{S-C}_3\text{A}$. (b) Composition area of Portland cement clinker. (c) Obtaining K with a binary raw meal. (d) Obtaining K with a ternary raw meal.

4.3.1.2 Making more clinker with less fuel

Fuel cost is a very important part of the production cost of clinker; Scheubel and Natchwey (1997) estimated this cost to be 30% of the production cost in 1996. The present increase in the price of petroleum has destroyed all the efforts of the cement producers to decrease this dependence on fuel cost.

We will not here look at the use of alternative fuels, which is a profitable business for the cement industry (sustainability creates business opportunities in that matter). However, the use of alternative fuels does not decrease CO_2 emissions, and does not permit us to make more clinker

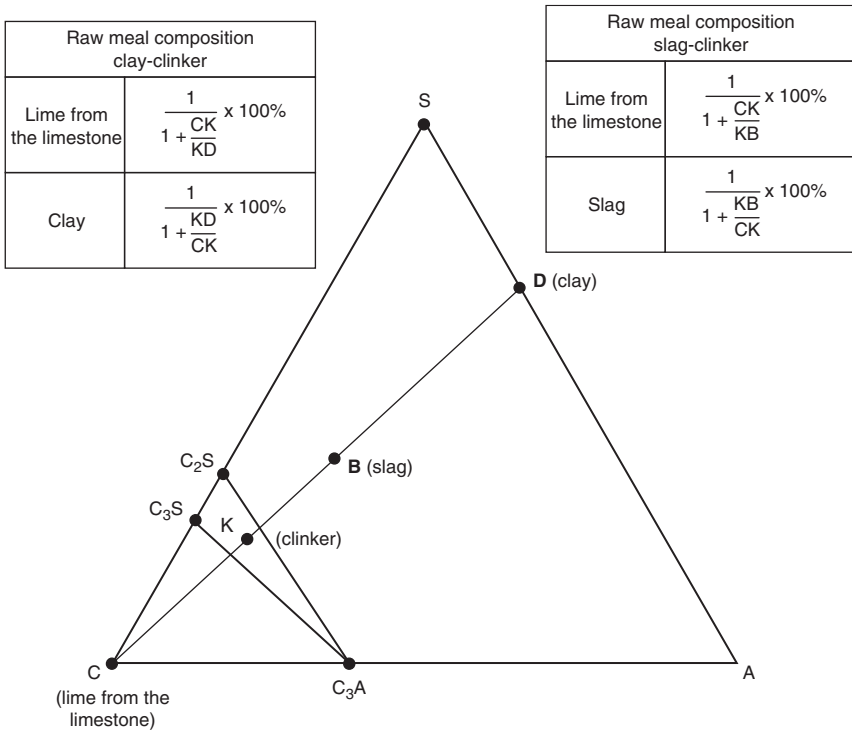


Figure 4.4 Calculation of the raw meal composition using the clay (D) or the slag (B) and limestone (C) to produce clinker K.

with less fuel; it is only a profitable business. We will instead briefly focus on the decrease of the clinkerization temperature through the use of mineralizers.

It is known that when some fluorine or sulfur are introduced in small quantities, a decrease of 100 to 150°C can be observed in the temperature that has to be reached in the kiln to produce a reactive clinker. The use of such mineralizers is advantageous at two levels: it decreases the cost of the fuel necessary to produce the clinker and it decreases the emissions of CO₂ and NO_x.

It seems that this is easier to say than to do this and that it could take some years before this technology becomes applicable in all cement plants, but the financial incentives are there so that cement companies should invest the necessary money in this research and development effort (Marciano, 2003). Also, making Portland cement clinkers having a lower C₃S content decreases CO₂ emissions.

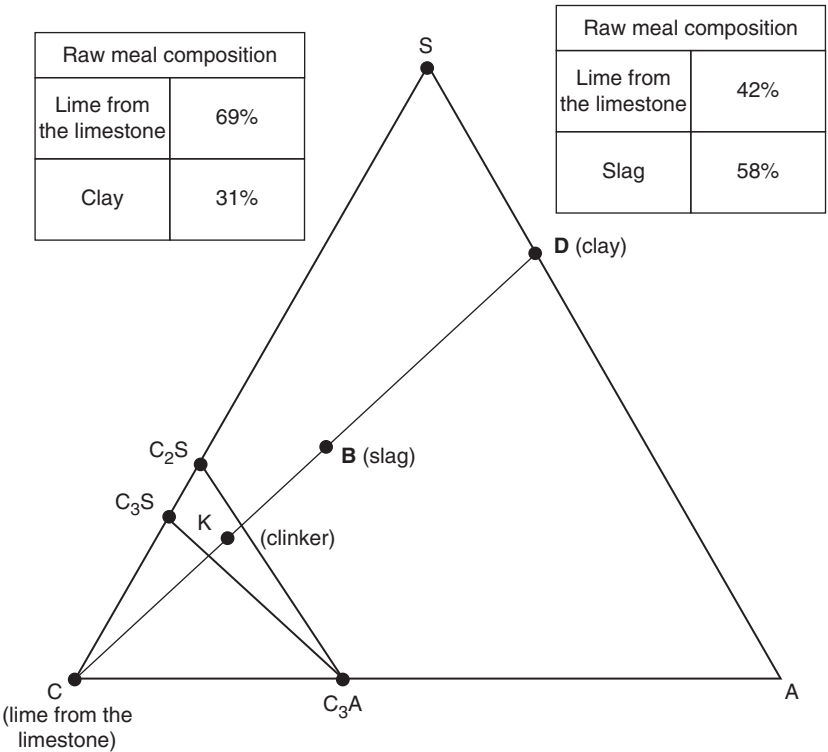


Figure 4.5 Raw meal compositions to produce the slag and clay clinkers.

Table 4.1 Comparison of the CO₂ emitted when producing a clay-clinker or a slag-clinker

Pure Portland cement clinker	CO ₂ emission (pure Portland cement)		
	Clinker	Combustible	Total
Limestone + clay	0.49	0.45	0.94
Limestone + slag	0.19	0.45	0.64

4.3.2 Making more cement with less clinker

It is not a revolutionary idea to blend Portland cement clinker with other cementitious materials, once the verb dilute is replaced with the verb blend (Mehta, 2000; Malhotra, 2006) (Figure 4.6).

Europe is well ahead in this matter; the Netherlands and Belgium are the countries in which the average substitution rates are the highest, about 35% in the Netherlands and 30% in Belgium. In these two countries contractors

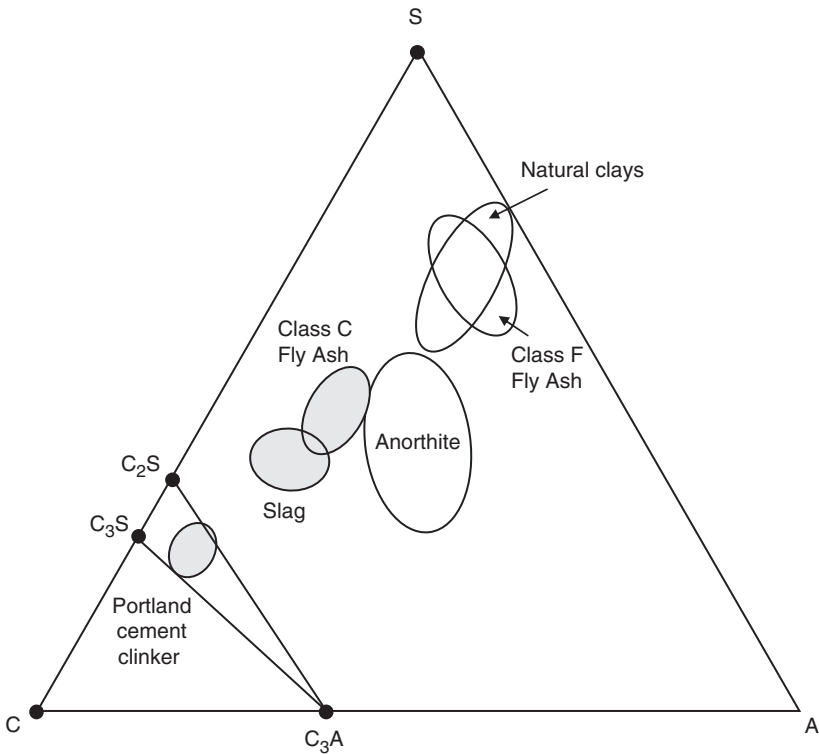


Figure 4.6 Schematic representation of the composition of slag, class F and class C fly ash, anorthite, and natural clays.

have been educated to use competitively these blended cements that are less “nervous” and more robust than pure Portland cement. Of course, pure Portland cements are still produced and used in the Netherlands and Belgium, as well as cements containing more than 50% of cementitious materials other than Portland cement clinker. With the present state of technology for decreasing the w/c ratio, an average level of 50% of substitution is possible. This means that with the present amount of clinker produced annually by cement companies twice as much cement could be put on the market and at least twice as much concrete.

What about a totally non-clinker cement? Such a cement is already marketed in Belgium and the Netherlands by the Obourg Cement Company (Gebauer *et al.*, 2005). It is a mixture of finely ground blast furnace slag, anhydrite, and an alkaline activator. Of course, such a cement is presently used only for very special marine works, but, as it also obeys the w/c law, its use in traditional construction should come earlier than the developers of this cement believe.

Looking at the long term, we would like to mention the reflections of a Canadian environmentalist about transforming limestone into a useful construction material (Hawken *et al.*, 1999). There are presently three ways to do so. The first way is to cut limestone blocks in a quarry, preferably with slaves for profitability and preferably of cubic or rectangular parallelepiped shape to be able to pile them more easily to build pyramids, bridges, castles, and cathedrals. This is not a very rapid and efficient process, but it is highly ecological and good for sustainability. There is practically no significant CO₂ emission associated with the process except for the CO₂ from the lungs of the slaves. There is a second way that is much more efficient. It consists of blasting the limestone, grinding it to a fine powder, mixing it with an appropriate amount of clay, firing it to around 1450°C, and grinding the result of this firing to a fine powder with 5% of gypsum. This is a very efficient process but not very ecological and sustainable. The third way is to give finely ground limestone to a hen and 24 hours later it produces a very strong limestone shell at the temperature of its body!

Birchall and Kelly (1983) pointed out that abalone are able to do even better: they are able to extract calcium ions from sea water and to combine them with the CO₂ dissolved in sea water to transform them into a very hard shell at a much lower temperature. But as human beings are not fish and need air to live, we prefer the example of the hen. However, the idea of Birchall and Kelly has some merit from an environmental point of view. We should start sea farming of abalone to allow more CO₂ to dissolve in sea water, eat the abalone and grind the abalone shells to give them to hens to produce eggs. Then we could make truffle omelettes and crème brûlées. This would be an excellent and sustainable solution to the transformation of limestone into a building material!

4.3.3 Making more concrete with less cement

From a technical and sustainability point of view, the Portland and blended cements actually marketed today exhibit a major weakness: the surfaces of their particles are covered with a great number of unsaturated electrical charges, negative and positive, that are generated during the final grinding. When these highly charged particles enter into contact with highly polarized water molecules they tend to flocculate (Kreijger, 1980). The mechanical action of the blades of a mixer can destroy these flocs but as soon as the cement particles are no longer sheared by the blades, the electrostatic charges recover their powerful forces and the cement particles flocculate again. A consequence of this flocculation is that a certain amount of water remains trapped in these flocs. These water molecules are no longer available to lubricate the fresh cement paste and tend to keep the cement particles far away from each other. This is deleterious for the compactness of the hardened cement paste because it increases its porosity, and this is not good for either durability or strength.

In order to increase the flowability of concrete, through laziness, facility and ignorance, some (too many) concrete producers increase the amount of mixing water, an approach that worsens the situation, since there is a much more clever and efficient solution to solve this flocculation problem. To fight the tendency of cement particles to flocculate it is necessary to fight the physical phenomenon that is at its origin: it is only necessary to use a chemical compound that will neutralize one type of electrical charge existing on the surface of cement particles. Thereafter, due to the electrostatic repulsion of the non-neutralized sites, the cement particles will be well dispersed and the formerly trapped water in the flocs can exercise its lubricating function.

As alite (impure C_3S) is the most abundant phase in clinker and is mostly saturated with negative charges (as will be seen in Chapter 7), dispersive agents usually have an active negative site that neutralizes the positive sites of the belite (C_2S) and the interstitial phase, C_3A and C_4AF . Moreover, as the interstitial phase is the most reactive from a chemical point of view, it is particularly advantageous to use a dispersant that can act upon the sulfate ions of the calcium sulfate that is added during the final grinding to control cement setting. This explains the success of sulfonate and carboxylate radicals in dispersing cement particles: when a few liters per m^3 of concrete (or even less) of such dispersive agents are introduced, the concrete slump can be increased, or the same slump can be obtained with about 10% to 15% less water.

This decrease in the amount of mixing water necessary to make a concrete of given slump can be used either to save some cement or to increase concrete durability. Till now, the admixture companies have promoted the saving of cement in order to find a niche for their business in the concrete industry: use a water reducer, they say to concrete producers, and you will decrease the production cost of your concrete.

Since cement is not a particularly expensive product, for a long time admixture companies marketed primarily lignosulfonates, a cheap industrial by-product of the pulp and paper industry, to disperse cement particles and to make a profit from this application. It worked well for many years, until both a Japanese and a German company started, almost at the same time, to manufacture synthetic polysulfonates specially designed for the cement and concrete industry. (It is interesting to note that these powerful dispersant polymers are also used in the pulp and paper, leather, and many other industries.) In the concrete industry, these dispersing agents are sold as **superplasticizers**. Their use in rich mixes (low w/c mixes) results in a decrease in the mixing water of 15% or more. They are the key products used to make high-performance concrete; due to their strong dispersing action it is possible at the same time to decrease the w/c ratio and to increase the slump. Their dispersing action is so powerful that it is possible to make fluid concrete with much less water than necessary to fully hydrate Portland cement ($w/c = 0.42$ according to Powers) or even

less water than necessary to stoichiometrically hydrate cement particles ($w/c = 0.22$).

All of the present cements now used need to be deflocculated when they are mixed with water. This deflocculation is very easily achieved when using a dispersing agent. However, because this dispersing agent is not systematically added at the cement plant and because the admixture industry has not yet succeeded in educating concrete producers to use them (particularly in emerging countries), we estimate that on a worldwide basis about 100 million tonnes of cement are wasted annually. The idea is not to close 100 cement plants; the idea is to make more concrete with the 100 million tonnes of cement that could so easily be saved.

If the cement industry is really interested in making Portland cement and concrete sustainable they should start to add a dispersing agent during the final grinding. Some detractors to this idea of adding anything other than “gypsum” during final grinding have told me that the North American cement industry tried without success to add air entraining agents during the final grinding of Portland cement to promote the use of air entrained concrete, and that it is not necessary to repeat the same error. They are wrong, however, because the entrainment of air depends on a large number of factors that have nothing to do with the cement characteristics, while adding a dispersing agent during the final grinding corrects a fundamental weakness of cement particles. Of course, each cement company will have to find the appropriate amount of dispersant for each of its cements because it is the physicochemical and morphological characteristics of the cement particle that dictate the amount and type of dispersing agent to be used.

This does not mean that superplasticizers will no longer be added in concrete plants to make durable low w/b concretes, but they will be used more appropriately and in smaller quantities; the basic deflocculation will have been eliminated by the dispersing agent introduced into the cement during its final grinding. The dispersing agent will not be used exclusively to save cement when aiming for a given slump and strength, but rather to decrease the w/c and improve concrete durability. Concrete durability is a direct function of the w/c : the lower the w/c the greater the durability of concrete (and its strength). Only in those cases where strength and not durability is the critical design criterion could some cement be saved.

From a sustainable development perspective, we would like to rename water reducers as “ w/c reducers” to emphasize the essential role they can play in making concrete more durable and more sustainable. Using the same amount of cement, a concrete of a given slump will require less mixing water so that its w/c will be lower. The microstructure of the hardened paste in general will be more compact, particularly in the transition zone (interface between the paste and the aggregate). This concrete will be less permeable to aggressive agents and of course stronger. Its life expectancy will be increased.

4.3.4 Supporting more kN with less cement and aggregate

The strength of concrete has nothing to do with the cube strength of a particular cement. As Féret and Abrams showed us a 100 years ago, the strength of concrete is directly linked to its w/c ratio; the lower the w/c the stronger the concrete. In fact, the w/c determines the distance between the cement particles in the fresh paste. The lower the w/c the closer the cement particles, the lower the amount of “glue” necessary to create strength, and the smaller the distance that the ettringite needles and C-S-H will have to grow to create this “glue”, as already shown in the preceding chapter. Moreover, when the cement particles are closer to each other there is less water to hydrate them, so the hydration goes from a dissolution–precipitation process that produces beautiful bundles of ettringite and quasi-perfect hexagonal platelets of Portlandite to a diffusion process that produces an amorphous-like mass of glue. Cement and concrete microscopists do not like to observe low w/c hydrated pastes because they cannot take any beautiful pictures from them!

In spite of the fact that not all cement particles will be hydrated and that some of the initial cement will act as a filler (an expensive one), practical results show that from a strength point of view (MPa’s obtained per kg of cement), when building a structure with a low w/c concrete, less cement and aggregate have to be used to sustain a given load. This is very good for cement and concrete sustainability. Therefore, when designing structures with low w/c concretes it is possible to build more structures with the same amount of cement and these structures will last longer (Mitchell, 2006).

4.3.5 Making more durable concrete structures with a longer life cycle

It is not sufficient to design a structure with a low w/c to make it durable. Durability depends also on the harshness of the environment and on the placing and curing of this low w/c concrete. The mix must be appropriately designed to be sure that the concrete will last and maintain its design strength throughout the life cycle of the structure. There are special binders that are designed and recommended for use in special environments. Entrained air must be used to protect concrete against freeze–thaw cycles and de-icing salts, fibers must be used to improve the abrasion resistance and so on. But all of these special concretes share one thing in common: to be durable they must be placed and cured with care, which is not so often done currently because curing is too frequently neglected, and this results in the poor durability of concrete structures. When concrete is not properly cured, it shrinks. Plastic shrinkage cracks the surface of freshly finished concrete, autogenous shrinkage cracks the surface of low w/c concrete, and drying shrinkage cracks hardened concrete.

It is very simple to cure concrete. It is only necessary to prevent the water it contains from evaporating by using a curing compound or to provide an external source of water by fogging (as in nurseries when growing roses), water spraying, or by the use of wet burlap. Internal curing can also be achieved by the partial replacement of some aggregates (coarse or fine) by a saturated lightweight aggregate. In this case, the curing is internal to the concrete but external to the cement paste. During cement hydration the water present in the pores of the lightweight aggregate is sucked up by the cement paste so that concrete swells instead of shrinks.

The uncontrolled development of autogenous shrinkage can result in serious durability problems. Autogenous shrinkage is not a new type of shrinkage: all uncured concretes are subjected to autogenous shrinkage whatever their w/c. But, for high w/c concrete having a w/c greater than 0.50 it is negligible, representing only about 10% of the drying shrinkage, so that it can be ignored. On the contrary, in low w/c concrete it can be as great as the usual drying shrinkage, and what is very dangerous is that it develops at a time when the concrete is not very strong. Due to an absence of proper curing many low w/c concrete structures are built with highly durable concrete in between the cracks! Aggressive agents can easily penetrate into the concrete through these cracks and attack the first layer of reinforcing steel.

4.4 What about profitability?

Profitability depends essentially on how well you understand the “rules of the game” to be able to take advantage of them. The game of producing cement and concrete is still much the same game, but with new rules, and simply fighting the new rules is not a responsible attitude. It is better to learn as soon as possible how to play within the new rules. It is important that the cement and concrete industries remain profitable, but what is very attractive when this profitability is linked to sustainability is that our society, we as taxpayers, our children, and grandchildren (and those of the shareholders and of the presidents of the cement and concrete companies) will all profit from this “profitability”.

4.5 Conclusion

The new challenge faced by the cement industry to reduce the CO₂ emissions associated with the use of cement and concrete is not an insurmountable one; we have already mastered all of the technologies to produce three to four times more concrete with the same amount of Portland cement clinker, and we know how to make more clinker with less limestone. This challenge will not necessitate large financial investments, because it is essentially a matter of education. This does not mean that the necessary adjustments will be easy and rapid; education requires time and stubbornness. Our industry is based on tradition, codes, and experience, not on innovation,

but since it has succeeded in overcoming drastic changes in the past, why not again now.

Acknowledgement

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5 Modern binders

5.1 Introduction

The binder is one of the two most important components of concrete because, along with water, through the w/b ratio, it influences essentially all of the mechanical properties of both fresh and hardened concrete, and its durability. Since the sustainability of concrete must now be improved, it is no longer possible to continue to produce concrete as was done during the twentieth century, when short-term profit was the only driving force. It is essential to put into practice all of the knowledge available to minimize the waste of materials and the emission of greenhouse gases, mainly CO₂ associated with the production and use of concrete.

In 1900, only about 10 million tonnes of cement were produced world-wide. At that time, the production of each tonne of cement was accompanied by the emission of many tonnes of CO₂ because of the very low efficiency of the production process, but globally the cement and concrete industries did not emit much CO₂ because of the relatively small quantity of Portland cement produced. Currently, due to the technological progress achieved in the production process of Portland cement clinker, the production of 1 tonne of Portland cement clinker represents approximately the emission of 1 tonne of CO₂ (0.80 tonnes in the most modern and efficient plants). However, as may be seen in Figure 5.1 and Table 5.1, the world consumption of cement is now (a century later) more than 2.5 billion tonnes annually, which represents the emission of more than 2.5 billion tonnes of CO₂ (Aitcin, 2008).

Presently, the emission of CO₂ by the cement industry represents about 6% to 8% of the worldwide CO₂ emissions. This is not as great as the CO₂ emissions from the energy or the transportation industries, but it is a lot for a single industry.

In industrialized countries, it is possible to decrease significantly the waste of materials and the production of CO₂ linked to the production of modern binders and concrete, as will be seen throughout this book. Several technological solutions are already available and in some cases are now at the implementation stage in the industry. It should not be too difficult to decrease the CO₂ emissions linked to the production of binders and the use of

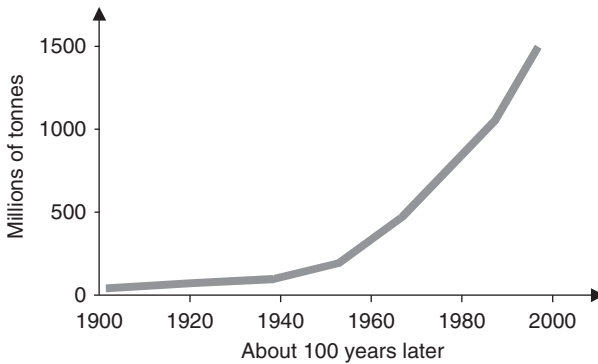


Figure 5.1 Increase in worldwide Portland cement production during the twentieth century. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

Table 5.1 Increase in the worldwide Portland cement production during the twentieth century

Year	Millions of tonnes	Source
1900	10	Estimation
1906	13	Candlot (1906)
1913	39	Davis (1924)
1924	54	Davis (1924)
1938	86	Bogue (1952)
1948	102	Gourdin (1984)
1955	215	ATILH
1965	430	ATILH
1973	717	Gourdin (1984)
1980	850	Gourdin (1984)
1990	1140	CEMBUREAU
1995	1440	CEMBUREAU
1998	1520	CEMBUREAU

Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

concrete in industrialized countries because their consumption of concrete is stagnating or even decreasing slightly as can be seen in Table 5.2. In contrast, this is not the case in some developing countries where the production of binders has drastically increased, as in China, or has started to increase, as in India, in order to satisfy the socio-economic needs of these countries. In developing countries, concrete is the most used construction material to build the needed infrastructure. What is alarming is that development in these countries is accompanied by a massive urbanization and urban

Table 5.2 Per capita consumption of cement, in kg

Country	1987	1992	1997	2004
Luxembourg	895	1247	1123	1221
Portugal	564	769	948	867
Greece	604	739	716	963
Spain	522	666	681	1166
Ireland	345	409	628	1000
Japan	584	656	622	453
Austria	595	669	605	565
Italy	522	770	593	795
Belgium	415	579	566	557
Switzerland	738	658	528	569
Germany	380	455	419	353
China	168	263	388	712
Netherlands	334	344	355	313
United States	342	292	347	409
France	404	376	320	366
Denmark	311	241	270	296
United Kingdom	260	209	217	216

(Source: CEMBUREAU) Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

development, which is well known to be synonymous with huge concrete consumption.

As a general rule, as can be seen from Figure 5.2, the consumption of cement increased with the per capita gross national income until it reached about \$10 000; thereafter the per capita consumption started to decrease, and stabilized at around 300 kg of cement/per capita/per year in most industrialized countries (Scheubel and Nachtwey, 1997). It is therefore imperative to encourage the developing countries not to repeat the past errors of the industrialized countries, and to help them to produce more concrete with less CO₂ emission (Malhotra, 2006) and less waste of materials. In the developing countries, if the already available technologies to decrease the emission of CO₂ were applied when producing concrete, it would be possible to double the amount of concrete used without emitting a single additional tonne of CO₂. The current challenge of the cement and concrete industries is to find a rapid way to introduce these technologies in the developing countries.

For the cement industry, this is not so difficult a task. This change is well under way as a consequence of the globalization of the markets and of the consolidation of the cement industry. Cement production in developing countries is coming under the control of large multinational cement companies that are building very modern plants to satisfy this emergent market. Indeed, some of the most modern and efficient cement plants are found in developing countries, with the oldest and less efficient ones in industrialized countries! The presence of three large cement groups

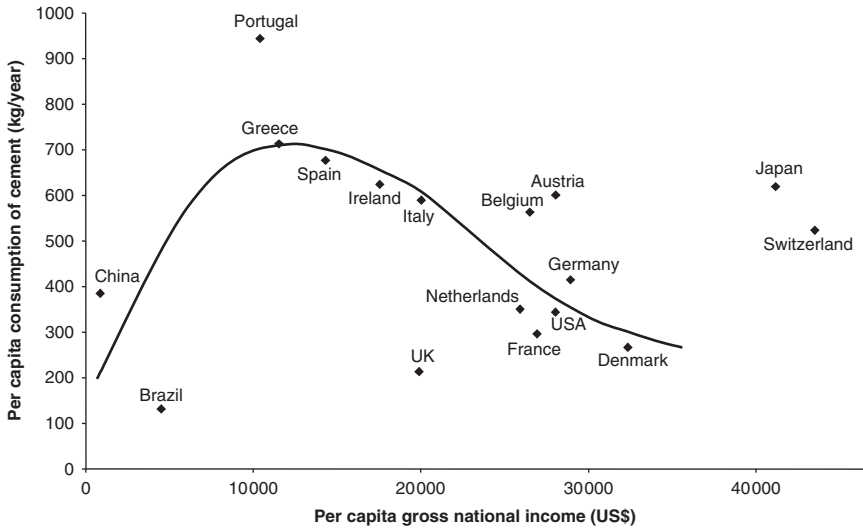


Figure 5.2 Correlation between the per capita consumption of cement and the per capita gross national income in 1997. Reproduced from Scheubel and Nachtwey, 1997.

(Cemex, Holcim, and Lafarge, listed in alphabetical order) in more than 100 countries will help the worldwide cement industry globally to improve its performance in terms of CO₂ emissions per tonne of Portland cement clinker and binder produced.

On the concrete side, the situation is not so encouraging; it will take a longer time to see these objectives reached because worldwide, the concrete industry is very fragmented, mostly in “low-tech” industries that operate at a local scale. There are very few global concrete companies, and the few that existed have been bought by the large cement groups. This involvement of large cement groups in the concrete industry will, we hope, help the development of the new concrete industry.

In order to better understand the transformations occurring presently in the cement and concrete industries, it is useful to start with a brief historical review of the evolution of the cement industry during the last century. In this way, it is possible to understand from where we must start to fulfill the new objective of making concrete more durable, sustainable, and profitable.

5.2 Production of Portland cements and binders

We will here limit the analysis of the production of Portland cement and binders to North America and Europe, because these are the areas that we know best and for which it is possible to get precise statistical data. It is also

very interesting to compare the production of Portland cement and binders on these two continents because it was, and still is, so different.

In North America, Portland cement had little competition throughout the twentieth century although, by the end of the century, it was primarily European cement companies that controlled the major part of the production of Portland cement in the USA and in Canada. In contrast, in Europe, the use of blended cements was developed earlier and is very common presently. For example, the use of slag cement was standardized as early as 1903 in Germany. The production of blended cements increased drastically after World War II to allow a more rapid reconstruction of the infrastructure following the massive destruction during the war. By favouring the blending of Portland cement clinker and various cementitious materials (mostly fly ashes, slag, and natural pozzolans), it was easy to increase the production of the sorely needed binders without investing too much in the construction of expensive new cement plants. The motivation then to increase the supplementary cementitious material (SCM) content in the blended cement was essentially of an economic nature; it had nothing to do with sustainability.

5.2.1 *North America*

In 2000, the situation of the cement market was very simple in the USA; the cement industry was producing and engineers were specifying primarily only the Portland cement known as Type I/II Portland cement, in spite of the fact that five types of Portland cements have long been standardized (Tennis, 1999). In Canada, the situation was similar, though the incorporation of 5% of limestone in “pure” Portland cement has been permitted since 1980. This 5% limestone content was in fact the only difference between Canadian Type 10 cement and its Type I USA counterpart. The clinker used in both cements was the same. Another difference between Canada and USA was the introduction in the market in the early 1980s of a blended silica fume cement containing 7% to 8% silica fume. This very efficient cement was almost exclusively used in eastern Canada because of its short supply. It was used for the construction of large concrete structures such as the Hibernia offshore oil platform and the Confederation Bridge between New Brunswick and Prince Edward Island.

By about 1940, five types of Portland cement had been standardized in the USA:

- *Type I*: ordinary Portland cement
- *Type II*: Portland cement with a moderate heat of hydration and a moderate resistance to sulfate
- *Type III*: Portland cement with a high early strength
- *Type IV*: Portland cement with a low heat of hydration
- *Type V*: Portland cement resistant to sulfates.

This does not mean that all of these cements were available on the market or that they were produced as such. For example, there were many years in which Type IV cement was not available. Moreover, when looking at the statistics of the production of Portland cement in the USA, it can be seen that in 1998, only one type of cement was mostly manufactured, the so-called Type I/II cement, a Portland cement satisfying the requirements of ASTM C 9 for both types of cement in the small common area in which their respective requirements overlapped.

As seen in Table 5.3, this production represented 90% of the production of cement in the USA. The remaining 10% was divided between Type III cement, Type V cement, and masonry cement. Type III cement was mainly used in prefabrication plants and in winter in the northern USA and Canada, Type V in areas where sulfate attack was common as in California, and masonry cement was used in masonry work. Masonry cement has been and still can be composed of a blend of a finely ground mixture composed of 50% Type I/II Portland cement and 50% limestone filler to which different chemical admixtures such as an air entrainment agent, and a viscosity modifier are added. However, there is a tendency to come back to a 50%:50% mixture of Portland cement clinker and hydrated lime for masonry cement.

The production of non-Portland cement binders was negligible when compared to the 90 millions tonnes of Portland cement. Since 2000, the situation has changed, but not too much. The USA is a long way from the use of blended cement as compared to the Netherlands and Belgium, the two countries in which the penetration of blended cement in the construction industry is presently the greatest (Aïtcin, 2007).

5.2.2 *Europe*

In 2000, the situation was totally different in Europe. Many types of blended cements were produced, including binary cements containing high amounts

Table 5.3 Production of different cements in 1998 in the USA

<i>Cement type</i>		<i>Millions of tonnes</i>	<i>%</i>
Types I and II	Normal and moderate	85.07	90
Type III	High early strength	3.15	3.3
Type V	Sulfate resistant	2.76	2.9
Oil well		0.80	0.8
White		0.79	0.8
Concrete blocks		0.59	0.6
Blended		0.67	0.7
Expansive and regulated set		0.05	Negligible
Others		0.08	Negligible

of limestone filler. The current European standard recognizes 164 different types of binders! Such a large number was reached because when establishing the European standards it was necessary to take into account all of the peculiarities of the different national standards, and the four strength classes of cement. Considering this complexity, it is far from certain that the right binder is always used in a particular application!

5.3 Manufacturing modern binders from a sustainable development perspective

The implementation of sustainability in the cement and concrete industries will bring considerable changes in the composition of the binders. In the long term, it will be practically impossible to find “pure” Portland cement. Instead there will be binders containing different proportions of Portland cement clinker blended with different cementitious materials. In fact, as shown previously, the direct substitution of 1 kg of Portland cement clinker by 1 kg of any other cementitious material will decrease by 1 kg the amount of CO₂ emitted during the fabrication of the binder. Of course, for the foreseeable future, the binders that will be used will contain at least a certain amount of Portland cement clinker.

5.3.1 Manufacturing Portland cement clinker

Portland cement clinker is obtained through the firing at about 1450°C of a properly proportioned mixture of limestone and clay or shale. This mixture must have a well-defined chemical composition in CaO, SiO₂, Al₂O₃, and Fe₂O₃ to permit the formation of the four following minerals:

- tricalcium silicate, 3CaO·SiO₂ (C₃S)
- dicalcium silicate, 2CaO·SiO₂ (C₂S)
- tricalcium aluminate, 3CaO·Al₂O₃ (C₃A)
- tetracalcium aluminoferrite, 4CaO·Al₂O₃·Fe₂O₃ (C₄AF).

In this simplified chemical notation (C) represents CaO, (S) represents SiO₂, (A) represents Al₂O₃, and (F) represents Fe₂O₃.

When observed as a thin section in an optical microscope (Figure 5.3) or in a scanning electron microscope (Figure 5.4), it is easy to see polygonal crystals of C₃S and rounded crystals of C₂S (Figure 5.3). Generally, C₂S crystals are striated (Figure 5.5) and C₃S crystals quite smooth (Figure 5.6). C₃S and C₂S crystals are embedded in an interstitial phase (Figures 5.3 and 5.4) that can be entirely vitreous or can contain some C₃A and C₄AF crystals.

In Figure 5.7, it can be seen that some smaller crystals have been deposited on the surface of the C₃S and C₂S crystals. Usually these are alkaline sulfates.

Interstitial phase

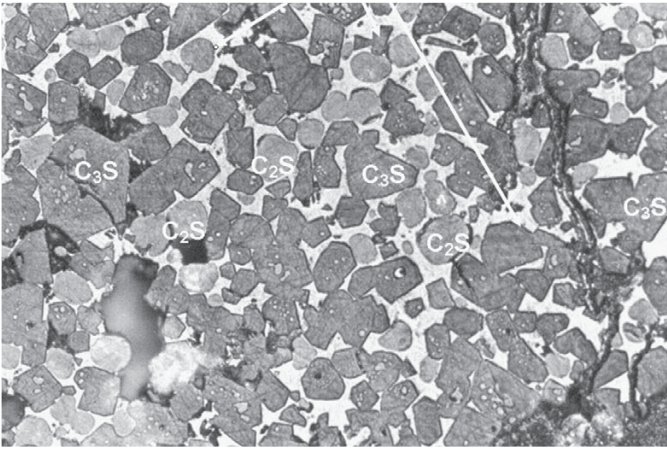


Figure 5.3 Polished surface of a clinker particle after its attack with succinic acid. (Courtesy of A. Tagnit-Hamou).

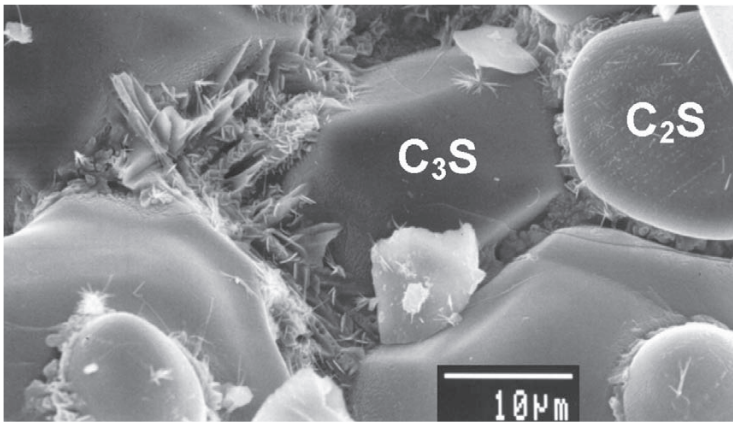


Figure 5.4 Portland cement clinker seen through an electron microscope. (Courtesy of A. Tagnit-Hamou).

In some cases, lime clusters can be seen where a coarse limestone particle was unable to react completely with silica (Figure 5.8).

Figure 5.9 represents belite nests corresponding to an agglomeration of several contiguous C_2S crystals where a large silica particle was unable to react entirely with lime to form C_3S as seen in Figure 5.6. Secondary belite formed during the slow cooling can be seen on some alite crystals (Figure 5.10).

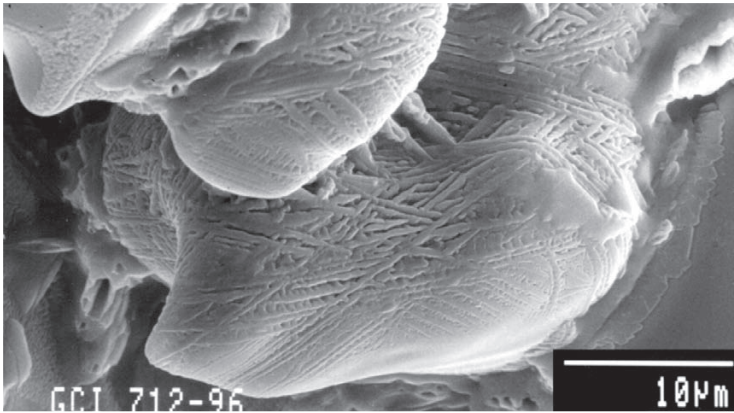


Figure 5.5 Striated belite crystals. (Courtesy of A. Tagnit-Hamou).

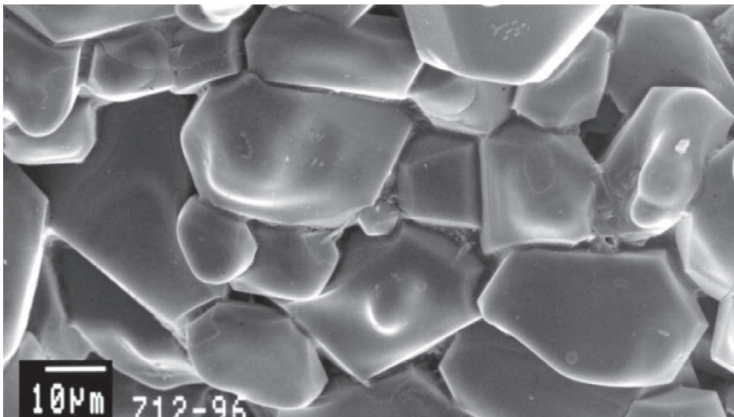


Figure 5.6 Large alite crystals. (Courtesy of A. Tagnit-Hamou).

Clinker nodules have morphologies that depend on:

- the composition of the raw meal;
- the impurities contained in the raw meal;
- its fineness when it enters the kiln;
- the duration of its stay in the different parts of the kiln;
- the temperature reached in the clinkering zone;
- the atmosphere of the kiln (oxidizing or reducing);
- the duration of its stay in the clinkering zone;
- the rate of quenching of the clinker after its passage through the clinkering zone; etc.

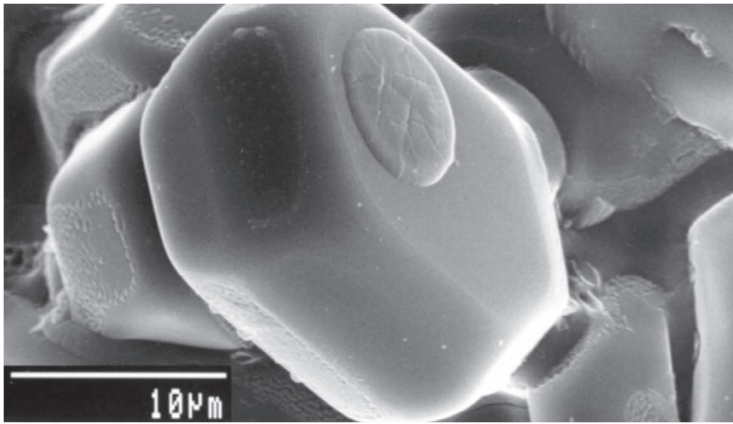


Figure 5.7 Deposits on alite crystals. (Courtesy of A. Tagnit-Hamou).

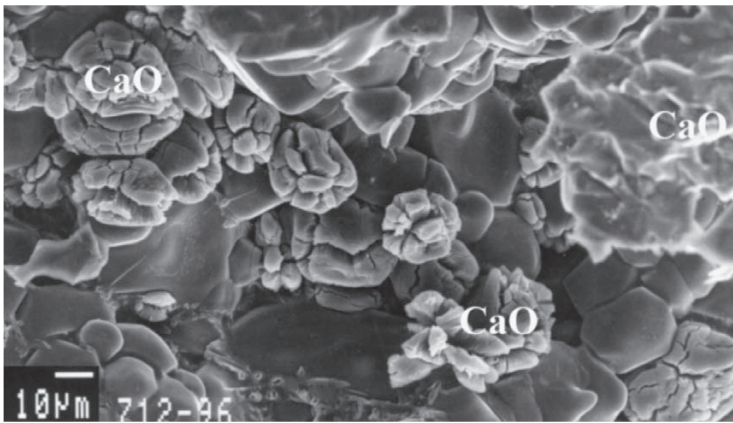


Figure 5.8 Lime cluster (free lime). (Courtesy of A. Tagnit-Hamou).

Therefore, it is impossible to produce two identical clinkers in two different cement plants. Even in cement plants that operate several kilns, the clinkers produced by each particular kiln have their own specific characteristics, even though these clinkers are produced from the same raw meal and the same fuel.

It is important for a cement producer to control the chemical composition of the raw meal; this is a necessary condition for the consistent production of clinker, but it is not a sufficient condition. Clinker having a constant chemical composition can have different properties because as has been shown, there are many factors other than the chemical composition that can influence its properties. To produce a consistent

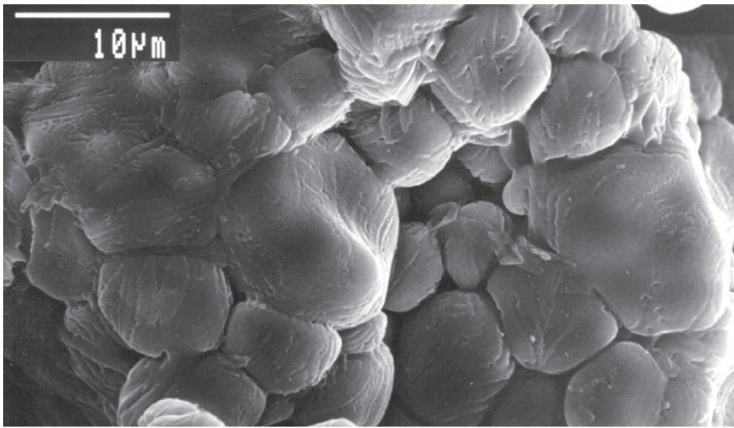


Figure 5.9 Belite nests. (Courtesy of A. Tagnit-Hamou).

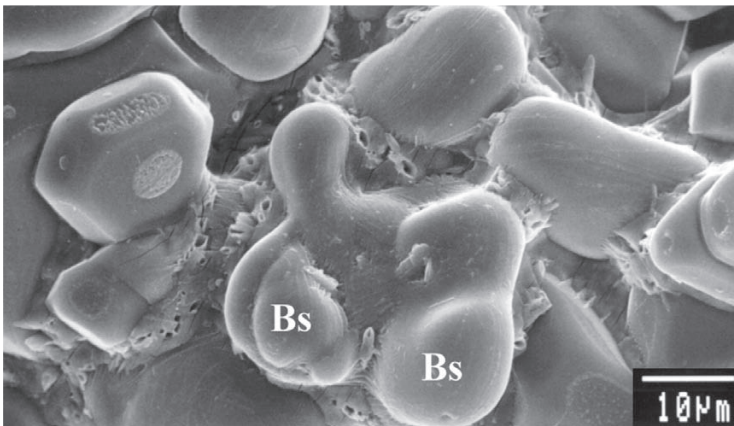


Figure 5.10 Secondary belite (Bs) formed during a slow cooling of the clinker. (Courtesy of A. Tagnit-Hamou).

clinker, it is absolutely necessary that cement producers control *all* of these other factors. In order to limit the variations in the production of clinker, cement producers are obliged to build clinker silos to homogenize their clinker production. They also homogenize the Portland cement by keeping this cement in motion within the cement silos before blending or shipping it.

Figure 5.11 represents schematically the chemical reactions that transform the raw meal into clinker. Figure 5.12 shows how this chemical reaction takes place in a kiln equipped with a precalcinator.

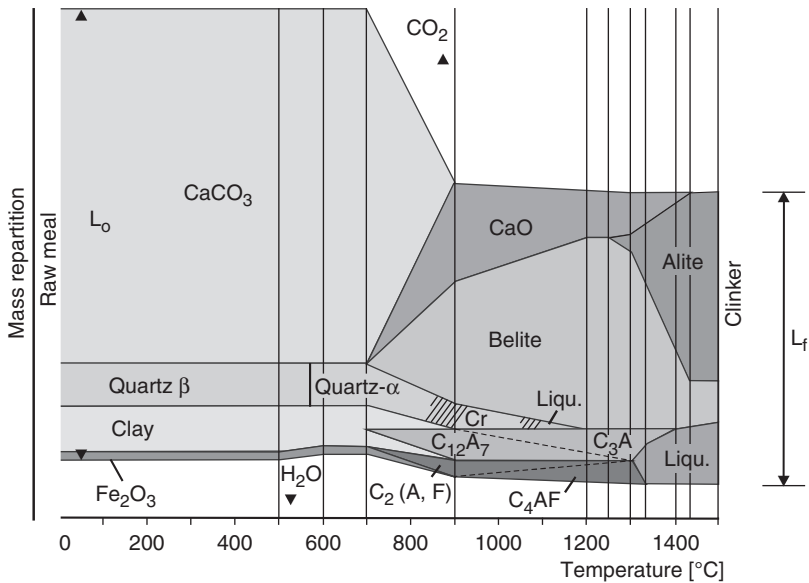


Figure 5.11 Transformation of the raw meal into clinker. (Courtesy of KHD Humboldt Wedag, 1986).

Because of the introduction of a precalcinator that decarbonates the raw meal within a few minutes, it is possible:

- to shorten cement kilns;
- to increase their diameter; and
- to increase significantly their daily production.

Some modern kilns in Asia are able to produce 10 000 tonnes of clinker per day; in the middle 1960s a large cement kiln typically produced only 2000 tonnes of clinker per day.

Table 5.4 gives the chemical composition of several different Portland cement clinkers. It can be seen that it is mostly the C_3A and C_4AF contents that vary much from one cement to the other. This variation corresponds to variations in their Al_2O_3 and Fe_2O_3 contents.

The silica contents of all of the cements in Table 5.4 range between 24% and 29%, while their CaO contents are about 70%. Proportionally, the Al_2O_3 and Fe_2O_3 contents of the different cements presented in Table 5.4 are much more variable. For example, the Fe_2O_3 content of a white Portland cement is less than 1% (the lower this content the whiter the Portland cement). The Fe_2O_3 content of a Portland cement resistant to sulfates, on the other hand, is as high as 4.5%; this is the highest Fe_2O_3 of all of the cements

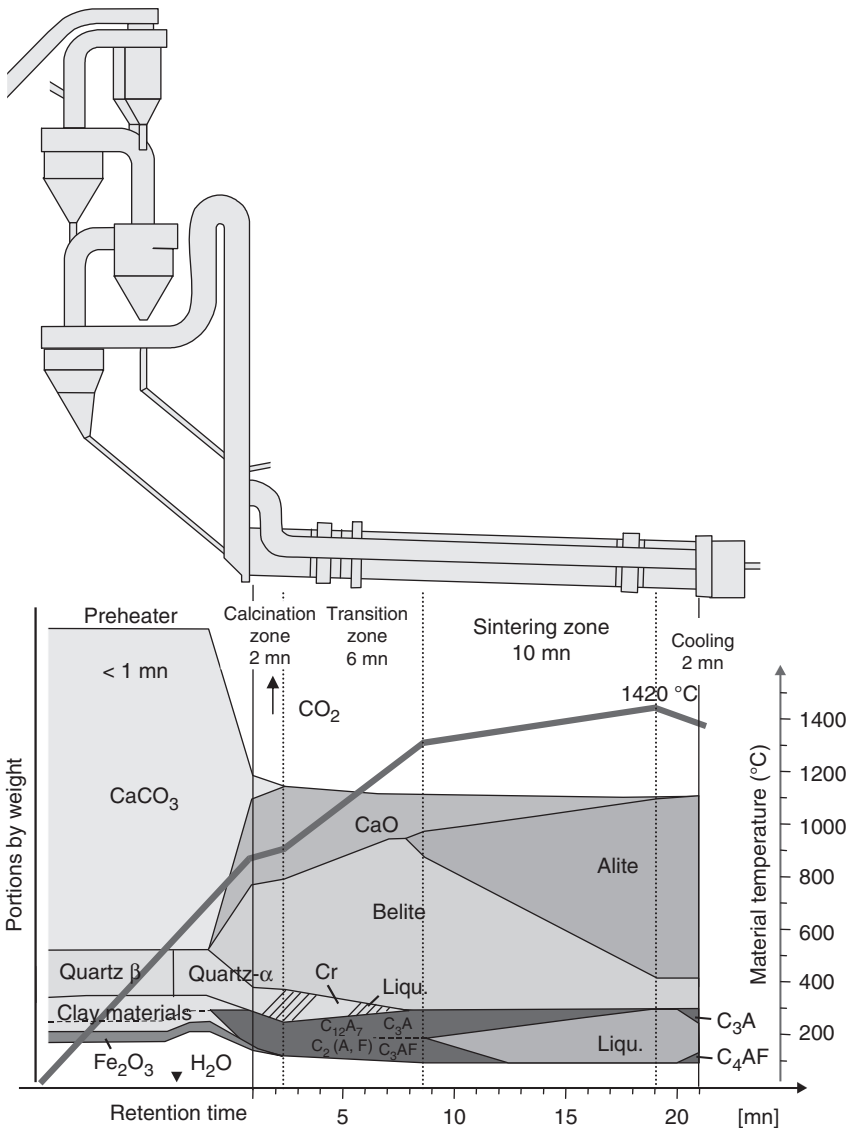


Figure 5.12 Formation of clinker in a short kiln equipped with a precalcinator. (Courtesy of KHD Humboldt Wedag, 1986).

presented in the Table; it is a dark-coloured cement. In this type of cement, the formation of C_4AF is favoured in the interstitial phase, rather than the formation of C_3A . When this cement reacts with the gypsum added to control its rheology, it forms ettringite-like crystals that are more stable vis-à-vis the sulfates than the ettringite crystals formed when C_3A reacts with gypsum.

Table 5.4 Average chemical and Bogue compositions of some Portland cements

Oxide	Cement type							
	CPA 32.5	CPA 52.5	US Type I without limestone filler	Canadian Type 10 with limestone filler	Type 20M low heat of hydration	US Type V sulfate resisting	Low alkali cement	White
CaO	64.40	66.28	63.92	63.21	63.42	61.29	65.44	69.53
SiO ₂	20.55	20.66	20.57	20.52	24.13	21.34	21.13	23.84
Al ₂ O ₃	5.21	5.55	4.28	4.63	3.21	2.92	4.53	4.65
Fe ₂ O ₃	2.93	3.54	1.84	2.85	5.15	4.13	3.67	0.33
MgO	2.09	0.90	2.79	2.38	1.80	4.15	0.95	0.49
K ₂ O	0.90	0.69	0.52	0.82	0.68	0.68	0.21	0.06
Na ₂ O	0.20	0.30	0.34	0.28	0.17	0.17	0.10	0.03
Na ₂ O equiv.	0.79	0.75	0.63	0.74	0.30	0.56	0.22	0.07
SO ₃	1.60	2.40	3.44	3.20	0.84	4.29	2.65	1.06
L.O.I.	—	—	1.51	1.69	0.30	1.20	1.12	1.60
Free lime	1.50	—	0.77	0.87	0.40	—	0.92	—
Insolubles	—	—	0.18	0.64	—	—	0.16	—
Bogue composition								
C ₃ S	61.0	70.0	63.0	54.0	43.0	50.0	63.0	70.0
C ₂ S	13.0	6.1	12.0	18.0	37.0	24.0	13.0	20.0
C ₃ A	8.9	8.7	8.2	7.4	0.0	0.8	5.8	11.8
C ₄ AF	8.9	10.8	5.6	8.7	15.0	12.6	11.2	1.0
C ₃ S + C ₂ S	74	76	75	72	80	74	76	90
C ₃ A + C ₄ AF	17.8	19.5	13.8	16.1	15.0	13.4	17.0	12.8
Specific surface area m ² /kg	350	570	480	360	340	390	400	460

Reproduced from *Binders for Durable and Sustainable Concrete*, Aircin 2008. (Courtesy of Taylor & Francis)

Table 5.4 shows that the alkali content of cements also varies. It depends on the level of alkaline impurities present in the raw meal. Usually, it is expressed as the Na_2O equivalent content which can be calculated as follows:

$$\text{Na}_2\text{O equiv} = \text{Na}_2\text{O} + 0.658\text{K}_2\text{O}$$

where Na_2O and K_2O are the Na_2O and K_2O contents of the clinker. Usually, the phase composition of a cement can be calculated using the Bogue formulas. It is then called the **Bogue potential composition**. The adjective “**potential**” is used because Bogue’s calculations assume certain hypotheses that are not always met in the kiln. The Bogue compositions of the Portland cements presented in Table 5.4 shows that these cements have quite different phase compositions, even though their total silicate content ($\text{C}_3\text{S} + \text{C}_2\text{S}$) only varies between 75% and 80%, and their interstitial phase content ($\text{C}_3\text{A} + \text{C}_4\text{AF}$) represents about 15% to 16% of the mass of the clinker. This phase difference between the silicates and the interstitial phase results in the optimization of the output of the kiln and gives robustness to the process.

This is not the case for the type 20 M clinker produced specially for Hydro Québec in the province of Quebec to build its dams. It must have a C_3A content less than 3% in order to limit even more its heat of hydration. This clinker must also have a low alkali content. The production of this clinker requires careful attention from the cement manufacturer, and it cannot be produced at the same rate as an ordinary clinker. In such a clinker, the interstitial phase is so liquid that it always has the tendency to separate from the silicate phase in the firing zone.

A much more detailed description of the manufacture of Portland cement may be found in *Binders for Durable and Sustainable Concrete* (Aïtcin, 2008).

5.3.1.1 *The ideal Portland cement*

The ideal Portland cement is a cement that does not need to be particularly fine, because it is much better from a cracking and durability point of view to bring the cement particles closer to each other and because it is not necessary to produce the maximum amount of C–S–H to get the desired strength and durability. For usual applications, we would impose a **maximum Blaine fineness** of $350 \text{ m}^2/\text{kg}$.

The same SO_3 maximum content that is presently fixed at 2.3% for ASTM Type V cement that has a C_3A content less than 5% should be enforced.

As far as the compressive strength of standard mortar cubes, rather than specifying minimum strength requirements, we would instead specify

both minimum and maximum strength requirements. This requirement is somewhat redundant, because we have already specified maximum C_3A , C_3S , and fineness values.

Moreover, we would add an essential requirement that is presently lacking in all cement standards: a test that would ensure that the initial cement rheology is not altered during the first 1½ hours that follow the mixing of the water and cement. The current initial and final setting times are inappropriate tests to control the initial rheology of a cement during the period when it must be controlled. Initial and final setting times are, indirectly, tests that measure the rate of hardening of a particular cement, not its rheology. When cements are beginning to set, they have already been in the forms for 2 to 5 hours.

5.3.1.2 Perverse effect of C_3A

5.3.1.2.1 ON THE RHEOLOGY OF CONCRETE

It is well known that C_3A is the most reactive phase of Portland cement and that the addition of some form of calcium sulfate is the simplest and most economical way to neutralize the early hydration of C_3A and of the interstitial phase. In the absence of calcium sulfate, C_3A hydrates nearly instantaneously to form hydrogarnet. In contrast, when sulfate ions are available, the C_3A is transformed into ettringite which slows down considerably the further hydration of the C_3A at the surface of the ground clinker grains. It is only when Portlandite starts to precipitate at the end of the dormant period that C_3A hydration starts to form more ettringite again. When the calcium sulfate added to the cement is exhausted, SO_4^{2-} ions become quite rare; ettringite then becomes a source of calcium sulfate and is transformed into monosulfoaluminate. When there are no more SO_4^{2-} ions provided by the ettringite, the remaining C_3A hydrates as hydrogarnet, but when these two minerals are formed, it is a long time since the concrete has been placed in the forms and it has already hardened. In principle, in a concrete that has just finished hardening (1 to 3 days) some monosulfoaluminate, some ettringite, and some hydrogarnets can be found. Usually, microscopic observations show us only ettringite because, for microscopists, photos of a hydrated cement paste look better when they contain beautiful needles of ettringite!

When a Portland cement has not been well sulfated, it can exhibit either a flash set phenomenon (undersulfated) because the C_3A hydrates instantaneously as hydrogarnet, or a false set phenomenon when, during grinding, too much gypsum has been transformed into hemihydrate. The conversion of this hemihydrate into gypsum causes a temporary loss of initial workability. In such a case, an increase of the mixing time restores the desired workability, but in the case of a flash set, it worsens the situation.

5.3.1.2.2 ON THE COMPATIBILITY AND ROBUSTNESS OF POLYSULFONATE
SUPERPLASTICIZERS

During grinding, numerous electrical charges appear on the fractured surfaces of the cement particles, mostly negative charges on C_3S and C_2S crystals and positive charges on the C_3A and C_4AF crystals. As a result of these numerous surface electrical charges, cement particles flocculate very rapidly when they come into contact with a liquid as polar as water. Consequently, **all cements** need to be dispersed in order to improve their performance, otherwise cement particles will flocculate and Portland cement will lose some of its binding potential. In order to avoid cement particle flocculation, it is only necessary to neutralize the surface electrical charges with organic molecules known as water reducers or superplasticizers. For 50 years, lignosulfonate water reducers have been used very successfully to deflocculate cement particles. Carboxylates have also been used for the same purpose, but to a lesser extent because some are slightly more expensive and because they delay somewhat the achievement of early strength.

Polysulfonate and polycarboxylate molecules are presently extensively used to lower the w/c or w/b ratio in order to produce high-performance concrete. Polysulfonates and polycarboxylates are very efficient dispersing admixtures, but as the cost/performance ratio of polycarboxylate is currently generally higher than that of polynaphthalene sulfonate, polysulfonates are the most widely used superplasticizers in ready-mixed concretes. It is only with cement having a high C_3A and C_3S content and a low soluble alkali content that in some precast applications, where air entrainment is not a prerequisite, some polycarboxylates are cost-effective when compared to polynaphthalene superplasticizers.

When cement particles are not allowed to flocculate, not only are cement particles well dispersed within the mass of concrete, but also all of the water trapped within the cement flocs acts as a lubricant, thereby improving concrete workability. The same workability can be obtained with less initial mixing water or a higher slump can be obtained with a lower amount of mixing water. Hence, water is no longer the only means of controlling concrete rheology; polysulfonates and polycarboxylates offer much more flexibility and possibilities.

Of course, the Portland cement hydration reaction is altered by the presence of these organic molecules that coat cement particles, and to a certain extent can act as a barrier to water molecules. It becomes a matter of equilibrium between the ionic species that are found in the interstitial solution of the fresh concrete. In some cases, it has been shown that the SO_3^- terminations of polysulfonate superplasticizers react with the C_3A to form an organomineral component resembling ettringite, but that does not crystallize into beautiful ettringite needles but rather looks like an “amorphous” material. When too many polysulfonate molecules react in that way with the C_3A , a more or less rapid slump loss is

observed depending on the number of superplasticizer molecules that are lost.

5.3.1.2.3 ON THE DURABILITY OF CONCRETE

Whenever damaged Portland cement concretes are observed under an electron microscope, it is always surprising to see large amounts of well crystallized ettringite needles. These ettringite crystals can be found in cracks, in the transition zone, or even in air bubbles. It is well known, but not well understood, that when ettringite is formed in the presence of high concentrations of lime, which is the case in Portland cement concrete, it crystallizes in an unstable and expansive form. However, when it forms in the presence of a reduced amount of lime, as in the supersulfated cements, it crystallizes in a very stable form and not in an expansive form (Gebauer *et al.*, 2005).

The observation of a fractured surface of a specimen of high-performance concrete ($w/b = 0.35$, spacing factor of $180 \mu\text{m}$) showed that when this specimen failed after 1960 cycles of freezing and thawing according to Procedure A of ASTM C666 (Freezing and Thawing in Water) it was full of ettringite. The inside of some air bubble had been invaded by beautiful ettringite needles. At least, this is proof that there is movement of the interstitial solution towards air bubbles during freezing and thawing cycles.

When certain cracked concretes that are still in relatively good shape are observed under an electron microscope, ettringite crystals are often found in these cracks. This ettringite is termed *secondary* ettringite because it crystallized after the formation of the crack.

The durability of concrete to sea water attack can also be linked to the C_3A content of the cement. Finally, the not very well understood phenomenon called delayed ettringite formation (DEF) is also caused by the presence of C_3A in Portland cement. Therefore, the less C_3A a clinker contains, the better it is.

5.3.1.3 Making concrete with an ASTM Type V cement

The range of concretes presently used by the concrete industry has widened significantly in recent years, following the use of very specific admixtures that have become more and more efficient in their effects. Low w/b concretes, self-compacting concretes, high-performance roller-compacted concretes, fibre-reinforced concretes, reactive powder concretes, and underwater concretes have been developed and are increasingly being used. Is it possible to make all of these “smart” concretes with a Portland cement and hydraulic binders made with a Type V Portland cement clinker? Of course, Type V Portland cement specifications, that in the United States represent 3% of the cement market, must still be satisfied; a maximum Blaine fineness of $300 \text{ m}^2/\text{kg}$ could be sufficient for such a clinker.

However, if a Type V clinker is ground to a fineness of $350 \text{ m}^2/\text{kg}$, it can be used for most applications in which a Type I or II cement is now used. The concrete will be somewhat darker and slightly less strong at 24 hours, but it will be less prone to cracking due to plastic shrinkage, autogenous shrinkage, and drying shrinkage if appropriately water-cured. In hot countries, such a clinker is ideal since it would be very easy to control its rheology because of its controlled “reactivity”.

Concrete users who find that the compressive strength of such concretes made with clinkers having C_3S and C_3A contents lower than those of the cements they are used to using would only have to lower slightly their w/c or w/b ratios or to increase slightly the initial temperature of their concrete. As this cement has low C_3A and Na_2O equivalent contents, it is compatible with any **good quality** polysulfonate superplasticizer; moreover, it requires only a small amount of superplasticizer to decrease significantly the amount of mixing water and increase significantly the initial compressive strength. Polymelamine superplasticizers usually increase initial compressive strength slightly more than polysulfonates and polycarboxylates.

For self-compacting concretes, the use of a Type V clinker is very advantageous because its lower “reactivity” and not very high Blaine fineness mean it requires less superplasticizer to reach a flowing state.

As far as reactive powder concretes are concerned, the various tests conducted by the U.S. Army Corps of Engineers (Coppola *et al.*, 1996) and the Université de Sherbrooke showed that Type V cements were the ideal and most economical cements to produce such concretes. The Sherbrooke *passerelle* was built with a special cement used by Hydro-Québec to build its dams that has a maximum C_3A content lower than 3%. The presence of rapidly soluble alkali sulfate in the ideal clinker is also very advantageous because it limits the early consumption of superplasticizer molecules.

It is only in cold weather that a Type V cement might display too low an early strength, but for winter concreting it is always possible to increase its fineness, to increase the initial temperature of the concrete, and/or to lower slightly the w/c or w/b ratios using a polymelamine superplasticizer.

In all of these cases, a Type V clinker has the great advantage of making a concrete whose initial rheology can be kept under control during the entire time necessary to place the concrete. It will no longer be necessary to add water in the field to restore an adequate slump to place the concrete easily in the forms. What a giant step in the direction of concrete durability!

For mass concrete, a Type V concrete is ideal, especially if it is blended with a slag, a fly ash, or a pozzolan. The blending can be adjusted to the desired maximum temperature or 28-day compressive strength. Moreover, such a cement that has enough rapidly soluble alkalis will be compatible with almost all Portland and blended cements and will be very economical with polynaphthalene superplasticizers.

Presently, as mineral components are available almost everywhere, **it will no longer be necessary to make a special low alkali cement**, because if the

only aggregates available in a given area are potentially reactive, the best way to get rid of an alkali/aggregate reaction is to use a blended cement. **Therefore, Type V clinker could be used with potentially reactive aggregates if it is blended with a mineral component.**

It is only in architectural applications, where a white clinker is a must, that a second type of clinker will be needed; it should look like that used by Aalborg Cement in Denmark to manufacture its white cement with a low C₃A content.

5.3.2 Cementitious materials

It has been well known, since antiquity, that some natural materials can react with lime to give a hydraulic binder, that is, a binder that can harden under water. The Phoenicians, the Greeks, and later the Romans used certain volcanic ashes that were found around the Mediterranean and mixed them with lime to produce a binder capable of hardening under water. What these materials had in common was that they all contained some vitreous (glassy) silica. The higher the vitreous SiO₂ content, the more reactive they were with lime. The best Roman volcanic ashes were extracted in the area of the modern city of Pozzuoli on the Bay of Naples; these natural products are now all referred to as pozzolans.

It must be emphasized that only *vitreous* volcanic ashes will react with lime; the crystalline ones are not reactive. For instance, shortly after the Mount St Helens volcanic eruption in the United States in 1980, the American Portland Cement Association (PCA) received hundreds of small containers containing what was described as a “potential source of cementitious material”, to evaluate the actual cementitious potential of these ashes. The PCA, however, found that the ashes from Mount St Helen had no cementitious properties, because they were totally crystallized. The volcanic lava from which they came had not been quenched (cooled rapidly) but rather had cooled so slowly so that it was well crystallized. Only incandescent ashes that are air cooled when projected in the air or quenched in water have some potential as cementitious materials, if their vitreous SiO₂ content is high enough.

The definitions of ACI Standard 116 for some of the supplementary cementitious materials that may be blended with Portland cement are:

- *Blast furnace slag*: the non-metallic product, consisting essentially of silicates and aluminosilicates of calcium and other bases, that is developed in a molten condition simultaneously with iron in a blast furnace.
- *Fly ash*: the finely divided residue resulting from the combustion of ground or powdered coal and which is transported from the firebox through the boiler by flue gases.

- *Silica fume*: very fine non-crystalline silica produced in an electric arc furnace as a by-product of the production of elemental silicon or alloys containing silicon.
- *Pozzolan*: a siliceous or siliceous and aluminous material which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

On the ternary diagram shown in Figure 5.13, it is possible to get an idea of the chemical composition of the different cementitious materials that are commonly blended with Portland cement.

5.3.2.1 Slag

Blast furnace slag is a by-product of the production of pig iron. The iron ore pellets and the metallurgical coke that are introduced at the top of a

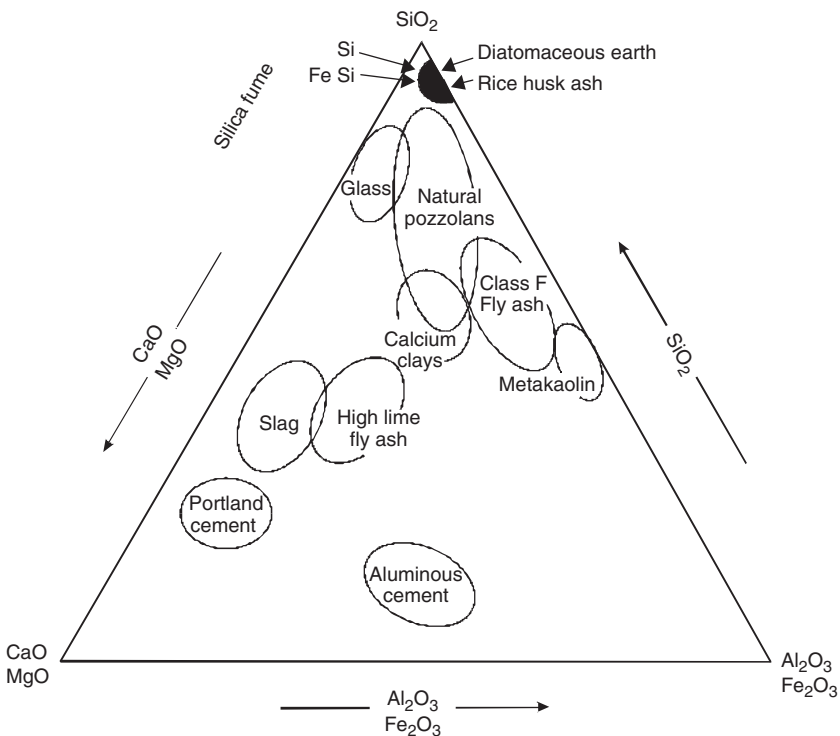


Figure 5.13 Chemical composition of hydraulic binder components. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

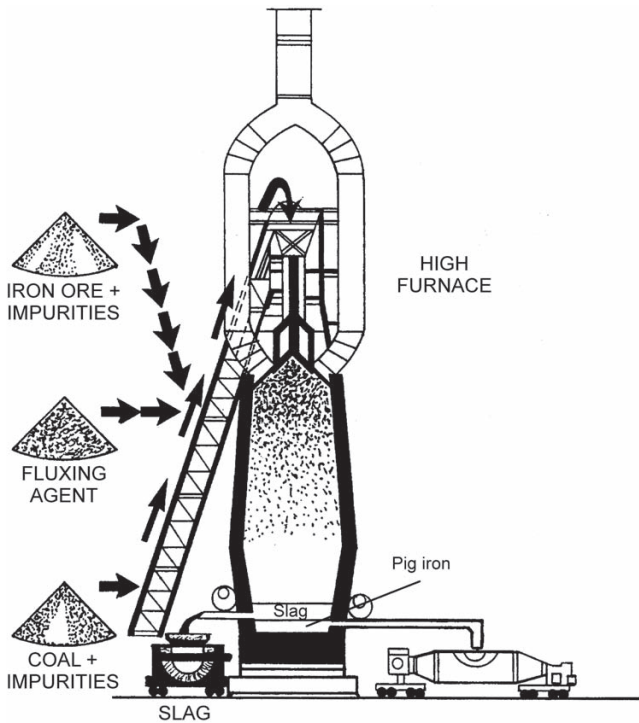


Figure 5.14 Schematic representation of a high furnace. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

blast furnace contain some impurities that must be melted in order to be eliminated (Figure 5.14). At the bottom of the blast furnace, the slag is a molten liquid that covers the layer of liquefied pig iron because of the difference in their specific gravities. Moreover, pig iron droplets are purified when they pass through the slag layer. Pig iron melts at 1050°C , while the slag melts at a much higher temperature.

In order to lower as much as possible the temperature of the molten slag, it is usually necessary to add a fluxing agent to obtain a slag composition in the range of the eutectic point E_2 in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram. (Figure 5.15). Consequently, the metallurgist pays close attention to the chemical composition of the slag in order to reduce the energy cost of the pig iron production.

To be able to use the liquefied slag as a cementitious material, it is necessary to quench it rapidly (usually with water) in order to prevent its crystallization in the form of melilite crystals. Melilite is a solid solution of gehlenite ($\text{CaO SiO}_2 \text{Al}_2\text{O}_2$) and ackemanite ($\text{MgO SiO}_2 \text{Al}_2\text{O}_3$).

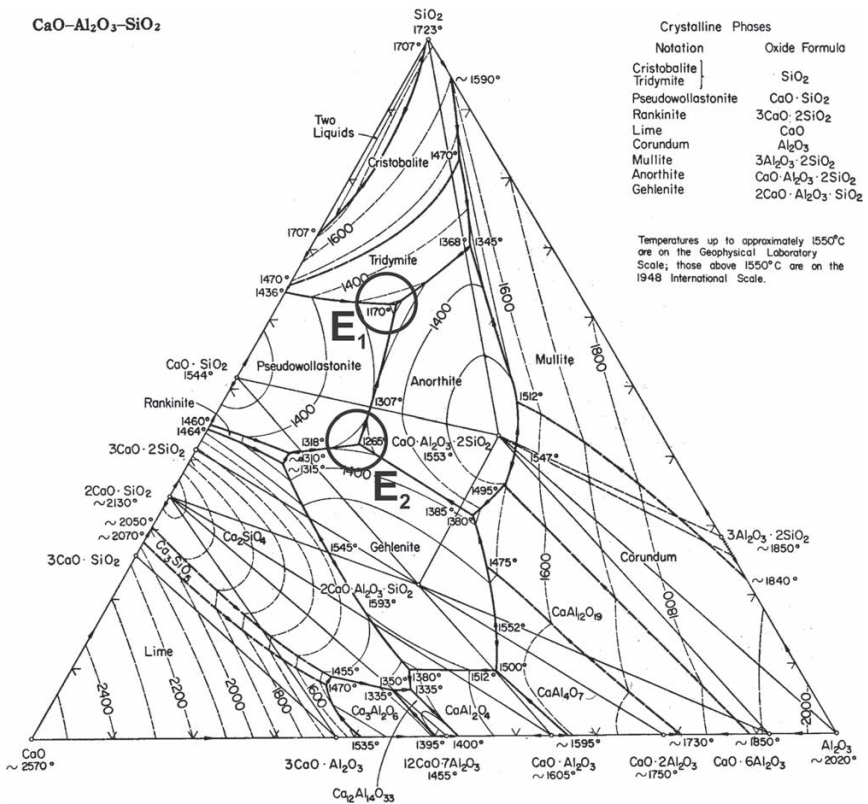


Figure 5.15 Position of the two eutectics having the lowest melting temperature in a $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ phase diagram. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

The quenching is usually carried out in gutters situated as close as possible to the slag output; water is projected onto the slag from the side of the gutter. The hotter the slag is when it is quenched, the paler it is and the more “reactive” it is; the darker the quenched slag, the less reactive.

To estimate the cementitious potential of a slag, knowledge of its chemical composition is not in itself very useful: it is better to examine its X-ray diffractogram to see if the slag is vitreous. Figure 5.16 shows the X-ray diagram of a fully vitrified slag: there are no peaks, but rather a “hump” in the vicinity of the principal diffraction peak of melilite. This means that on a short range basis, the silica tetrahedra are organized in a similar way as the ones found in melilite.

The thin section of a crystallized slag (Figure 5.17) shows prismatic melilite crystals. Figure 5.18 shows the conchoidal shape of quenched

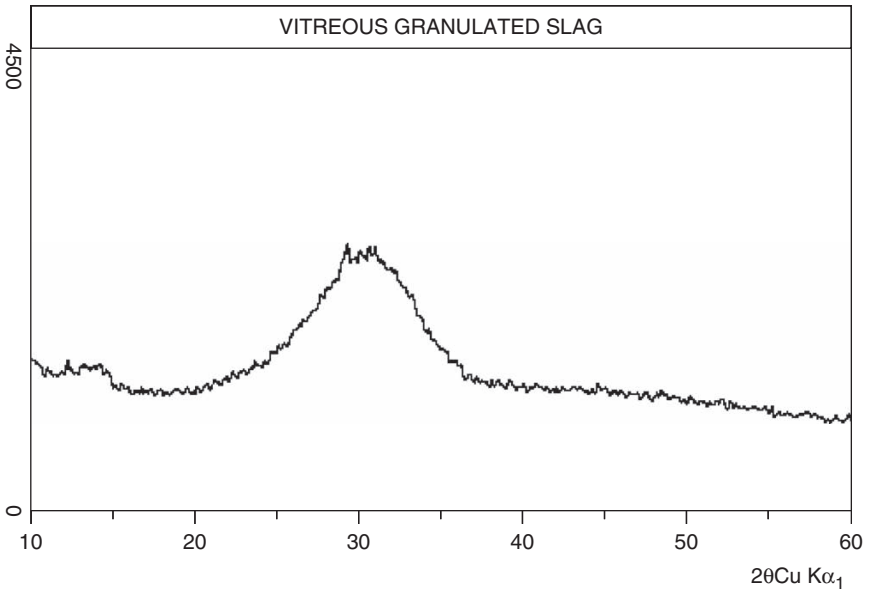


Figure 5.16 X-ray diffractogram of a hot slag after its quenching. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

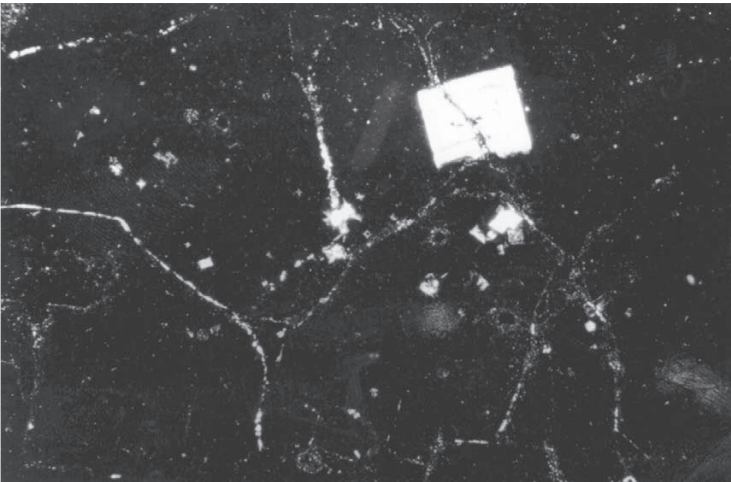


Figure 5.17 Melilite crystals in a slag particle after quenching. This slag was a cold slag quenched below the temperature of the liquidus. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

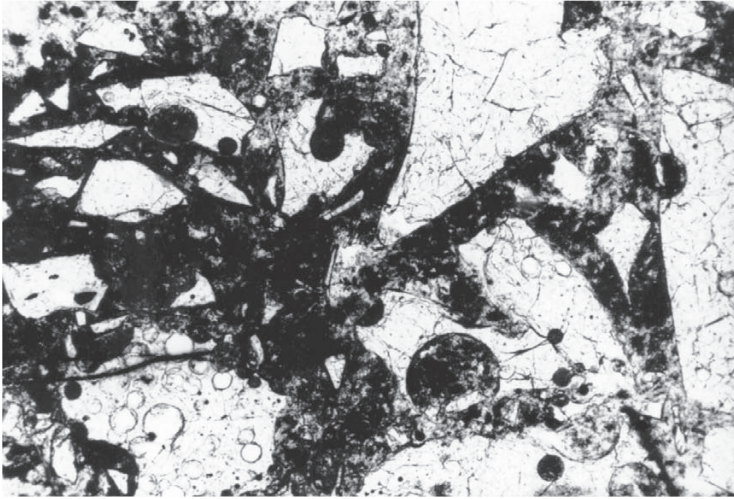


Figure 5.18 Vitreous angular slag particles (in white). This slag was quenched at a high temperature because no melilite crystals are visible. Such a slag is called a hot slag. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

vitreous slag, that looks like glass spalls. Also, it may be seen that numerous gas bubbles were trapped during the quenching with water. This helps during the grinding process. It was in Germany as early as 1868 (Papadakis and Venuat, 1968) that slags were used for the first time. It was also in Germany that the first standard on slag cement was issued in 1903.

Slag can be ground separately or simultaneously (co-grinding) with Portland cement clinker to produce slag cements. As slag is harder to grind when co-grinding it with Portland cement, it is the Portland cement part of the blend that is ground finer, and not the reverse which would be better. Separate grinding before blending is preferable because then it is possible to grind each separate part of the blend to its optimum fineness.

It is possible to blend slag with Portland cement at proportions up to 85% slag as in supersulfated cement. As mentioned earlier, the Obourg cement company of Belgium is presently marketing a 0% clinker binder composed of ground slag, anhydrite, and an alkaline activator (Gebauer *et al.*, 2005). By lowering the w/b ratio with a superplasticizer, it is possible to obtain with this 0% clinker binder compressive strengths of the same order as those obtained with pure Portland cement.

Those who wish to go deeper into the subject of slag should read Nkinamubanzi and Aïtcin (1999), Nkinamubanzi *et al.* (1998), and ACI Committee 233, *Standard on ground granulated blast furnace slag as a cementitious constituent in concrete*.

5.3.2.2 Fly ash

Fly ashes are the combustion residues captured in the dedusting systems of electric power plants that burn coal or lignite. The impurities contained in the coal and the lignite are heated to a high temperature in the burner and liquefied. Subsequently, when they reach the coldest part of the combustion chamber they condense in the shape of glassy spherical particles and are entrained by the effluent gas. Their spherical shape is due to their quenching since a spherical shape minimizes the surface energy of the particle (Figures 5.19 and 5.20). Figure 5.21 represents schematically the formation of fly ash.

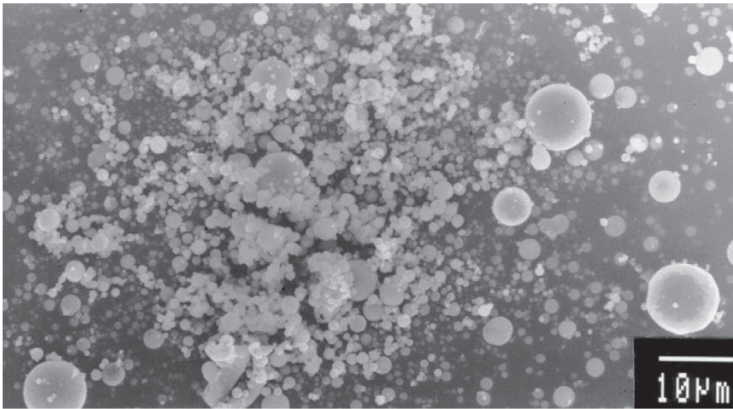


Figure 5.19 Spherical particles of fly ash. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

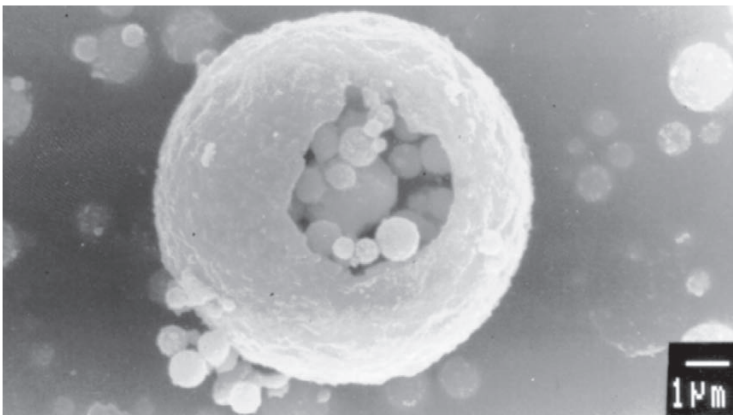


Figure 5.20 Plerosphere containing cenospheres in a fly ash. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

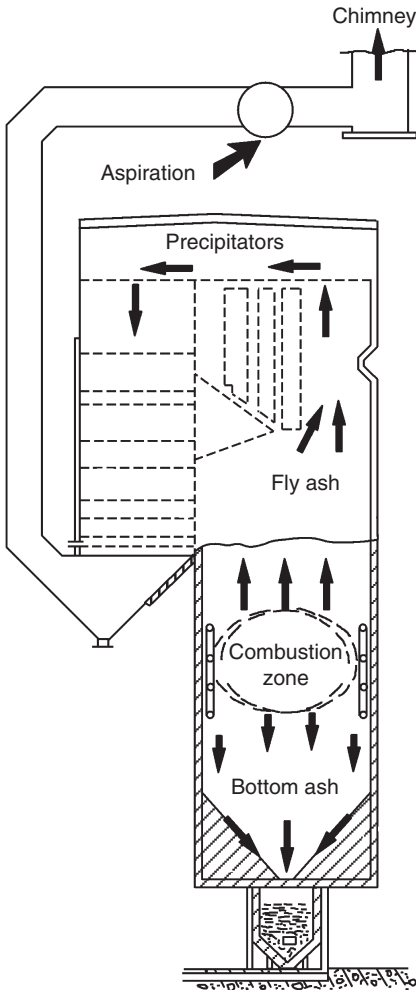


Figure 5.21 Schematic representation of the formation of fly ash. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

Fly ash chemical composition is variable: it is a function of the impurities present in the coal, which varies from one source of coal to another. It can also vary within the same source of coal. Fly ashes thus do not have any specific chemical composition, do not have a specific mineral composition, do not have a specific grain size distribution, do not have a particular specific gravity, do not exhibit the same degree of glassiness, and do not have the same amount of unburned carbon. Nonetheless, in North America they are classified according to their chemical composition into two

broad categories: class F fly ashes that have a low lime content and class C fly ashes that have a high lime content. ASTM defines these two classes as follows:

- *Class F*: fly ash normally produced from burning anthracite or bituminous coal that meets the applicable requirements for this class. This class of fly ash has pozzolanic properties.
- *Class C*: fly ash normally produced from lignite or sub-bituminous coal that meets applicable requirements for this class. This class of fly ash, in addition to having pozzolanic properties, also has cementitious properties. Some class C fly ashes may contain lime content higher than 10%. In Europe these two classes of fly ash are known instead as silicoaluminous and silicocalcic fly ashes; some fly ashes rich in calcium sulfate are called sulfocalcic fly ashes.

The expression “fly ash” is therefore a generic term that is applied to powders, essentially vitreous (Figure 5.22), having broad chemical and morphological characteristics. Aitcin *et al.* (1986) have shown that while some fly ashes have cementitious properties, others have none. Bédard (2005) has even characterized a fully crystallized fly ash (Figure 5.23). It was

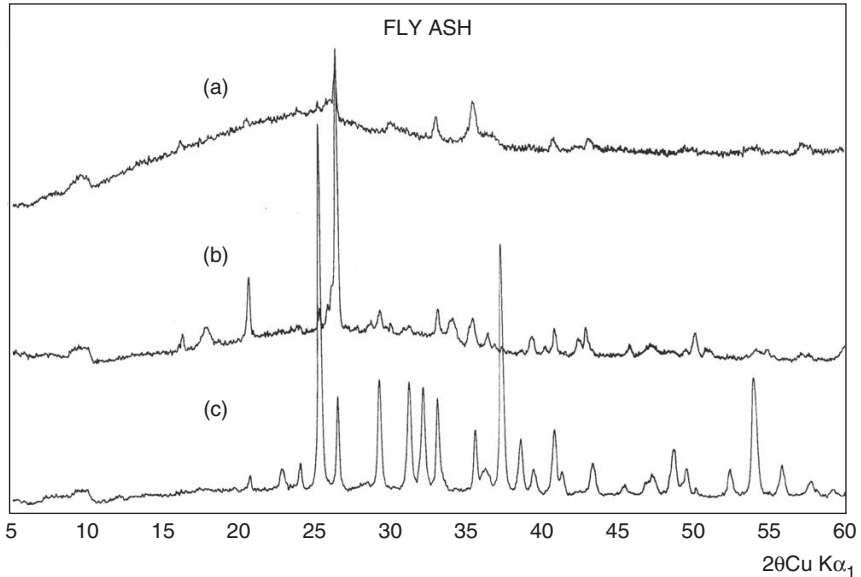


Figure 5.22 Typical X-ray diffractogram of different types of fly ash. (a) Class F or silicoaluminous. (b) Class C or silicocalcic. (c) Sulfocalcic fly ash totally crystallized. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

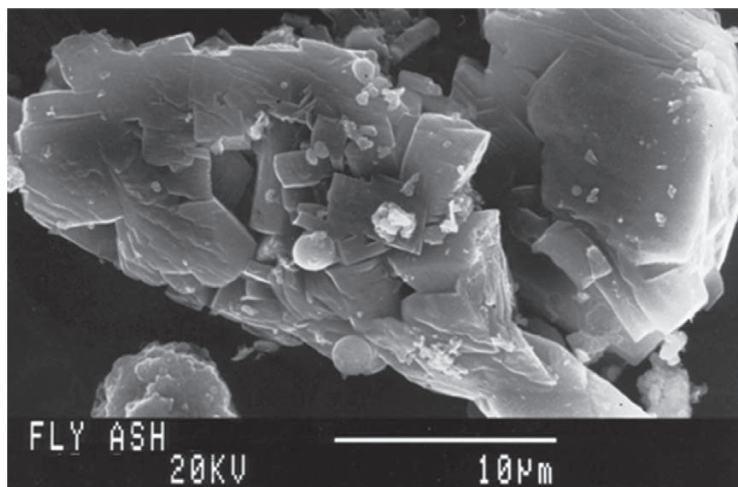


Figure 5.23 Coarse crystallized fly ash particles. (Courtesy of I. Kelsey-Lévesque).

called fly ash simply because it was collected in the dedusting system of a power plant. Of course, it had no cementitious properties at all.

An important characteristic of fly ashes is their carbon content, because if it is too high it can create many problems when using admixtures. In a fly ash, the carbon can be found essentially in two forms: as unburned coarse particles of coal or as soot that coats the fly ash particles. It is easy to eliminate the coarse particles of coal (with a cyclone), but it is rather more difficult from an economic point of view to get rid of the soot.

Fly ashes usually contain coarse particles that are crystallized. These particles come from the coarsest part of coal, that passed so rapidly through the burner that they had no time to become fused. These do not have any cementitious value and are very easy to eliminate with a cyclone. When this is done, the fine fly ash particles that are separated constitute a *beneficiated* fly ash. The coarse particles that are eliminated by this process can always be used to correct the raw meal composition. In some cases, they can also be attractive for their coal content.

More and more fly ashes now contain calcium sulfate, because some power plants blend their coal with limestone during the grinding of the coal, in order to lower the acid emissions associated with the presence of sulfur in the coal or in the lignite.

According to the European standard, no more than 35% fly ash can be substituted for Portland cement. However, higher amounts of fly ash can be incorporated in concrete when using a superplasticizer to produce high volume fly ash concretes (Malhotra, 2002; Mehta and Manmohan, 2006).

A more detailed account of fly ash can be found in ACI 232 2R, *Standard on the use of fly ash in concrete*.

5.3.2.3 Silica fume

Silica fumes are the by-product (Figure 5.24) of the production of silicon and ferrosilicon or of zirconium. They are collected in the dedusting system of the arc furnaces that are used to produce these metals or alloys. In these arc furnaces some SiO vapour is formed. It oxidizes when it comes into contact with air, and solidifies in the form of spherical particles whose average diameter is about $0.1 \mu\text{m}$. These particles are thus about 100 times finer than the particles of an ordinary Portland cement. In this case too, the spherical shape of the particles is the result of the minimization of the surface energy of each particle, as for fly ash particles. (Figure 5.25).

When the electric arc furnace is equipped with a heat recovery system, the collected silica fume is white. When the furnace does not have a heat recovery system (the general rule), it is grey. With a heat recovery system, the gas is extracted at a temperature greater than 800°C , so that most of the carbon particles are burned and the silica fume is whitish. Without a heat recovery system, the hot gas of the electric arc furnace is diluted with fresh air to lower its temperature below 200°C , so that it does not burn the dedusting sacks. At such a low temperature the carbon particles are not burned, and they give a grey colour to the silica fume. This carbon content

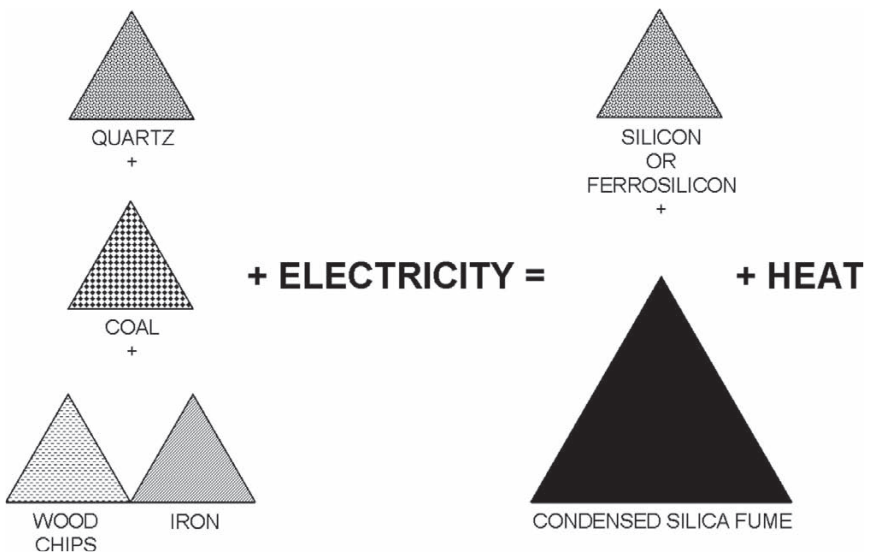


Figure 5.24 Principle of the production of silica fume. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

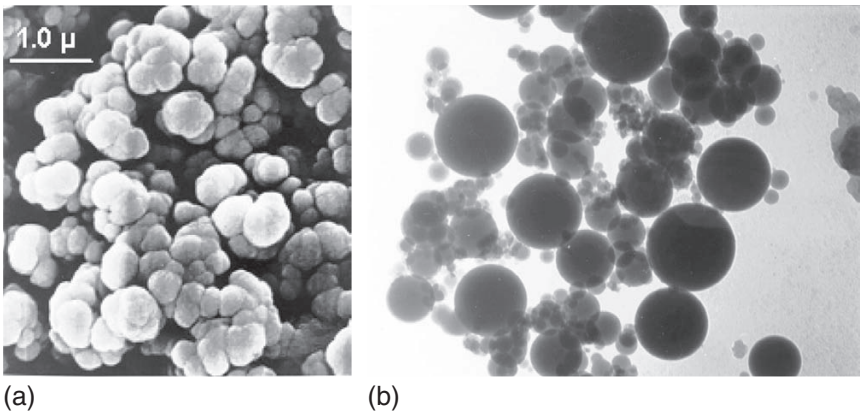


Figure 5.25 Silica fume as seen in an electron microscope. (a) Scanning electron microscopy. (b) Transmission electron microscopy. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

Table 5.5 Chemical composition of some silica fumes

	<i>Grey production of silicon</i>	<i>Grey production of ferrosilicon</i>	<i>White</i>
SiO ₂	93.7	87.3	90.0
Al ₂ O ₃	0.6	1.0	1.0
CaO	0.2	0.4	0.1
Fe ₂ O ₃	0.3	4.4	2.9
MgO	0.2	0.3	0.2
Na ₂ O	0.2	0.2	0.9
K ₂ O	0.5	0.6	1.3
L.O.I.	2.9	0.6	1.2

Reproduced from Papdakis and Vanuat, 1966, with permission.

comes from the coal used in the process, from the graphite of the electrodes, the binder of these electrodes, or from the wood chips that are used when producing silicon metal.

The chemical analysis of industrial silica fumes shows that they usually contain more than 90% of SiO₂ (Table 5.5). When they are produced in a furnace producing silicon metal, this value is higher than 90%; when they come from the production of an 85% ferrosilicon alloy their SiO₂ content is greater than 85%.

An X-ray diffractogram shows that silica fumes are vitreous (Figure 5.26). Their specific surface area measured by nitrogen adsorption (B.E.T. method) gives a specific surface area of the order of 15 000 to 20 000 m²/kg.

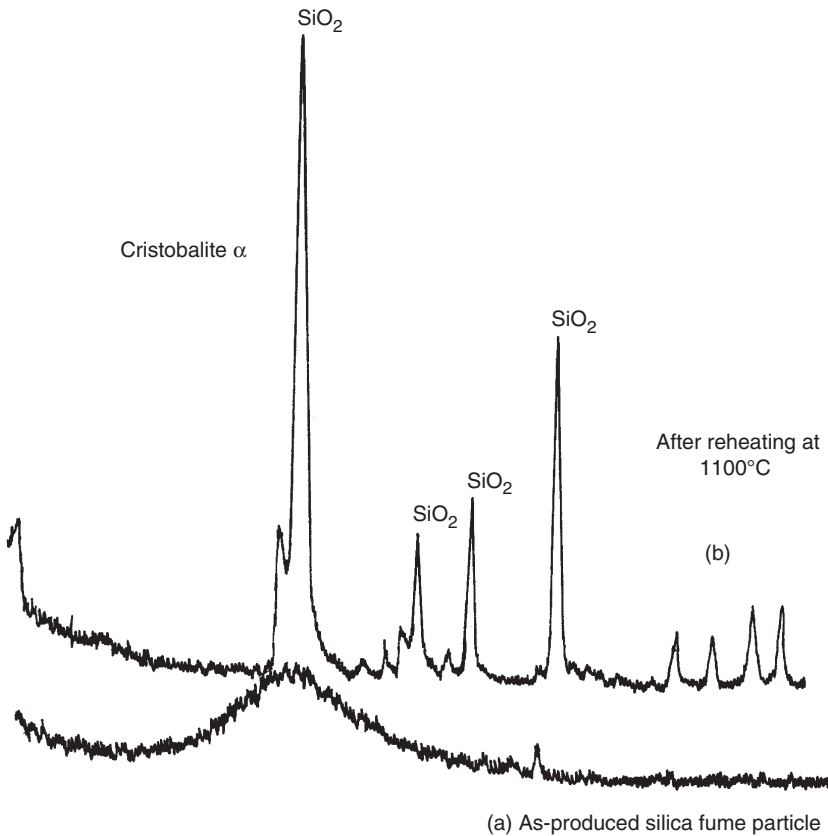


Figure 5.26 X-ray diffractogram of silica fume (a) as-produced and (b) after its reheating at 1100°C. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

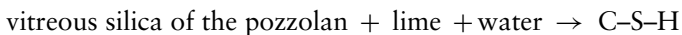
In comparison, Portland cement typically has a specific surface area of 350–450 m²/kg.

The major problem with using silica fume in the cement and concrete industry is its handling. As silica fume particles are extremely fine, they are very difficult to handle. The *Silica Fume Users Manual* (Holland, 2005) gives pertinent practical informations on the properties and the commercialization of silica fume. Interested readers might also consult ACI 234 *Standard guide for the use of silica fume in concrete or condensed silica fume* (Aïtcin, 1983).

5.3.2.4 Natural pozzolans

Natural pozzolans are materials, usually of volcanic origin or in a few cases of sedimentary origin, that essentially contain more than 25% reactive silica.

The basic chemical principle that makes the use of natural pozzolans possible is:



The hydraulic properties of natural pozzolans were discovered by the Greeks and the Romans and were used by them in a variety of structures, some of which still exist today.

Table 5.6 shows the chemical composition of some different natural pozzolans. Their chemical composition varies over a wide range. Presently, to the best of our knowledge, natural pozzolans are blended with Portland cement in Italy, Greece, Turkey, Morocco, Mexico, and Chile.

Malhotra and Mehta (1996) and Massazza (1998) have provided data on the effects of some natural pozzolans on concrete properties. But, as in the case of fly ashes, it would be dangerous to generalize these results to other kinds of natural pozzolans. ACI 232.1R *Standard use of natural pozzolans in concrete* provides more detail on this topic.

5.3.2.5 *Calcined clays and shales*

The use of calcined clay in concrete dates back to Phoenician, Greek, and Roman times. When a clay or a shale is calcined at 700°C to 750°C the crystals of which they are composed are dehydrated, and the crystalline structure becomes disorganized. Silicon tetrahedra then become reactive at ambient temperature with the lime liberated by the hydration of C_3S and C_2S .

Metakaolin comes from the calcinations of kaolin (china clay) (Figure 5.27). It is commonly used in Brazil where it is marketed by Metacaulin do Brazil. It is now also being produced in the United States and Canada, though its use is still limited.

As the shape of elementary calcined clay or shale particles is irregular and porous, blending with Portland cement increases the water demand in concrete unless a superplasticizer is used. However, in a saturated state they may be used both for internal curing, and for their pozzolanicity. In this case, they must be sold separately to concrete producers.

5.3.2.6 *Rice husk ash*

The husk that protects rice grains against rain has a siliceous skeleton representing about 20% of its mass. When rice husks are burnt at a temperature of 700°C to 750°C the resulting ashes are mainly composed of vitreous silica. It is very important to control the burning temperature because if the temperature goes too high the SiO_2 can recrystallize in the form of cristobalite, in which case the rice husk ash loses its pozzolanicity. Calcined rice husk ashes are more or less dark, according to their unburned carbon content.

Table 5.6 Chemical composition of some natural pozzolans and calcined clays

Oxides	Pozzolans		Canary Islands	Trass		Calcined Gaize	Calcined clay	Pumice
	Italy, Latium segni	Greece, Santorini Island		Rhenan	Romanian			
SiO ₂	48	65	47	55	62	84	58	55
Al ₂ O ₃ + TiO ₂	22	13	20	16	12	8	18	22
Fe ₂ O ₃	9	6	3	4	2	3	9	3
CaO	7	3	4	3	6	2	3	2
MgO	3	2	0.5	1	1	1	4	0.5
Na ₂ O + K ₂ O	5	6.5	9	9	3	—	4	11
SO ₃	0.5	0.5	—	—	—	0.7	1	—
Loss on ignition	5	4	16	10	14	0.8	2	6

From Papadakis and Venuat (1966).

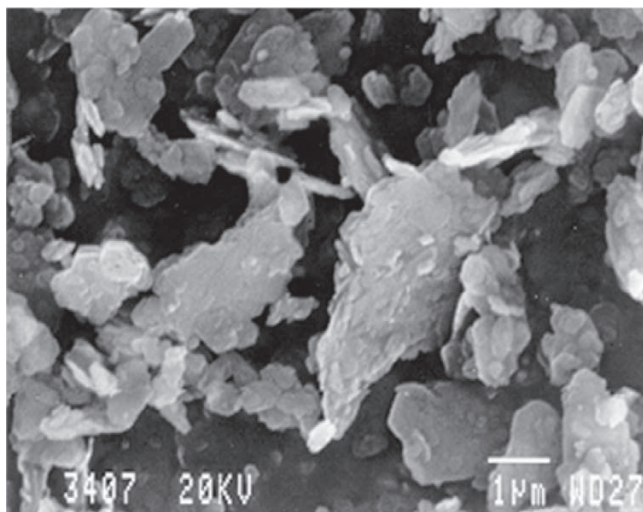


Figure 5.27 Metakaolin particles. (Courtesy of M. Cyr).

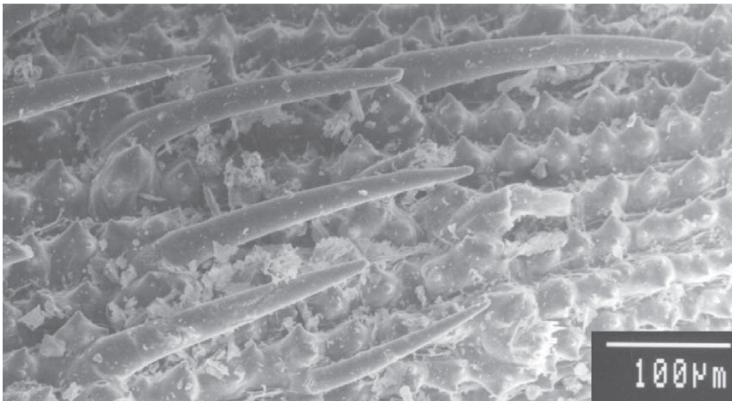
The vitreous silica displays excellent pozzolanic properties. However, due to their very particular texture and morphology (Figure 5.28a and b), the introduction of rice husk ash in a concrete mixture increases the water demand of the fresh concrete (Malhotra and Mehta, 1996). Saturated with water rice husk ash too could be used both for internal curing and for its pozzolanicity, but then it must be sold separately to concrete producers.

5.3.2.7 *Diatomaceous earth*

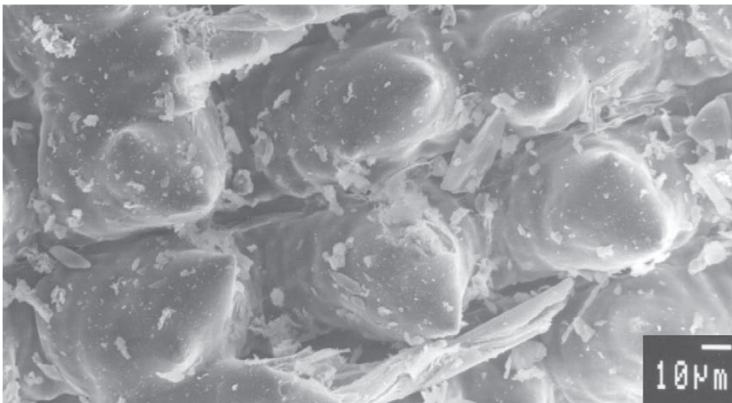
Diatomaceous earths are composed of the siliceous skeletons of microscopic algae that lived in either fresh or sea water. The examination of diatomaceous earth under an electron microscope shows different types of patterns (Figure 5.29). A chemical analysis and an X-ray diffractogram show that diatomaceous earth is essentially composed of vitreous silica. This silica is very reactive but its large porosity increases the water demand. Saturated with water, diatomaceous earth too could be used for internal curing and also for its pozzolanicity.

5.3.2.8 *Perlite*

Perlite is obtained by heating rhyolitic rock (a volcanic rock rich in silica). The rock is transformed into a spongy mass that can absorb a significant amount of water (Figure 5.30). Presently, perlite is mostly used as an ultra-light lightweight aggregate to make insulating concrete (thermal and acoustical insulation). Its very high absorptivity limits its blending with



(a)



(b)

Figure 5.28 (a) Rice husk ash and (b) enlarged view. (Courtesy of A. Tagnit-Hamou and I. Kelsey-Lévesque).

Portland cement. However, when saturated it may be used both for internal curing and for its pozzolanicity.

5.3.2.9 Pulp and paper sludge

Paper plants are now using more and more recycled fibres, but this creates a problem with the residues of the de-inking process. These residues contain organic or mineral pigments, very short cellulose fibres (too short to be recovered and recycled) and the filler used when making the original paper. The fillers used are either limestone or kaolin. When sufficiently dried using a filter press process, these residues have a combustion value and can be burned to generate electricity and water vapour (cogeneration process). But what

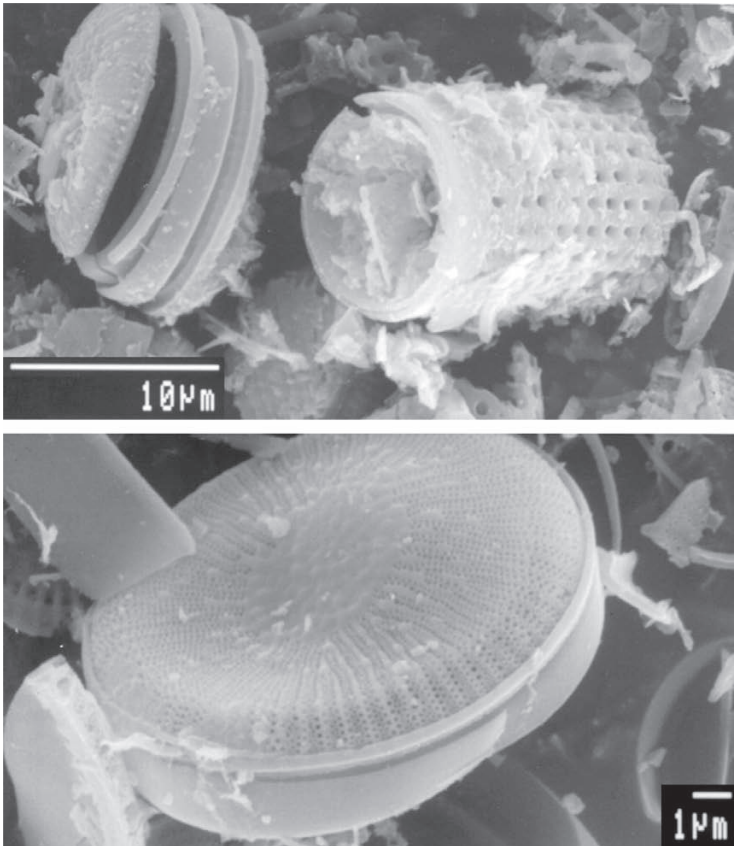
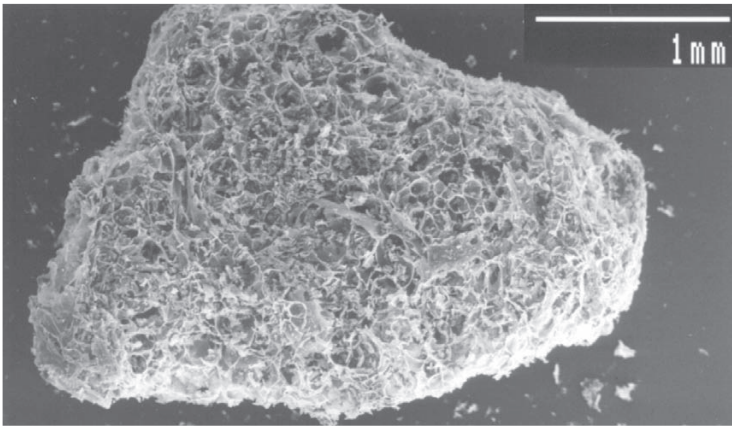


Figure 5.29 Diatomaceous earth. (Courtesy of I. Kelsey-Lévesque and A. Tagnit-Hamou).

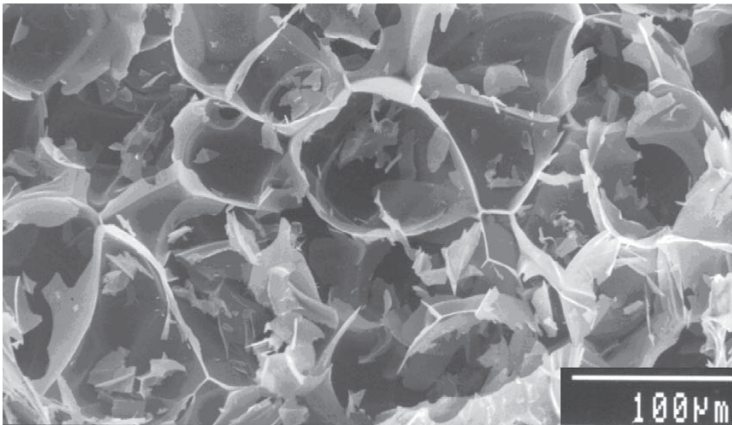
can be done with the final residue of the combustion? According to its chemical composition, it should be possible to recycle it as a pozzolanic material, or even as a cement if its chemical composition is adjusted to produce hydraulic calcium silicates. The Kruger Pulp and Paper Company, in collaboration with Tagnit-Hamou (2008), has developed an industrial process that transforms these sludges into a useful cementitious material. This cementitious material has already found a use in the construction of some basements in the Sherbrooke area with the cooperation of St Lawrence Cement, a Canadian company affiliated with Holcim.

5.3.2.10 *Spent pot-liners from aluminium smelters*

The electrolytic cells of aluminium smelters generate 2 tonnes of spent pot-liners for each 100 tonnes of primary aluminium produced. This means



(a)



(b)

Figure 5.30 (a) Perlite particle and (b) enlarged view. (Courtesy of A. Tagnit-Hamou and I. Kelsey-Lévesque).

that an aluminium plant that produces 500 000 tonnes of aluminium per year generates 10 000 tonnes of spent pot-liners. Spent pot-liners are mostly composed of refractory bricks and graphite but because they also contain some leachable cyanides and fluorides, they are classified as toxic wastes. They must be disposed of in special deposits under well-controlled conditions of storage, at a cost of about \$800 to \$900 per tonne (including transportation costs).

The company Nova Pb has developed a thermal treatment that eliminates all of the toxic components and leaves a residue called Glass FritTM. During this treatment, the chemical composition of the spent pot-liners is adjusted to be close to that of slag, except that it is less rich in lime and much richer

Table 5.7 Comparison of the chemical composition of Glass Frit[®] and a slag

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	CaF ₂	K ₂ O	Na ₂ O	Na ₂ O <i>eq</i>
Glass Frit	31.7	23.4	3.4	14.6	0.8	9.4	1.0	9.4	10.1
Slag	36.8	10.3	0.7	36.5	12.6	—	0.4	0.4	0.7

in alkalis. Table 5.7 gives the chemical composition of a treated spent pot-liner after such adjustment.

Glass Frit is quenched to get it into a vitreous state. When ground to the same fineness as a slag, Glass Frit becomes a very interesting cementitious material that has already been used in some demonstration projects (Tagnit-Hamou and Laldji, 2004; Laldji and Tagnit-Hamou, 2006, 2007). Due to its particular composition, Glass Frit has hydraulic and pozzolanic activities superior to those of slag when correctly activated with either soda or lime.

5.3.2.11 Rapid evaluation of the pozzolanicity of a material

By itself, chemical analysis does not provide even a hint about the pozzolanicity of a material; at most, it tells how much SiO₂ the material contains but it does not indicate the form of the SiO₂ or in what type of mineral it is included. Only an X-ray diffractogram can indicate if this SiO₂ is totally or partially in an amorphous (vitreous) reactive form. For example, chemical analysis shows that silica fume, diatomaceous earth, and rice husk ash all have an SiO₂ content greater than 90%, and their X-ray diffractograms (Figure 5.31) show a “halo de diffusion” at the location of the principal peak of cristobalite. (Cristobalite is the crystalline form of SiO₂ that is stable at high temperature. But an X-ray diffractogram reveals nothing about the morphological aspect of this SiO₂, which is also very important when evaluating the pozzolanic potential of a material.)

Observation under an electron microscope shows that in a silica fume the vitreous silica is in the form of very fine spherical particles, a hundred times finer than an average Portland cement particle. In contrast, in diatomaceous earth and rice husk ash, the vitreous silica represents the skeleton of the organic material that has disappeared by a natural process (diatomaceous earth) or by burning (rice husk ash). This vitreous silica is in the form of a very porous material.

When looking the pozzolanicity of a metakaolin, it is seen that its SiO₂ content is not high (52% only) but that the crystals of kaolin have been totally disorganized during its firing at 750°C. It is this total disorganization of the silica tetrahedra and alumina octohedra that is responsible for the pozzolanicity and high reactivity of the metakaolin. However, observation of metakaolin particles under an electron microscope shows that they have

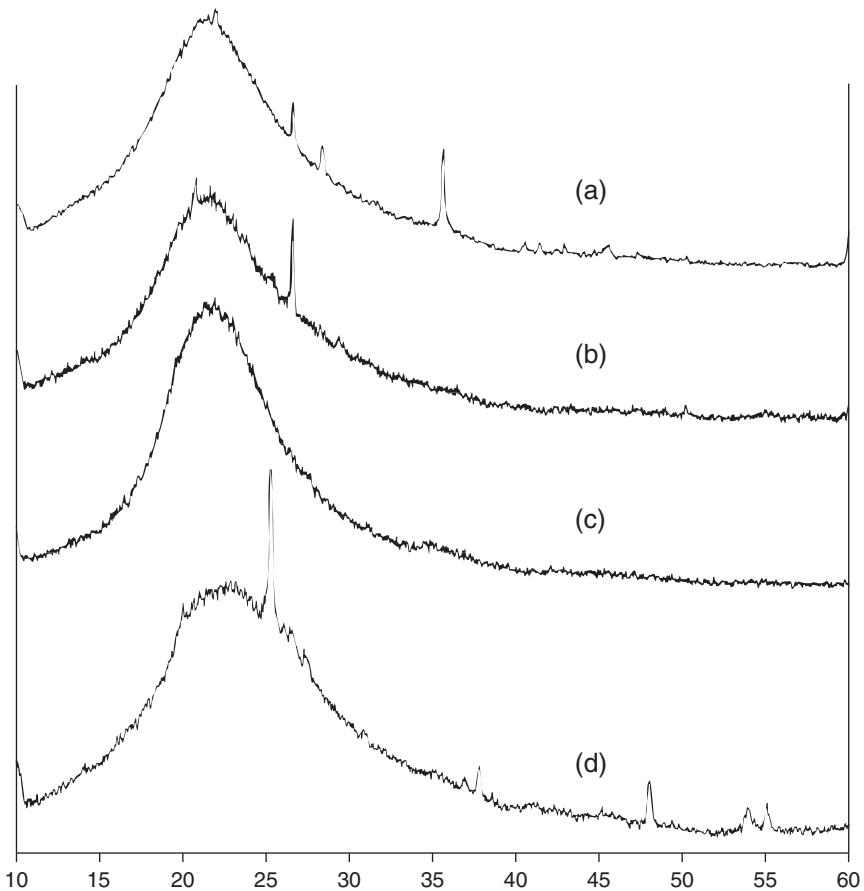


Figure 5.31 Typical diffractogram of various forms of amorphous silica. (a) Silica fume. (b) Rice husk ash. (c) Diatomaceous earth. (d) Metakaolin. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

a very irregular form so that, from a rheological point of view, they are not as advantageous as silica fume particles.

From these examples it can be seen that the morphological aspects of a pozzolanic material have a great influence on the way in which they can be used by the cement and concrete industry. ASTM Standard test method 311 *Sampling and testing fly ash and natural pozzolans for use as a mineral admixture in Portland cement concrete* provides a practical method of evaluating the actual pozzolanic potential of a material but it is a long process, requiring 28 days to determine the pozzolanic value of the material.

In conclusion, in order to evaluate the pozzolanic potential of a material, it is necessary:

- first, to make a chemical analysis to determine the SiO_2 content;
- second, to make an X-ray diffractogram;
- third, to observe the morphology of the particles under an electron microscope; and
- fourth, to test the material according to the ASTM 311 Standard Test method.

5.3.3 *Fillers*

In Europe and in Canada it is possible to introduce 5% of limestone filler into a Portland cement and still sell it as “pure” Portland cement. As well, in Europe, up to 35% limestone filler can be incorporated in some blended cements, and in Canada up to 15%.

5.3.3.1 *Limestone fillers*

To some researchers, limestone filler is not a totally inert filler, because it can react with C_3A to form carboaluminates. Goldman and Bentur (1993) and Venuat (1984) have shown that limestone fillers accelerate somewhat the hydration of C_3S . In addition, limestone filler particles have been found to be nucleation sites that favour the growth of C-S-H (Nehdi *et al.*, 1996). From an economical point of view for a cement company, it is the most advantageous filler because its production cost is very low.

5.3.3.2 *Silica filler*

When available as a by-product of another industrial process at a low price, silica filler can be blended with Portland cement in the same manner as limestone filler. Of course, this application involves only the crystallized form of silica. Silica filler has no particular binding properties; it acts as a pure filler. Crystallized SiO_2 is a very stable material even in the lime-rich environment provided by Portland cement hydration. From an economic point of view, it is not particularly worthwhile to grind any form of quartz, sandstone, or quartzite; these rocks are very hard to grind and very abrasive. But when the silica is already in a fine powder form, having about the grain size of Portland cement particles, it is possible to use it as a filler. It is very useful from an ecological perspective because 1 kg of silica filler eliminates the emission of 1 kg of CO_2 .

5.3.3.3 *Glass fillers*

There are countries in which the recycling of glass bottles causes a problem. The number of imported glass bottles (essentially in the form of wine bottles)

is much greater than the possibility of recycling them to make new bottles. In such countries, as in Canada, only transparent glass (also called white glass) can be recycled to make new bottles. Therefore, what can be done with all of the other bottles that have a chemical composition and colour so variable that is not possible to recycle them?

These bottles can be crushed and ground to a fineness of about 500 to 600 m²/kg (corresponding to a maximum grain size of 4 to 5 μm) and added to concrete as a filler. In spite of their high alkali content, there is no risk of alkali silica reaction because the alkalies are solidly trapped in the glass. In collaboration with the Liquor Board of the Province of Quebec, Tagnit-Hamou (2008) has developed very interesting field applications for pulverized glass. The Liquor Board of Quebec now requires that all concretes that are used in its stores contain glass filler.

5.4 Non-clinker binders

In the European standards, the cement type that contains the minimum amount of Portland cement clinker is CLK-CEM III/C, that contains no more than 5% of clinker blended with 95% of slag. However, Ciment d'Obourg in Belgium is producing a similar binder that does not contain any clinker at all that can be used in the same types of applications (Gebauer *et al.*, 2005). To the best of our knowledge this is the first of this new type of binder, but certainly will not be the last.

5.5 Testing Portland cements and binders

Portland cement is made from common materials found almost everywhere, but these raw materials contain impurities that vary from one source to the next and these impurities influence the final properties of the Portland cement. The thermal process that transforms these natural materials into clinker is quite straightforward from a theoretical point of view for anyone who can read phase diagrams, but the processed end product, namely Portland cement clinker, is not simple at all. In fact, it is a complex mixture of four main minerals (C_3S , C_2S , C_3A , and C_4AF) and a variety of secondary minerals (free lime, periclase, uncombined silica, alkali sulfates, calcium sulfates, etc.).

C_3S and C_2S may form as large crystals or as small ones; the interstitial phase (C_3A and C_4AF) may be relatively crystallized or more-or-less amorphous, or partially crystallized and partially amorphous. Belite (impure C_2S) nests and free-lime clusters can also be found. The nature of the atmosphere in the clinkering zone can go from slightly oxidizing to slightly reducing, and so change the morphology of the clinker (Aïtcin, 1998). Due to all of these differences (and many others), it is quite impossible to produce identical clinkers in two different cement plants. Once a clinker has been produced, cement manufacturers can play with the gypsum content and

the fineness of the Portland cement to control to a certain extent the final properties, but this game has its own limits.

Consequently, in order to produce a Portland cement that has controlled and predictable properties, it is necessary to homogenize the raw materials used, and the clinker and the Portland cement produced, and to monitor regularly some of its basic properties. When looking at the development of the cement industry, quite early on it became imperative to develop some acceptance tests to ensure a certain level of technical performance, in order to ensure a safe and secure use of Portland cement in the field.

With the development of blended cements that contain a significant fraction of various, more or less cementitious materials (slag, limestone filler, fly ashes, natural pozzolans, artificial pozzolans, silica fume, metakaolin, and rice husk ash), it has become increasingly imperative to control the variability of the technical characteristics of these blended cements. This variability is greater than that of “pure” Portland cement because these cementitious materials have chemical and morphological compositions that are more variable than that of Portland cement clinker.

Moreover, in order to decrease their energy costs, cement producers are using more and more so-called “alternative fuels” (scrapped automobile tires, animal flours, used paints and varnishes, biphenol chloride [BPC], domestic wastes, recycled plastics, etc.). The variability of these alternative fuels adds even more variability to the clinker. Finally, at present, many cement producers are using various sorts of calcium sulfates to control the setting of their cement, and this also influences the rheological and mechanical properties of the cement.

More than ever, it is absolutely necessary to ensure that the present acceptance standards result in the production of a binder having predictable rheological and mechanical properties. This can, in principle, be done with a performance standard, but what performance is to be specified? Is it necessary to continue to use present acceptance standards? Is it possible to eliminate some? To modify others? To add new ones? We do not think that it is necessary to change drastically the present acceptance standards; it is only necessary to adapt them somewhat and to modify the optimization process of the characteristics of the binder. Generally speaking, the standards developed over the years in North America to test pure Portland cement have served the industry well up to now, and we believe that it is not necessary to propose radical changes, except perhaps for the evaluation of the rheological behaviour in order to solve field problems with some cements when using them in 0.35 to 0.40 w/b concretes.

Until recently, it was appropriate to test cement pastes at a w/b of 0.48 to 0.50, because most concretes often had a w/b ratio of over 0.60, but this no longer always the case. More and more high-performance concretes having w/b between 0.35 and 0.45 are being used. The fabrication of these concretes necessitates the use of superplasticizers. With some cements there

is no workability problem during the first 1½ hours following the batching, while with others that have passed the same acceptance standard, the slump loss is unacceptable. When cement particles are brought closer to each other by decreasing the w/b as shown in Figure 3.1, the rheological and hydration conditions are considerably modified. When the cement particles are in close contact with one another in a low w/b paste, ettringite crystals or early C–S–H grow very rapidly and quickly create some initial mechanical bonds which are very negative from the rheological standpoint.

5.5.1 Prioritization of strength over rheology

Until now, generally speaking, the phase composition, the gypsum content and the fineness of cement are optimized to get the highest initial cube strength within a particular strength class of a Portland cement. Unfortunately, all too many cement producers still believe that the compressive strength of a concrete depends only on the cube strength of their cement. While this factor cannot be neglected, it is only secondary when compared to the influence of the w/b. The short- and long-term strengths of a cement paste or a concrete depend essentially on the w/b, and not on the cube strength of the binder used to make this concrete.

It is possible to manufacture a concrete testing 57.9 MPa at 18 h, 63.4 MPa at 20 h, and 65.3 MPa at 22 h using a Portland cement having a Blaine fineness of 340 m²/kg (which is not very high), a C₃S content of 52% (which is low for a modern binder), and a C₃A content of 0.5% (which is extremely low) (cement D*, Table 5.8). The secret of this ultra-high strength concrete was its very low w/b equal to 0.20. Coppola *et al.* (1996) found very similar results.

It is thus time for cement producers to abandon the optimization of the characteristics of their binder in terms of only *cube strength*, because quite often the only result of this is to complicate the task of those who try to make more durable concrete structures using this binder. Rather, it is time to optimize the composition and the characteristics of a binder in terms of its *rheological performance*: this is the most urgent need of

Table 5.8 Characteristics of some cements used to make reactive powder concretes with a compressive strength of about 200 MPa

		A	B	C	D*
Type	ENV 197/1	CEI 42.5R	CEI 52.5R	CEI 52.5R	—
	ASTM	V	V	III	II/V
C ₃ A	0	4.00	11.2	0.5	—
Blaine (m ² /kg)	340	530	520	540	—

Note: Cements A, B, C from Coppola *et al.* (1996). Cement D* from Aitcin *et al.* (1991).

the construction industry. Facing repeated rheological problems in the field costs millions of dollars to the construction industry. Moreover, rheological problems can result in durability problems necessitating early repairs, rehabilitation, or the premature destruction of structures, all because the characteristics of the binder were not optimized for the right criteria. In fact, concrete users do not need binders having a high cube strength; they need binders with an easily controlled rheology. This is the current challenge of the cement industry.

5.5.2 *Prioritization of rheology*

5.5.2.1 *Present situation*

Presently the control of the rheology of a binder is the weakest part of cement acceptance standards. The flow of a standard paste having a w/b of 0.48 or 0.50 is measured about 10 minutes after the first contact between water and binder particles. Then, the second step is to control the initial setting time 2 to 3 hours later. Nothing is checked in between as shown in Figure 5.32. However, it is during this period of time that concrete is transported and placed, a crucial time in the life of concrete for those who are preoccupied by the durability of concrete structures and the economics of concrete placement.

5.5.2.2 *The ideal binder*

For a contractor, the ideal binder is one that has the rheological characteristics represented in Figure 5.33. Of course, it is impossible to make such an ideal binder but there is still room for improvement when considering the present situation as indicated in Figure 5.32. It should, for example, be required that the standard paste not lose more than 30% of its initial flow during the 1½ hours following the mixing with water.

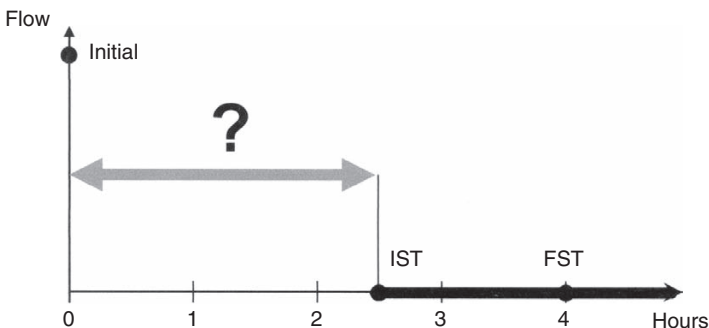


Figure 5.32 Testing the hardening of concrete.

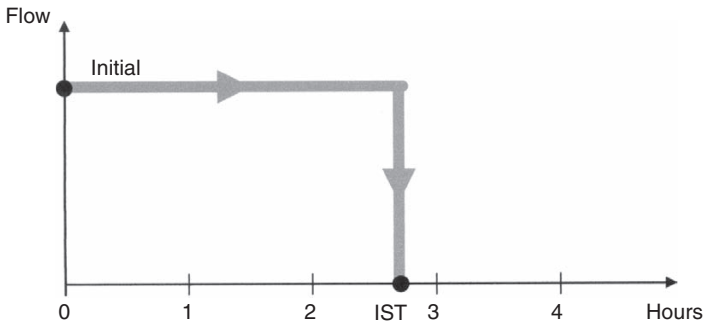


Figure 5.33 Hardening of an ideal binder.

5.5.2.3 *Is it appropriate to continue to test binders at a w/b of 0.48 or 0.50?*

It is now time to change the w/b at which binder pastes are tested. A w/b of 0.48 or 0.50 is too high to properly test the rheology of a binder paste: at that level the cement particles are too far apart in the paste and it is the water that essentially controls the rheology. The large distance between the binder particles can hide their strong interactions when they are brought closer to each other in a low w/b paste.

Powers (1958) showed that in order to reach full hydration (at least theoretically), it is necessary to have a minimum w/b of 0.42. Above this value, the paste contains water that will never participate directly in hydration or be part of the gel water that is adsorbed on the cement particles. Therefore, it would be more logical to test cement paste at a w/b of 0.42 (or 0.40 for those who like round numbers) or even at a w/c of 0.35 because, as demonstrated by Jensen and Hansen (2001), full hydration can be reached at such a low w/b if some external water is provided.

Of course, at such a low w/b it is necessary to disperse the binder particles with a water reducer or a superplasticizer to counteract the formation of cement flocs. When such a dispersant is introduced into the paste, binder particles no longer flocculate and the water trapped within the flocs is freed to fluidize the binder paste. Using a performance standard, the binder producers would have the necessary latitude to select the most efficient water reducer to improve the rheology of their binder pastes, as long as they are willing to tell their customer the brand and dosage of the water reducer used.

It is not only our opinion, but also the opinion of those who are preoccupied by the future of the cement and concrete industries within a sustainable development frame that all binders be tested at a w/b of 0.40 to 0.42 or even better 0.35. At such w/b levels, the rheological interaction of the binder particles can be seen and corrected for, because it is no longer exclusively the water that controls the rheology of the paste.

Those who are frightened by the idea of making flow tests with a water reducer will eventually be forced to do so, because, at some point in the future, all commercial binders will contain a water reducer introduced into the binder during the final grinding, as is currently done by at least one cement company in Pakistan. Ignoring the beneficial effects of water reducers decreases significantly the sustainability of present commercial binders. However, the decrease of the w/b of the standard binder paste will increase the cube strength, which will make the proponents of the cube strength very happy!

5.5.3 Monitoring of rheology up to initial set

As one of the most critical periods of time in the life of concrete is the 1½ hours that follow the beginning of mixing, it is important to pay careful attention to the rheology of the paste during this critical period. The closer the rheology of the paste approaches that presented in Figure 5.33, the more efficient the binder is. Therefore, it is necessary to adjust the phase composition, the fineness, and the calcium sulfate content to optimize the rheology, rather than the mechanical strength, because:

- It will be easier to place concrete in the field, and it will not be necessary to add a water reducer in the field because it will already be contained within the binder.
- It will be easier to build durable structures as long as the concrete is properly cured after its placement in the forms.
- Less concrete will be wasted.
- Sustainable development will no longer be an empty shell in the concrete industry.
- The economic performance of cement and concrete companies will be significantly improved because, as stated earlier, the worst enemy of concrete is not steel, wood, brick, glass, or aluminium, but rather bad concrete. A structure built with bad concrete will have to be repaired, rehabilitated, or demolished before reaching the end of its projected life. The repair or demolition of a bad concrete results in large manpower costs but only low material costs. All the money spent in repair or demolition is no longer available to build new infrastructure in which the amount of cement is 10 to 100 times greater than that in a repair or demolition project.

5.5.4 Monitoring slump loss

As a consequence of the research done on the rheology of low w/b concrete at the Université de Sherbrooke, the three cement producers of the Province of Québec now monitor daily the slump loss of a reference concrete (Class C2 under Canadian standard CSA A 23.1). It is essentially an air entrained

concrete with a w/b equal to 0.43 or 0.45 that contains a water reducer. Since this monitoring has been implemented, from a practical point of view, no catastrophic slump losses have been observed in the field. Generally speaking, a significant improvement of the rheology of the delivered concrete has been observed, which results in a significant increase of the productivity and of the durability of concrete structures in the harsh environment they face in the Province of Quebec.

5.5.5 Other considerations

The above suggestions do not constitute a great revolution; they are just a small step forward that should result in an improvement of the productivity of the concrete industry. This will result in the construction of concrete structures of better quality and consequently of greater durability. The future competitiveness of the cement and concrete industry will be influenced positively by such small changes.

In order to provide customers with a product having a low variability, it is absolutely necessary to develop a series of acceptance criteria that guarantee the achievement of a minimal performance in the field. The acceptance criteria can be prescriptive, as in the twentieth century or they can be performance based as will eventually be the case in the twenty-first century. It should be remembered that the need for acceptance standards goes back to the early beginnings of the cement industry. Professional associations of cement producers were created in Germany in 1877, around 1900 in France, in 1902 in the USA, and in 1935 in England. They practised a kind of self-discipline in order to provide a reliable product to their customers. Indeed, German Portland cement had such a reputation for quality that in 1884, 8000 barrels of cement (1360 tonnes) produced by Dickerhoff of Germany were shipped to the USA to build the foundation of the Statue of Liberty. The Metropolitan Opera Tower and the Waldorf-Astoria Hotel were built with German Portland cement. The New York Stock Exchange on Wall Street was built with a Portland cement made by Lafarge. Quality was at that time a rewarding investment, why not now?

Along with these national associations, national standards societies were created. The American Society for Testing and Materials (ASTM) published the first standards on Portland cement in 1904 (Kett, 2000). In France, the first cement standard was published in 1919 (Lafuma, 1951). Why should we not revisit these standards from a sustainable development perspective?

5.6 Introducing cementitious materials and fillers

Cementitious materials can be introduced directly into the concrete mixer at the batching plant or blended with the clinker at the cement plant. As long as the concrete containing cementitious material has been thoroughly mixed it does not make any difference which procedure is used. Each method of

using cementitious materials has its own advantages and disadvantages, and both are commonly used.

5.6.1 At the concrete plant

From a technical point of view the main advantage of introducing the cementitious material at the concrete plant is that it is the concrete producer who then controls the substitution rate according to the needs of the customer, the temperature, the initial strength required, the maximum temperature that the concrete would reach within the forms, and so on. For example, the percentage of cementitious material could be increased in summer, for mass concrete applications, or for high performance applications, while it could be decreased for winter applications or precast applications where a very high early strength is required. Indeed the addition rate can be adjusted from one batch to another.

When the cementitious material is added at the concrete plant, it is necessary to have a special silo for each of the cementitious materials. This is a non-negligible investment. In some existing concrete plants there is simply no space to add a new silo or it would be very expensive to modify the batching system to accommodate the introduction of one or two additional cementitious materials. In addition, from an operational point of view, it is necessary to properly manage the delivery schedule of the cementitious materials and to check their quality and consistency.

5.6.2 At the cement plant

When a cementitious material is added at a cement plant to make a blended cement its quality and consistency are checked regularly by the cement producer, its dosage is quite precise, and the cementitious material is thoroughly mixed with the Portland cement clinker. But the addition rate is usually fixed. Concrete producers then do not need any additional silos, nor do they need to be concerned about the control of the quality and consistency of the characteristics of the cementitious material.

In order to offer a more flexible dosage rate some cement producers have developed blending units where they can blend the binder “à la carte” or provide the cement “du jour” according to the needs of their customer when loading the cement trucks or the railway cars. In such a case the cement producer must grind and/or store separately the cementitious materials, which means adding one or more new silos at the cement plant or allocating one particular silo for each cementitious material.

When the cementitious materials are added at the cement plant, the cement producer has two options for the final grinding: grind the cementitious material and the Portland cement clinker together or grind the Portland cement clinker and the cementitious materials separately, store them separately in temporary silos and then mix them and store the blended cement in

a special silo. The latter complicates the production process and it involves the use of several silos, but from a technical point of view it allows an optimization of the grinding of the Portland cement clinker and of the cementitious material. The specific surface areas of the Portland cement and of the cementitious materials can be adjusted according to the degree of reactivity that it is necessary to achieve. Usually, when separate grinding is carried out the specific surface area of the cementitious material is greater than that of the Portland cement.

When the cementitious materials and Portland cement clinker are introduced simultaneously into the final grinding mill the fineness of the particles of each of them depends on their respective grindability. For example, when a blended cement containing some slag is produced it is necessary to increase the specific surface area of the blended cement to make it more reactive. In such a case the clinker is ground finer than the slag because the slag is harder to grind, which is the opposite of what should be done.

There is no universal rule at present that favours one mode of introduction of cementitious material over the other. In France, in Belgium, and in Québec in Canada, cementitious materials are blended at the cement plant. In Germany, slag is blended at the cement plant but fly ashes are introduced at the concrete plant. In the USA and in the rest of Canada, both methods are presently used.

When clinkers other than the ones we are now familiar with will be produced, it will add new variations to the type of binders offered in the market. This will complicate the selection of the most appropriate binder for each special application.

5.7 Concreting with blended cements

5.7.1 Cementitious material blended at the cement plant

In this case, the cement company optimizes the composition and the characteristics of its blended cement in order to satisfy acceptance standards. The practical behaviour of such a cement is not too different from that of Portland cement because its properties are controlled by the acceptance standards tests. However, the concrete early strength might be slightly lower than that of a pure Portland cement.

5.7.2 Cementitious material added at the concrete plant

In this case, the Portland cement–cementitious material blend has not been specially optimized and it is always dangerous to generalize the results from the technical literature when substituting a cementitious material for a certain part of the Portland cement clinker in a concrete plant. In fact, concrete properties depend not only on the properties of each component of the blend but also on their interactions. Trends can be anticipated but

only experience with the actual materials in the actual conditions of use can provide the real answer about the efficiency of the cementitious material added at the concrete plant.

5.7.3 Properties of the fresh concrete

It is not always true that concretes in which some of the Portland cement has been substituted by a cementitious material more easily hold their slump, bleed more, or require a smaller dosage of water reducer or superplasticizer, because they contain a fraction of cementitious material that is less reactive than Portland cement. Moreover, in some cases, it is more difficult to entrain air, in other cases not. In some cases, the initial setting is shorter, in others longer. Thus, when using cementitious materials, it is always dangerous to generalize!

5.7.4 Curing

Whenever a cementitious material has been introduced into a concrete mixer, it is very important to enforce strictly the water curing procedures because water is absolutely essential to get the full potential of the cementitious material. This is too often forgotten by contractors who treat a concrete made with a blended cement in the same way as a concrete made with a pure Portland cement. Any use of concrete made with a blended cement that is not accompanied by strict curing conditions will be a failure. Without water, there is no pozzolanic reaction. So, how easy is it to enforce proper water curing? There are two solutions:

- *First*, you motivate contractors to water cure the concrete structure (external water curing) by paying them specially to do so. When they realize that water curing can be a source of profit like their other concreting activities, they become zealous.
- *Second*, you can incorporate internal curing within the concrete mix by substituting a part of the natural sand by a saturated lightweight sand.

These two solutions are discussed in more detail in Chapter 12.

5.7.5 Properties of the hardened concrete

The greatest difference in the compressive strength of concretes made with pure Portland cement or blended cements is observed mostly in the short term. For example, after 2 or 3 days, silica fume concretes are stronger than pure Portland cement concretes of the same w/b. After 7 or 14 days, slag concretes are as strong as pure Portland cement ones, of the same w/b, depending on the level of substitution. But in the case of natural pozzolans and fly ash, it is generally necessary to wait more than 28 days, for their compressive strength to reach that of a pure Portland cement of the same w/b.

In some cases, it is necessary to wait 56 days, in other cases 91 days for the same w/b. But, as will be seen in the next paragraph, there is always the option of lowering the w/b ratio of the concrete made with the blended cement to make it gain strength more rapidly.

Another question that will be discussed later is: Is it fair to test concretes containing a certain amount of cementitious material substituted for pure Portland cement at 28 days? Will it be better and fairer to test these concretes at 56 or 91 days, since concrete structures are never fully loaded before such times, except of course for pre-stressed or post-tensioned structures?

5.7.6 *Increasing early compressive strength*

There are five solutions to this problem:

- using the synergistic effect of certain blends of cementitious materials
- lowering the w/b ratio
- increasing the initial temperature of the concrete mix
- heating the structural element with water vapour (low pressure steam curing)
- using insulated forms.

In many cases, contractors and pre-casters favour the low pressure steam curing technique, because it is the easiest one, or the only one that they know. However, from a sustainable perspective, it is the worst (waste of energy, loss of durability) and is also the most inefficient because the heat is applied from the exterior, and fresh concrete is not a good heat conductor.

5.7.6.1 *Synergistic effect of some cementitious material combinations*

It is well known that silica fume increases the early strength of concrete. But it is not so well known that a mixture of fly ash and slag gives higher compressive strength than their equivalent counterparts (in terms of total percentage) containing only fly ash or slag. This explains also the use of ternary or quaternary blended cements on two recent prestigious projects using particularly high-performance concretes: the Burj Tower in Dubai and the Liberty Tower in New York. As far as we know, the HPC used to built the Burj Tower in Dubai is a ternary blend made of Portland cement, fly ash, and silica fume while, the Liberty Tower in New York is built with a quaternary blend composed of pure Portland cement, slag, fly ash, and silica fume.

5.7.6.2 *Lowering the w/b*

The easiest and most sustainable way to increase early compressive strength is to lower the w/b. As was seen in Chapter 3, lowering the w/b ratio results

in the cementitious particles being closer to each other in the binder paste (reread the hidden meaning of the w/b). During hydration, the hydrates have a shorter distance to fill the gaps between them so that both early and final compressive strengths are increased. The resulting concrete is also more durable. From a sustainability point of view, this is the best solution.

5.7.6.3 Increasing initial temperature of concrete

Since the hydration reaction is a self-activated chemical process obeying the Arrhenius law, an easy way to increase early concrete strength is to increase its initial temperature. An advantage of this method is that the source of heat is uniformly distributed throughout the mix. There are some limitations to this temperature increase, because it can affect adversely the rheological behaviour of the concrete. However, it can be convenient in a precast plant where the placing time is very short.

5.7.6.4 Heating structural elements

This is the usual method used in precast plants. As already stated earlier this is a less sustainable and less efficient method. We do *not* recommend it except in extreme conditions, where it is not possible to use any other solution or combination of solutions.

5.7.6.5 Use of insulated forms

When using insulated forms, it is possible to take advantage of the acceleration of the hydration of Portland cement due to its heat of hydration. This heat of hydration is kept inside the concrete and not dispersed through the forms. When the binder contains some cementitious material, the increase of the temperature increases the reactivity of these cementitious materials and consequently increase the early strength of the concrete. In such a case, this early compressive strength is function of the amount of cementitious material and the thickness of the insulating material.

This method has the advantage of providing almost homogenous and isotropic hydration conditions: there is in reality a very small temperature gradient within the forms due to the unavoidable small heat losses. Moreover, as will be seen later, this method can be used to eradicate autogenous shrinkage in low w/b concrete when it is combined with a partial substitution of the sand by a saturated lightweight sand.

This is also a very sustainable method because it uses the internal heat generated by cement hydration without generating CO₂ emissions. This is the method that we favour, along with the reduction of w/b ratio, whenever it is easy to implement it. In the future, with the widespread use of blended cements this method will be implemented more and more often.

5.7.7 Durability

All other things being equal, concretes containing cementitious materials are usually more durable than pure Portland cement concretes if they have been well cured, because a part of the lime liberated by the Portland cement hydration (Portlandite crystals) reacts with the cementitious material to form secondary C-S-H, which is stronger and more stable than Portlandite. Portlandite itself is a mineral that is not particularly desirable in concrete from either a mechanical or a durability point of view.

The resistance to freeze-thaw cycles and deicing salts of blended cements containing silica fume and fly ash is well documented. In the case of a blended cement containing slag, some caution must be exercised if the substitution rate is over 25%. Slag concretes can withstand the procedure of ASTM C 666 (300 rapid freeze-thaw cycles under water) without any problem if they are well protected by a good air bubble system having a low spacing factor (the spacing factor represents half of the average distance between individual air bubbles). However, in the case of mixes containing more than 25% slag, it is not always certain that the air bubble system provides adequate resistance to freezing and thawing in the presence of deicing salts (ASTM C 457-88 Test Method).

Until recently, slag concrete has not been much used in Nordic countries where winter conditions are extreme. It has been quite extensively used in Germany, France, the Netherlands, and Belgium where winters are not particularly severe from a freezing and thawing point of view. As this weakness of highly substituted slag cement has not yet been fully studied, it is better to be cautious. It is hoped that this point will receive the necessary attention from researchers.

Finally, it is well known that slag cement concretes perform very well in a marine environment: it is their preferred use. Silica fume and fly ash blended cement also perform well under marine conditions. This is, however, not the case with blended cements rich in limestone filler.

5.8 Testing concrete containing cementitious materials

With the exceptions of silica fume and slag, blending Portland cement and clinker with any other cementitious material delays the achievement of the full strength of the concrete. When standard specimens made with such blended cements continue to be cured in lime saturated water or in a fog room beyond the standard period of 28 days they continue to increase in strength until 56 or even 91 days. After this the strength increase is not so significant. This strength increase between 28 days and 56 or 91 days is due to the fact that cementitious materials react slowly at room temperature with water and with the lime liberated by the hydration reactions. Therefore, there are now suggestions that f'_c should be measured at 56 or 91 days instead of the sacrosanct 28 days which has been the rule till now.

The idea is:

- *First*, in the design process use the “true” long-term compressive strength and not a lower value, because at 28 days the standard specimens have not reached their potential strength.
- *Second*, delaying the age at which f'_c is defined makes concrete more sustainable because a given f'_c measured at 56 or 91 days may be obtained with less binder than when it is measured at 28 days, regardless of the composition of the binder. This will decrease the CO₂ emitted when making concrete to support any particular load.

In principle, we are not opposed to this idea. However, we must emphasize that if a concrete containing a blended cement is not cured properly in the field it will *never* reach its full potential strength, because water is a very important part of the pozzolanic reaction; this reaction cannot develop in a dry concrete. Therefore, any move to lengthen the test age should be accompanied by tougher curing regulations. If the concrete industry is not ready to agree to cure concrete properly, and owners are unwilling to pay specifically for curing the concrete properly, we would oppose lengthening the testing age, because then field concretes containing cementitious materials will never reach their full potential strength.

5.9 Concluding remarks

This chapter is the longest one in this book because it is at the level of their nature and of their composition that modern binders will be different from traditional Portland cement. This will necessitate modifications in the way we treat concrete in the field. This major change is a consequence of improving the sustainability of concrete. The easiest and most efficient way to do this is to reduce the amount of Portland cement clinker when manufacturing blended cement. The ecological equation is very simple:

$$1 \text{ kg less of clinker} = 1 \text{ kg less of CO}_2 \text{ emitted.}$$

It is also the simplest, the fastest, and the least onerous means of making more concrete within a CO₂ emission quota which is particularly important in developing countries.

In countries such as the Netherlands and Belgium, an average substitution rate of 40% has already been reached without impairing the competitiveness of the construction industry. In these two countries, over the years, engineers and contractors have learned how to use blended cements appropriately. With the technology presently available in manufacturing and using blended cements, an average substitution rate of 50% is feasible if superplasticizers and other admixtures are properly used. The development of the use of blended cement does not imply the elimination of pure

Portland cement: there are circumstances in which the use of Portland cement will be mandatory, but this use will shrink as the technology to use blended cement improves.

Now that we can get the binder particles closer to each other using powerful dispersants such as superplasticizers, it is possible to increase very easily and very ecologically the early strength of concretes made with blended cement. Moreover, in these concretes, it is not necessary to develop as much “glue” to get a given strength because the hydrates can bridge the gap between the binding particles more rapidly and more strongly. Along the same lines, the use of insulated forms will become common even in hot countries because it is a very simple, efficient, inexpensive, and sustainable means of increasing concrete early strength, by taking advantage of the self-activation of the hydration and pozzolanic reactions.

Finally, it will be necessary for cement producers to modify drastically the way in which they optimize the “gypsum content” of their blended cement. The gypsum content will be optimized not to increase the early compressive strength of small test cubes, but rather to improve the rheology of the concrete during the first 1½ hours after it is mixed. The present practice of optimizing the gypsum content of Portland cement based binders for early strength favours high C₃S and C₃A contents as well as high fineness. Optimizing the gypsum content to improve the rheology will favour sustainability: lower C₃S and C₃A contents, and lower fineness.

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6 Water

6.1 Introduction

In concrete, water is a component that is as important as the binder; it influences the properties of both the fresh and the hardened concrete. As already seen in Chapter 3, it is the mass ratio of the mixing water (see Chapter 2 on definitions) to the binder that will determine, with the help of admixtures, the essential properties of the fresh and hardened concrete. The beauty of the notion of w/b is that, first, it places the two essential components of concrete on the same level as far as their importance is concerned; and, second, it emphasizes that their actions are tightly bound.

It is very easy to add water to a mixer through a meter, but it is not so easy to evaluate precisely all of the forms of “hidden” water contained in the other components introduced into the mixer. In Chapter 7, it will be seen how to calculate the water introduced into the mixer when using a superplasticizer and, in Chapter 8, the different forms of water present in the aggregates will be described.

From a practical point of view, when batching concrete, the real difficulty that arises is to take into account the variation of the water contained in the aggregates, particularly in the sand. When introducing 800 kg of wet sand into a concrete, a variation of 2% of its total water content corresponds to a variation of 16 litres of “hidden water”, which represents about 10% of the effective mixing water and a variation of 10% in the w/b ratio. Such a variation of the w/b ratio will influence significantly the strength, durability, and sustainability of the concrete.

Therefore, when batching concrete, it is very important to monitor as precisely as possible the variation of the water content of the fine aggregate. This is the only difficult thing, because weighing out different amounts of materials or metering the water introduced into the mixer is easy.

In this chapter, the quality of the water necessary to make durable concrete is not covered. This information is readily available in reference books (e.g. Kosmatka *et al.*, 2002). We will instead concentrate on the role played by water in the fresh, the hardening, and the hardened concrete. The crucial role of water during the curing process will be covered separately in Chapter 13.

6.2 The crucial roles of water

Water plays a crucial role at every stage of the life of concrete. In the fresh state, water largely controls the following aspects:

- the rheology of the fresh concrete (in conjunction with admixtures);
- the relative positions of the binder particles in the paste before hydration begins;
- the initial solubility of the different ionic species of the binder;
- the electrical and thermal conductivity of the fresh concrete; and
- segregation and bleeding.

During the hardening process, water plays a governing role in:

- the development of the hydration reactions and their physical, thermodynamic, and volumetric consequences;
- the development of autogenous shrinkage; and
- the electrical and thermal conductivity of concrete.

In hardened concrete, water continues to participate in the hydration processes of the different phases of the Portland cement clinker and of the various cementitious materials present in the binder.

Hydration stops when:

- there are no more anhydrous particles to hydrate, usually in the case of high w/b concretes;
- there is no more water available, as in low w/b concretes; or
- the hydrated paste already formed is so dense that water cannot migrate to hydrate the remaining anhydrous particles.

As already stated, water is necessary to continue the slow hydration process of the cementitious materials blended with Portland cement clinker in modern binders. Capillary water is also the medium by which aggressive ions can penetrate into concrete and attack it by percolation or osmotic pressure. As will be seen in Chapter 12 devoted to shrinkage, water plays a key role in the development of all forms of shrinkage, except for carbonation shrinkage. It is through the tensile forces developed in the menisci within the pore network that water makes concrete shrink.

From a practical point of view, the major problem with water is that its beneficial action is inversely proportional to its facility of use: while it is very easy and inexpensive to introduce it into fresh concrete, it is necessary to use it with parsimony because if its optimum content is not used, the properties of the fresh and hardened concrete will be significantly altered, as well as its durability and sustainability. On the other hand, when its action is beneficial, as for curing, and when it can be used abundantly, its use is

often considered to be a costly nuisance. Moreover, the better the concrete (low w/b), the more difficult it is for water to penetrate into the concrete in order to improve the efficiency of the hydration process or to counteract autogenous shrinkage.

In Chapter 13, it will be seen that in the case of low w/b concrete it is necessary to develop specific stratagems to provide adequate curing to the entire mass of concrete. It will also be seen that it is very important to pay contractors specifically to water cure concrete in order to make concrete structures more durable and more sustainable.

6.3 Water and fresh concrete rheology

The water present in a mixer is used not only to hydrate binder particles but also to influence the rheology of the fresh concrete, particularly its workability. When water starts to wet the particles of the binder, it provides a certain amount of cohesion to the fresh concrete, a cohesion that is not found when a limestone or a silica filler having the same grain size distribution as Portland cement is mixed with the same amount of water. This is why in masonry cements made of 50% of limestone filler blended with 50% of Portland cement clinker, it is necessary to add a viscosity modifying agent to compensate for this lack of “physical action” of water on the limestone filler and to provide the kind of plasticity that the mason wants to see when laying blocks or bricks.

In Portland cement, it is the water that is fixed to the surface of cement particles as soon as they are wetted that creates the cohesion that makes concrete workable, while decreasing the risk of segregation and bleeding. This cohesion originates from the first hydrates that are formed on the surface of the cement particles and from the electrical forces developed between the cement particles by the very polar water molecules. As shown in Figure 6.1, a water molecule can be considered as an electrical dipole because due to its particular structure, the centres of gravity of the positive and negative charges are not one and the same.

A concrete which does not develop enough cohesive forces as soon as water is introduced into the mixer will be prone to segregation and bleeding. Currently, admixtures can be used to fulfill this physical role.

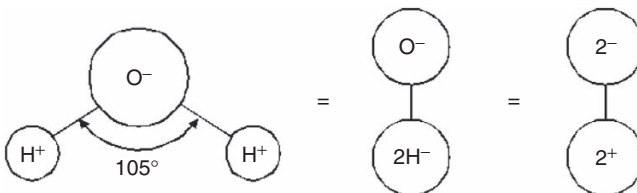


Figure 6.1 Schematic representation of a water molecule.

It is very important to have full control of the rheology of the fresh concrete when cementitious materials are added at the concrete plant, because the cementitious materials do not automatically create the necessary cohesive forces that would have been created by the substituted portion of Portland cement. In such a case it is quite often necessary to use an admixture to compensate for this weakness by adding, for example, a certain amount of entrained air or a viscosity modifier.

The cohesive forces developed initially by the water molecules do not result in too large and too rapid an increase of the viscosity of the concrete mixture. But if during transportation these first links become too numerous and too strong, the concrete can end up with insufficient workability at the job site. Any attempt to restore the necessary workability by addition of water is catastrophic from a strength, durability, and sustainability point of view. It corresponds to an increase of the w/b and a greater separation of the binder particles in the binder paste. It is imperative to restore the workability through the use of a water reducer or, even better, a superplasticizer. In some extreme cases, as in very hot weather, it is better to control the slump loss through the use of a set retarder.

In the previous chapter it was shown that many field problems related to concrete workability come from the fact that the optimization of the binder at the cement plant is carried out on a pure paste having a relatively high w/b of 0.485 to 0.50, without any admixture. Moreover, considering the large influence of temperature on concrete rheology, it is not easy to optimize the cement characteristics all year round. As a result, some cement producers of Quebec may have a summer and a winter formulation for their ordinary Portland cement.

6.4 Water and hydration

The hydration reactions will be described in detail in Chapter 11. Here, the chemical reactions with water will be briefly explained in general terms. The chemical reactions start by the liberation of the unsaturated ions present at the surface of the four main mineral phases of Portland cement clinker (C_3S , C_2S , C_3A , and C_4AF) and also by the entry into solution of the different sulfates present in the cement: the calcium sulfate added to control the rheology of the fresh concrete and the alkali sulfates that are always present in Portland cement clinker. The consequences of these two phenomena can be observed physically and thermodynamically in the cement paste: the temperature of the cement paste increases as well as its electrical conductivity. In concrete, it is rather difficult to observe a temperature increase because of the “sink” effect of the aggregates that have a huge thermal inertia. However, it is easy to notice the increase of the electrical conductivity of the concrete, as seen in Figure 6.2.

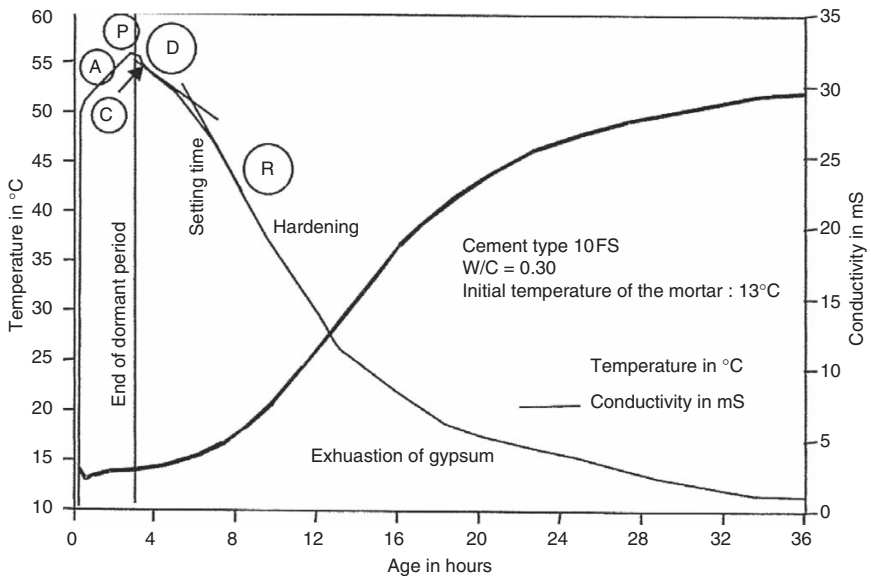


Figure 6.2 Electrical conductivity and heat release of a blended cement containing 8% silica fume. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

6.5 Water and shrinkage

From a practical point of view, there are four different types of shrinkage that can develop in specific circumstances during the life of concrete:

- plastic shrinkage that can occur in any freshly poured concrete;
- autogenous shrinkage that occurs in any concrete when the hydration reaction starts;
- drying shrinkage that occurs when water evaporates from the hardened concrete; and
- carbonation shrinkage when the cement paste carbonates.

In what follows, carbonation shrinkage will not be considered. Here it will only be shown how water plays a key “physical” role in the development of the other three forms of shrinkage. (The specific effects of these three types of shrinkage on the properties of concrete will be described in detail in Chapter 12.)

It is primarily the tensile forces developed in the menisci that appear in both the fresh and the hardened cement paste that cause shrinkage. The tensile forces are linked to the diameter of the pores through the

Laplace law:

$$p = \frac{2\sigma \cos \theta}{r}$$

where p is the capillary pressure, s is the surface tension of the liquid, q is the contact angle between the liquid and the solid, and r is the radius of the capillary pore.

In fresh concrete, the evaporation of the surface water creates the menisci in the capillary network and the associated tensile forces that generate cracking, because the cohesive forces in the fresh paste are not very strong. Different approaches can be taken to avoid or limit plastic shrinkage:

- water evaporation can be prevented through the use of vaporizers such as the ones used in a nursery when growing flowers (see Chapter 13 on curing);
- a curing compound can be applied immediately on the fresh concrete to create an impervious membrane that inhibits water evaporation; or
- an evaporation retarder can be applied on the surface. Evaporation retarders are aliphatic alcohols that cover the surface of the concrete with a mono-molecular film to prevent water evaporation.

In the hardening concrete, the cement paste undergoes a volumetric contraction known as *chemical* contraction (Le Chatelier, 1904). In the absence of an external source of water, that is, external to the cement paste, this chemical contraction results in the creation of some porosity. When the paste becomes rigid, this porosity leads to the occurrence of menisci and the creation of tensile forces; the consequent shrinkage is known as autogenous shrinkage. Autogenous shrinkage develops as soon as the hydration reaction starts in all uncured concretes, whatever their w/b . It is negligible in high w/b concretes but it can be very significant in low w/b concretes (Aïtcin, 1999). The uncontrolled development of autogenous shrinkage can be catastrophic from a durability and sustainability point of view, because it develops at a time when the tensile strength of concrete is very low and consequently it can result in severe cracking of the exposed surface of a concrete structure.

However, when there is an external source of water, the porosity created by the chemical contraction will be filled by water as soon as it is created, no menisci are formed there are thus no tensile forces, and so there is not any autogenous shrinkage (Aïtcin, 1999). From a practical point of view, to avoid autogenous shrinkage, it is necessary to provide either an external source of water by using external water curing (external to the concrete), or internal water curing (internal to the concrete), as will be described later.

In hardened concrete, drying shrinkage occurs when the capillary water evaporates from the concrete due to ambient conditions that favour this

evaporation: dry air, hot air, dry wind. In order to avoid drying shrinkage, it is necessary to cover concrete surfaces with an impervious film or a pore filler.

6.6 Water and alkali/aggregate reaction

As far as alkali/aggregate reactions are concerned, there is at least one point on which all researchers in this area agree: water is necessary for it to develop. Very often to stop or limit the development of an alkali/aggregate reaction, it is simply necessary to treat the surface of concrete exposed to rain or the other source of water so that it becomes impermeable.

6.7 Internal curing

In an effort to counteract the early cracking of low w/b concrete due to the uncontrolled development of autogenous shrinkage, different water curing approaches have been proposed (Klieger, 1957; Bentz and Snyder, 1999; Mather, 2001; Kovler and Jensen, 2005). Since the efficiency of external curing decreases rapidly because of the densification of the hydrated cement paste, another type of water curing has been proposed: internal curing. This technology will be described in detail in Chapter 13. Here, only its most important features will be presented. It consists essentially of introducing into the mix a material that can store a significant amount of water as, for example, lightweight aggregates or superabsorbant polymers. This “hidden” water does not change the mixing conditions. It is only when chemical contraction creates a porosity that it can be sucked up by the hydrating cement paste to fill this porosity. In this way, no menisci are formed and no autogenous shrinkage is developed. It is essential that this hidden water can easily be sucked up by the cement paste and be present in such a quantity that it can fill all of the porosity created by chemical shrinkage. This is a very important technological breakthrough that will contribute to making low w/b concrete more durable and more sustainable. When autogenous shrinkage is controlled, the life cycle of concrete structures is lengthened.

6.8 Use of special waters

6.8.1 Seawater

Can seawater be used to make concrete? The answer is a highly qualified “yes”. While seawater should be avoided if at all possible, there is sometimes no other option. It can be used in plain (unreinforced) concrete, though its use will result in about a 20% loss in strength compared to concrete made with fresh water (Mindess *et al.*, 2003).

6.8.2 Washing water in a ready-mix plant

Increasingly, concrete producers are not being allowed to direct their washing waters (i.e. the water used to wash out a concrete mixer after discharging a load of concrete) into the sewer system; they thus have to recycle it into the concrete they are producing. The elimination of the solid particles contained in the wash water is not so difficult using specialized flocculants. However, the water that is recovered is not pure. It is rich in different ionic species and organic molecules or polymers derived from the preceding concrete batches. Too large an amount of these organic molecules or polymers can alter the properties of the next batch of concrete because they are still active.

In such a case, it is important to limit the volume of the wash water in the new concrete so that its dilution could reduce its action to a tolerable level. Its use is permissible in the less sophisticated “ordinary” concretes but should be avoided in “high-tech” concretes because it could complicate the achievement of the special properties which are required for such concretes.

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7 Superplasticizers

7.1 Introduction

It is not necessary here to devote a chapter to the use of admixtures in general. The interaction between Portland cement and most admixtures has already been thoroughly treated from both a theoretical and practical point of view in various specialized books, such as Dodson (1990), Rixom and Mailvaganam (1999), and many others. Admixtures such as air entraining agents, water reducers, accelerators, and retarders will continue to be used as they have been for many years in normal strength concrete without any changes. But this is not the case for superplasticizers. This chapter will thus be devoted exclusively to superplasticizers because:

- they are key components of durable and sustainable concrete;
- their behaviour in blended cements has not been studied thoroughly (Saric-Coric, 2001; Roberts and Taylor, 2007; Bédard, 2005); and
- the new family of polycarboxylates is still (2011) in development.

Of course, the use of superplasticizers is not new; it has been growing since the early 1970s, though not enough in our opinion. In the introduction of this book, it was shown that concretes having a low w/b ratio are more environmental friendly than the usual 25 to 30 MPa concretes. Their use when designing concrete structures results in a dramatic saving of materials and reduces significantly the greenhouse gas emissions associated with the use of concrete. However, a low w/b concrete cannot be made without the use of a superplasticizer.

From a practical point of view, the use of superplasticizers is inhibited mostly by the problems due to cement/superplasticizer compatibility and robustness, which are key factors for their successful use in the production of high-performance concrete. Experience has shown that not all cements are compatible with all commercial superplasticizers, and conversely that not all superplasticizers are compatible with a particular cement. In Chapter 5, we presented one reason to explain, at least partially, why this occurs. Compatibility and robustness problems are due to the fact that, at present, too many cement producers are obsessed by the cube strength rather

than by the rheology of their standard cement paste when they try to optimize the characteristics of their clinker and Portland or blended cements. The necessary requirements to optimize a binder become more and more contradictory when the w/c decreases. This is the principal source of the field problems encountered with the use of superplasticizers.

For many years, the superplasticizers available on the market were primarily polysulfonates, purified lignosulfonates (LS), polynaphthalene sulfonate (PNS), and polymelamine sulfonate (PMS); all of these work essentially by electrostatic repulsion. Their interactions with Portland cement have been studied extensively, so that it is now possible to guess, with some confidence, whether a cement/superplasticizer combination is likely to be compatible and robust.

Recently, a new family of superplasticizers, known as polycarboxylates or polyacrilates, has been developed. The dispersion of cement particles by polycarboxylates does not result from electrostatic repulsion but rather from steric repulsion, so that the knowledge acquired on polysulfonates is not applicable when dealing with polycarboxylates. This new family of superplasticizer is still in the development process, and the best molecular configuration of the polymers that have so far been tested is not definitively fixed.

Superplasticizers can be used to increase the slump at a given w/b (indicated by ① in Figure 7.1), to lower the w/b for a given slump (indicated by ② in Figure 7.1), or to increase the slump and decrease the w/b ratio at the same time (indicated by ③ in Figure 7.1).

7.2 Definitions

7.2.1 *Compatibility*

A cement/superplasticizer combination is said to be *compatible* when it does not result in a drastic slump loss a short time after good initial workability has been obtained. As stated above, not all cements react in the same way with a given superplasticizer and not all commercial superplasticizers react in the same way with a particular cement. It is now possible to explain such differences at least in the case of polysulfonates. It is even possible to give some general rules that can be used to guide the selection of a potentially compatible cement/polysulfonate combination. Some cement/polycarboxylate combinations have also been found to be compatible while others are not, but our knowledge in this area is not as well documented as in the case of polysulfonates.

7.2.2 *Robustness*

Generally speaking, an industrial process is said to be *non-robust* when a small variation in one production parameter significantly affects the stability of the process and/or the quality of the final product.

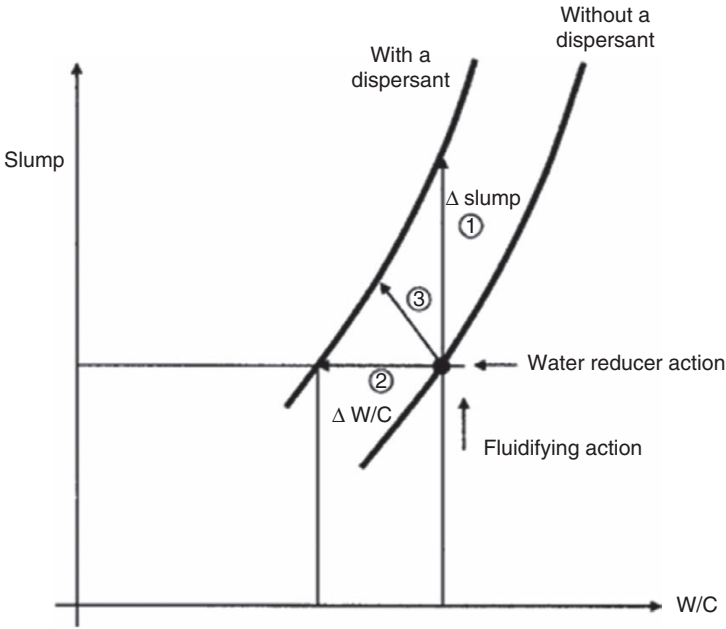


Figure 7.1 Different uses of a dispersant.

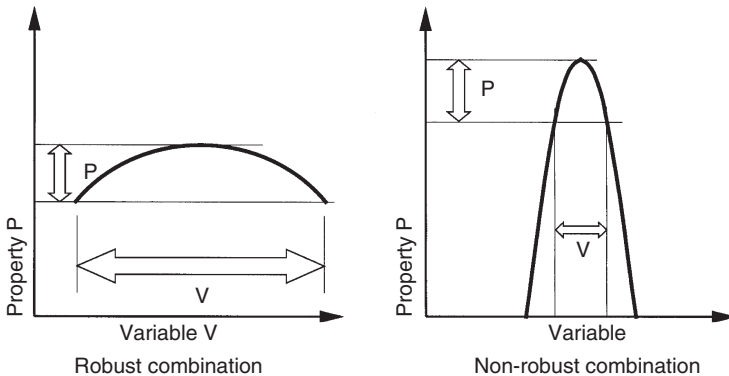


Figure 7.2 Notion of robustness. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

In contrast, an industrial process is said to be *robust* when a large variation in one parameter does not have much effect on the stability of the process; the larger the acceptable variation for these parameters, the more robust the process. Process engineers prefer a robust process rather than a more efficient but less robust one (Figure 7.2), and so do concrete producers.

7.3 Dispersion of cement particles

All commercial cements have in common a technological weakness that decreases their binding efficiency: when they are mixed with water they have a strong tendency to flocculate. It is very easy to demonstrate that without a superplasticizer cement particles flocculate when put in contact with water: it is only necessary to place 50 g of cement in a 1-litre flask full of water, agitate it and let it settle. After 5 to 15 minutes, it is possible to see the formation of large cement flocs that quickly settle to the bottom of the flask. At the end of the sedimentation process, the volume of flocculated cement is much larger than the initial volume of the dry powder (Figure 7.3).

When 5 cm³ of superplasticizer is added to the flask, the cement particles no longer flocculate, but rather settle according to Stokes' law. Usually, 24 hours later, most of the cement particles have reached the bottom of the flask. The coarse particles can be seen at the bottom with the finest ones at the top of the cement layer. The final volume of the settled particles is almost equal to or even less than the initial volume of the dry cement. Superplasticizers are simply chemicals that disperse cement particles. In this chapter, they will also be called *dispersants* in order to focus on their real physical action on cement particles rather than on their effects on concrete rheology. Water reducers are simply less efficient dispersants than superplasticizers.

7.3.1 Why do cement particles flocculate?

Cement particles flocculate when they come into contact with water for two reasons:

- *First*, they have highly electrically charged surfaces with both positive and negative sites; and
- *Second*, water molecules are highly polar so that they can act as electrical dipoles. The centres of gravity of the positive charges H⁺ and of the negative charge O²⁻ in a water molecule are distinct, as already seen in Figure 6.1. Therefore, a water molecule can be considered as an electrical dipole. In a cement floc water molecules can bond quite strongly to adjacent cement particles that have opposite charges. Moreover, a certain amount of water is trapped within these flocs, as seen in Figure 7.4. This water does not contribute to the rheology of the mixture, so that it is necessary to use more water to obtain the desired workability. It is this extra water that decreases concrete strength, durability, and sustainability.

7.3.2 Why are cement particles highly charged?

Portland cement clinker is a mixture of four main minerals: di- and tricalcium silicates (C₂S and C₃S), tricalcium aluminate (C₃A), and tetracalcium

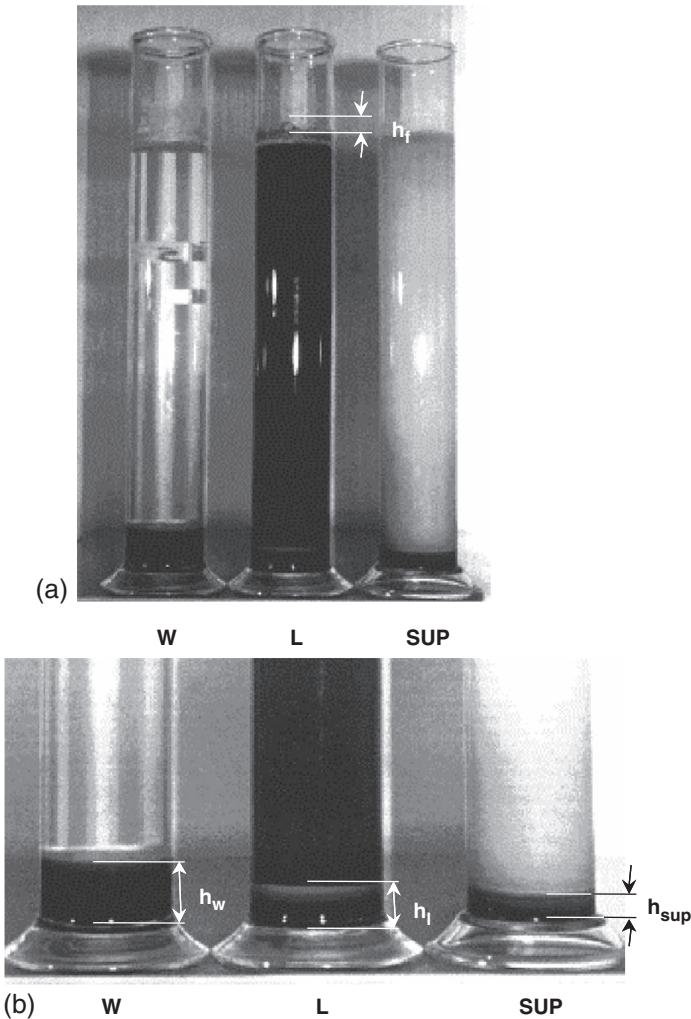


Figure 7.3 Flocculation of cement particles (W) in water; (L) in water + water reducer; (SUP) in water + superplasticizer. Reproduced from *High Performance Concrete*, Aitcin 1998. (Courtesy of Taylor & Francis).

aluminoferrite (C_4AF). When clinker nodules are ground to transform them into Portland cement, these minerals are fractured and appear on the surface of the cement particles. Figure 7.5 shows the type of surface charges present on the elementary cell of each of the four principal minerals found in Portland cement: C_3S has mostly negative surface charges, while C_2S , C_3A , and C_4AF have mostly positive surface charges. Consequently, cement particles have more negative surface charges than positive charges

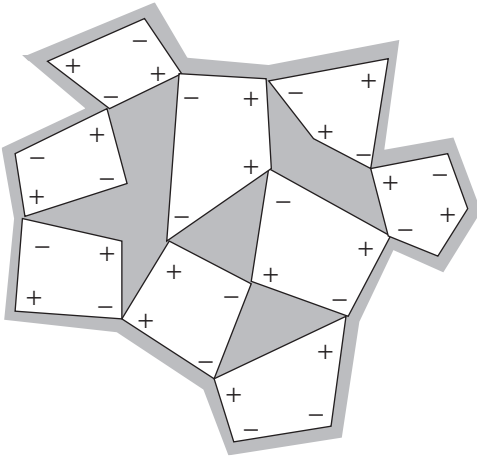


Figure 7.4 Flocs of cement particles. Reproduced from *High Performance Concrete*, Aïtcin 1998. (Courtesy of Taylor & Francis).

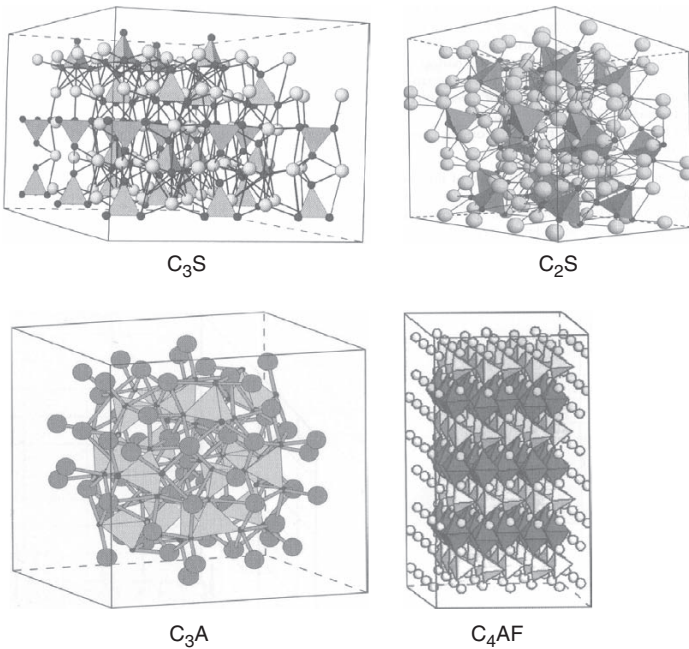


Figure 7.5 Crystal structure of the four principal minerals found in Portland cement clinker. Reproduced from Bensted and Barnes, 2002. (Courtesy of Taylor & Francis).

because C_3S is usually the most abundant phase in Portland cement, and the most highly charged.

7.3.3 How can we eliminate flocculation?

There are basically two ways to eliminate flocculation. The first consists of using an organic polymer that covers all of the cement particles with a single type of electrical charge so that they repel each other. As C_3S is the most abundant mineral in Portland cement, it is better to use a polyelectrolyte that neutralizes positive charges, as seen in Figure 7.6, so that all cement particles are negatively charged overall.

The second way is to cover all cement particles with a polymer whose free end is neutral from an electrical point of view, so that it acts basically by steric repulsion; this is what polycarboxylates do, as shown in Figure 7.7.

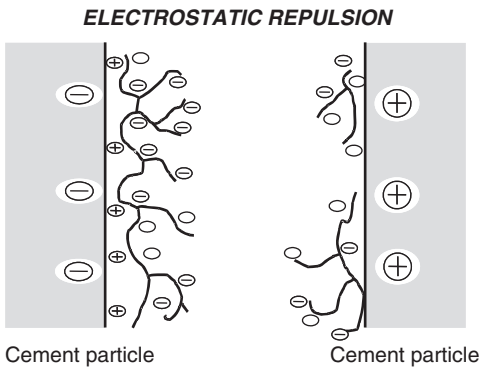


Figure 7.6 Electrostatic repulsion. After Jolicoeur *et al.* (1994). (Courtesy of Pierre-Claver Nkinamubanzi).

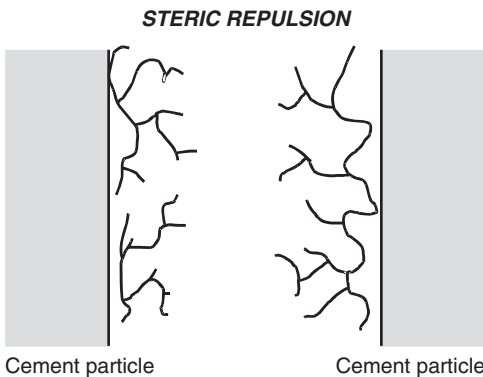


Figure 7.7 Steric repulsion. After Jolicoeur *et al.* (1994). (Courtesy of Pierre-Claver Nkinamubanzi).

In reality, the mode of action of these two families of superplasticizer is not so clearly differentiated; polysulfonates provide some steric repulsion and polycarboxylates some electrostatic repulsion.

7.4 Compatibility and robustness

7.4.1 *Why are some cement/superplasticizer combinations compatible and robust while others are not?*

Experience has shown that not all cement/superplasticizer combinations are equally efficient in dispersing cement particles. Some combinations are *compatible*; that is, they maintain concrete slump long enough to place it easily in the field. However, in some cases, even when the superplasticizer dosage is increased, it is impossible to maintain the initial slump for more than 15 minutes. Such a combination is said to be *incompatible*. Experience has also shown that some cement/superplasticizer combinations are said to be *robust* because small variation in the cement, water, and superplasticizer dosage have little effect on the rheological behaviour of the concrete. On the other hand, in other combinations, only a slight variation in the cement, water, or superplasticizer dosage has a catastrophic effect on concrete rheology, resulting in a drastic loss of slump, or segregation; these combinations are said to be *non-robust*. As stated earlier, from a practical point of view, it is much safer to work with a slightly less efficient combination that is robust, than with a very efficient combination that is not robust at all.

These different behaviours of cement/superplasticizer combinations are due to the fact that not only do the main phases of the Portland cement interact with superplasticizer molecules, but the minor components, such as calcium and alkali sulfates, also interact, as shown in Figure 7.8. Since clinkers are made from natural products and fuels containing different amounts of impurities, their phase composition and the composition of their minor components varies from one clinker to another. It is thus impossible to make exactly the same Portland clinker in two different plants; indeed, it is quite difficult to produce the same clinker all year round even in the same kiln. Both the impurities of the raw material and the fuel, as well as the thermodynamic conditions within the clinkering zone, influence the rheological and binding properties of Portland cement clinker.

In addition, two clinkers might have the same phase composition but not the same grindability, because the thermodynamic conditions existing in the kiln when they were formed were not exactly the same. Consequently, after grinding, the morphology of the cement particles could be different. Figure 7.9 represents schematically four clinkers having the same phase composition but different morphologies. A phase difference on the surface of the cement particles is very important from a practical point of view, because initially superplasticizer molecules act only at the surface of cement particles, regardless of what lies beneath. In the cases shown in Figure 7.9,

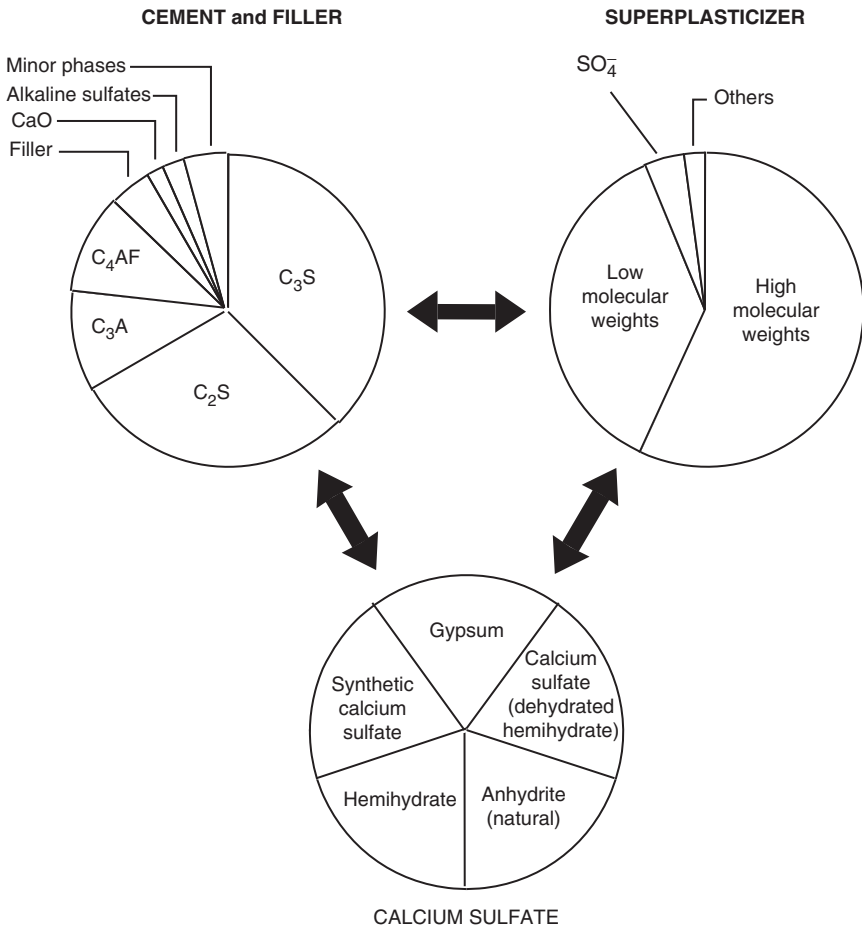


Figure 7.8 The complexity of the interaction of cement, polysulfonate, and calcium sulfates. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

superplasticizer molecules act as if the cement particle were composed exclusively of C_3S or C_3A , or a mixture of C_3S and interstitial phase, depending on the morphology of the cement particles.

One last point that does not favour the compatibility between polysulfonates and some cements is that too many specifiers are convinced that the alkali/aggregate reaction is the most dangerous and common concrete disease and that it must be avoided at almost any cost. That is why many specifiers systematically specify low alkali cement even when not a single potentially reactive aggregate exists in their area. Such an attitude is also favoured by certain cement producers who have the opportunity of

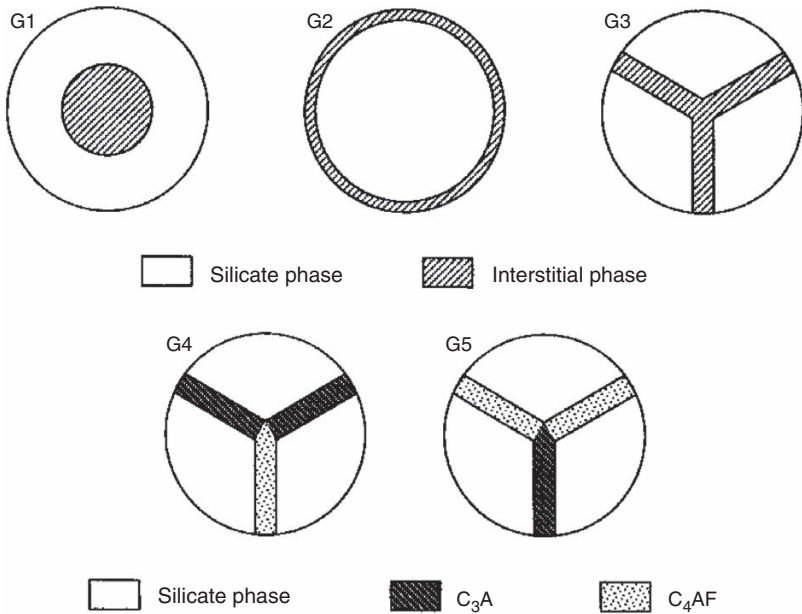


Figure 7.9 Hypothetical cement particles.

exploiting raw materials having low alkali contents; they base the marketing of their Portland cement on its very low alkali content. However, it is not always true that a Portland cement with an alkali content of 0.2% is safer than one with a content of 0.6% (the maximum limit set to qualify a cement as a low alkali cement). But, by using a cement with a very low alkali content, the action of the very soluble alkali sulfates that are so useful in controlling C_3A hydration is eliminated, so that these cements are very sensitive to slump problems. In reality, the alkali/aggregate reaction is a very minor cause of concrete deterioration compared to the use of a high w/c ratio and bad curing procedures. There are currently other efficient ways of avoiding alkali/aggregate reactions besides specifying a low alkali cement as, for example, the use of supplementary cementitious materials. Portland cement having an alkali content of about 0.8%, half of which is rapidly soluble (alkali sulfates) would be a preferable cement.

7.4.2 *How do we evaluate cement/superplasticizer compatibility and robustness?*

As cement/superplasticizer compatibility and robustness depend on certain very specific properties of the cement and the superplasticizer, as well as on their conditions of use, it is not so easy to predict precisely the actual

behaviour of a particular cement/superplasticizer combination. However, as a result of the research carried out over the past 15 years on the interaction of polysulfonates with Portland cement, it is possible to estimate with a good degree of certainty the kind of behaviour that can be expected.

Cement/superplasticizer interaction can be studied using two simple comparative tests: the mini-slump test and the Marsh cone test (Figures 7.10 and 7.11). These tests have been described in detail in the literature (Aïtcin, 1998). It is better to perform these tests on a 0.35 w/c paste in both a static mode (the mini-slump test) and in a dynamic mode (the Marsh cone test) at a constant temperature.

When performing these tests, it is useful to use a reference cement and a reference superplasticizer and compare the combination under study to

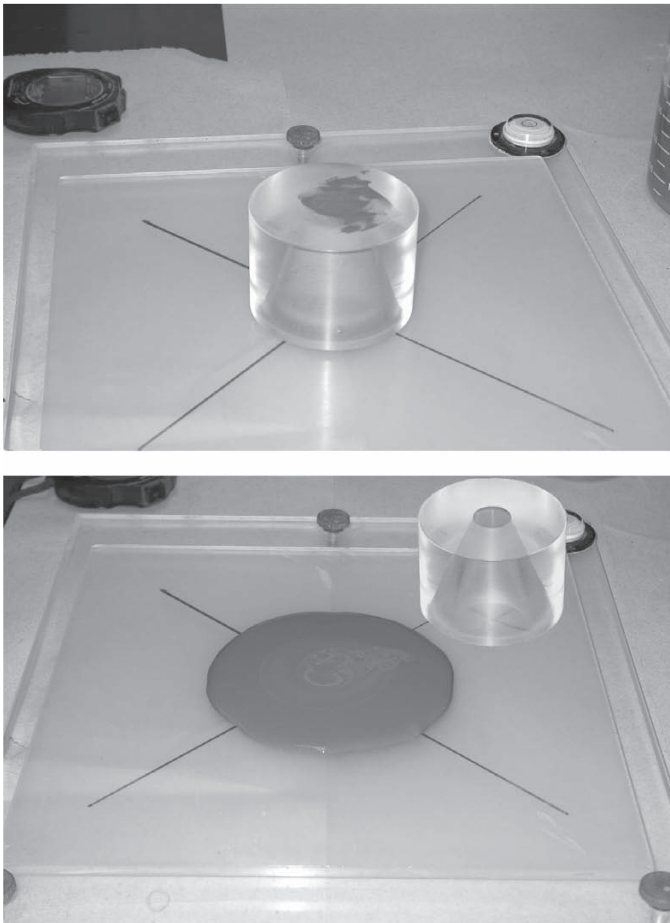


Figure 7.10 Mini slump testing. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).



Figure 7.11 Marsh cone test. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

that of these reference products. Of course, the selection of the reference products is critical; they must be produced by cement and admixture plants that control their products very tightly. An in-depth study of these two reference products must be conducted in order to interpret the difference between the products being studied and the reference products.

Using the mini-slump and Marsh cone tests, it is possible to determine what is called the *saturation point* of the superplasticizer, as shown in Figure 7.12. A higher superplasticizer dosage does not significantly improve the rheology of the grout; it begins to retard cement hydration instead. A much higher dosage can result in the entrainment of an excessive amount of large air bubbles (the *champagne* effect). These rheological tests must be performed during a period of 1½ hours to follow the behaviour of the combination over a period of time corresponding to the transport and placing of the concrete. It is also important to maintain the grout at the same temperature throughout the experiment.

If the saturation point dosage at 10 minutes is low and does not increase too much at 1½ hours, and if the flow/dosage curve is smooth, the combination is said to be compatible, economical, and robust as shown in Figure 7.13. On the other hand, if the saturation point dosage at 10 minutes is high and even higher after 1½ hours, and if the flow/dosage curve presents a well-defined break point separating a steep part for the lower dosages and

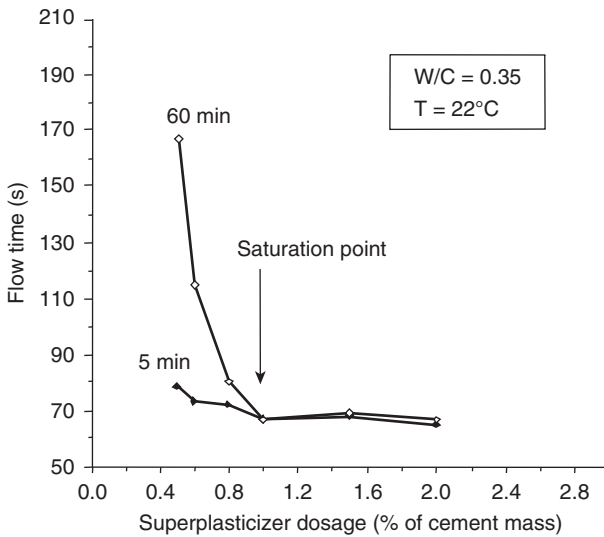


Figure 7.12 Flow time as a function of the superplasticizer dosage. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

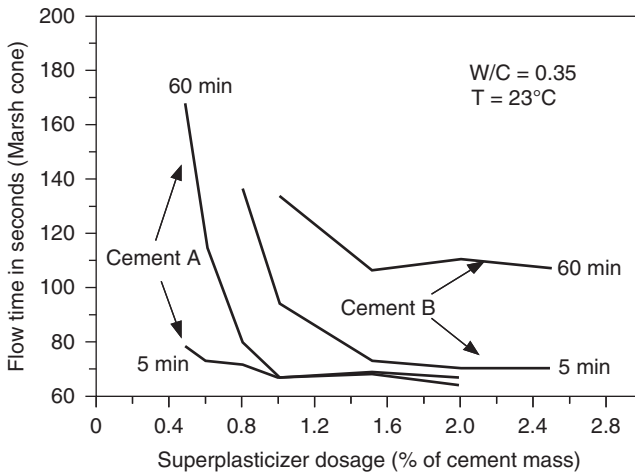


Figure 7.13 Examples of flow time at 5 and 60 minutes. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

a quite horizontal part for the higher dosages, the combination is said to be non-compatible, non-economical, and non-robust.

7.5 Utilization of superplasticizers

Superplasticizers can be used either:

- to increase concrete slump,
- to decrease the w/b ratio for a given slump, or
- to decrease the w/b ratio and increase the slump at the same time.

The first use is typical in the precast industry or when making self-levelling concrete. The third use is exploited when making low w/b concretes.

With compatible combinations it is possible:

- to increase the slump up to 180 to 200 mm without any sign of segregation in mixtures containing about 300 kg of cement per m^3 . When the cement dosage is lower it is better to use a mid-range water reducer that is slightly less efficient but more robust;
- to make 0.35 w/b concretes having slumps as high as 220 to 240 mm. In some cases, it is even possible to make 0.30 w/b flowing concrete. In such applications, the substitution of a part of the Portland cement clinker by one or several cementitious materials can be advantageous from a rheological point of view.

For a w/c ratio lower than 0.40 a small amount of silica fume or metakaolin is useful to fight segregation when increasing the slump. For a w/c ratio lower than 0.35, 7% to 8% silica fume helps to obtain both a good rheology and a high strength. Recently, it has been found that in quaternary blended cements (Portland cement clinker, slag, fly ash, and silica fume) the amount of silica fume can be decreased to 4% to 5%.

With a w/b ratio of 0.35, it is possible to make flowing concretes having a compressive strength between 65 and 85 MPa. To obtain a 100 MPa concrete, it is necessary to lower the w/c ratio to about 0.30. In this case, it is important also to check the compressive strength of the coarse aggregate. To make even stronger concrete, on some occasions it has been found possible to lower the w/c ratio in the range of 0.25 to 0.30. In one particular case, the first author was able to make a flowing concrete having a w/c of 0.19 and a compressive strength of 150 MPa using a particularly strong aggregate.

There also exist other ways of complementing the improvement of the rheology of low w/b ratio concretes that can be used in conjunction with superplasticizers. Entrained air is particularly recommended in low w/b ratio concretes because it decreases the shear resistance of the fresh concrete. Of course, it decreases concrete strength but it is easy enough to increase the strength by further lowering the w/b ratio. The use of

entrained air is described in more detail in Chapter 10. Viscosity modifiers are also commercially used in self-levelling low w/b concrete to improve the flowability of the concrete.

7.6 Commercial superplasticizers

Commercial superplasticizer can be made either from a pure base or from a mixture of a pure base and other admixtures. These other admixtures are supposed to “improve” the efficiency of the base with certain types of cements. In some cases, admixture companies add a small amount of retarder, accelerator, defoaming agent, etc. Sometimes, in order to decrease production costs, admixture companies substitute a part of the superplasticizer base by a less expensive water reducer. A less efficient and less expensive water reducer is also used to produce what is called a midrange water reducer that is used when the w/b is not too high (0.40 to 0.50).

In spite of these variations in the composition of commercial superplasticizers, it is useful to focus on the action of pure bases on pure Portland cement to better understand the mode of action of the principal polymers used as superplasticizers. This basic knowledge is very useful when the efficiency of a particular cement/superplasticizer combination has to be studied. It also helps during the necessary discussions with the admixture and cement producers to facilitate the production of low w/b concretes. It is a great pity that currently, concrete producers do not try to impose their rheological needs on the admixture and cement companies more vigorously!

7.7 Polysulfonates

Currently, three different types of polysulfonates are used as bases for commercial superplasticizers:

- lignosulfonates
- polynaphthalenes
- polymelamines.

Historically, the first patented dispersing agent was a polynaphthalene sulfonate (PNS), but commercially, lignosulfonates have been used since the 1950s. Then, the powerful dispersive properties of polynaphthalene sulfonate were rediscovered in Japan, while polymelamine sulfonate (PMS) was patented in Germany. Polysulfonates are efficient dispersive agents that are not very expensive to produce, but their SO_3^- terminations (Figure 7.14) can react with C_3A , a role normally reserved for the SO_4^{2-} ions provided by the dissolution of alkali and calcium sulfates. This side reaction can significantly decrease polysulfonate efficiency.

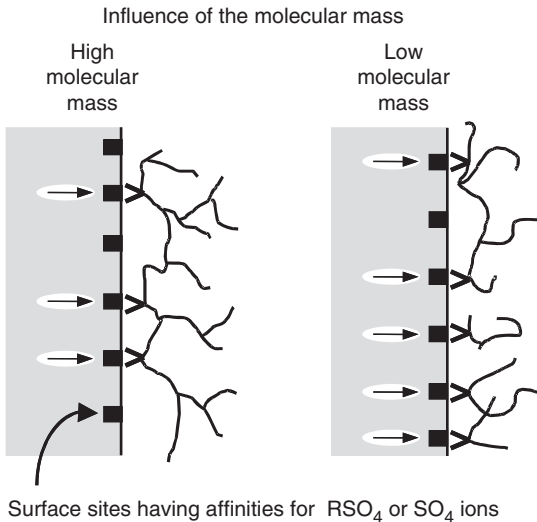


Figure 7.14 Inhibition of reactive sites. After Jolicoeur *et al.* (1994). (Courtesy of Pierre-Claver Nkinamubanzi).

7.7.1 Lignosulfonates

For a long time and still today, many water reducers were based on lignosulfonate. This is a very inexpensive dispersant, being a by-product of paper mills operating with the bisulfite process. In this process, the lignin that glues the cellulose fibres together in the wood is dissolved using a hot bisulfite liquor. After this treatment, the cellulose fibres are recovered while the lignin and all the undesirable chemical products found in wood (sugars, surfactants, and so on) are eliminated as a brown liquid that can be used as a water reducer. Sometimes, this liquid is treated to extract the sugars and surfactants that interact with the hydration process: the lignosulfonate is then said to be beneficiated.

Due to their molecular configuration (Figure 7.15), lignosulfonates are not very efficient dispersants; their use usually results only in a 5% to 8% water reduction. Exceptionally, when they are refined, some lignosulfonates can reduce the amount of water necessary to obtain a given workability by 10% to 15%.

The dispersive properties of lignosulfonate are affected by the particular chemical process, the species of the trees used, the mixture of these species, the time of the year when the trees were felled, the time span between their felling and their use in the paper plant, and so on. The quality of commercial lignosulfonates is also affected by their treatment (or not) to eliminate sugar and surfactants.

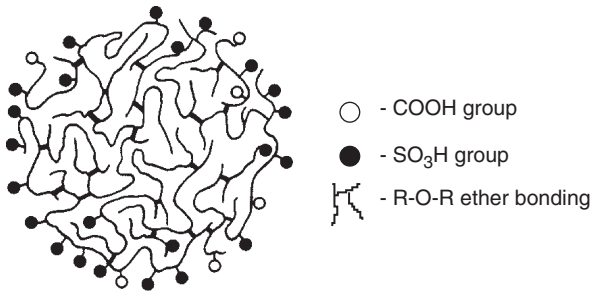


Figure 7.15 Micelle of lignosulfonate. Reproduced from Rixom and Mailvaganam, 1999. (Courtesy of Taylor & Francis).

As the bisulfite process is increasingly being abandoned by the pulp and paper industry because of its inefficiency and the pollution it produces, soon only a few old paper plants will remain to supply lignosulfonate for the concrete industry.

Currently, most pulp and paper mills operate with a thermomechanical process that is much more efficient and less polluting. The lignin is no longer eliminated, but is included in the paper. Moreover, as polynaphthalene, polymelamine, and polycarboxylates are much more efficient dispersants, it is not worthwhile spending too much space on lignosulfonates. Rather we will concentrate on the most efficient superplasticizers currently on the market.

7.7.2 *Polynaphthalene sulfonate*

Polynaphthalene sulfonates (PNS) are synthetic polymers used as dispersants in several industries, including the concrete industry, the gypsum industry, the pulp and paper industry, the leather industry, and the paint industry, among others. In each industry, a special configuration of the polymer has been found to be the most efficient (Figure 7.16).

Polynaphthalene sulfonate is synthesized by a simple chemical process from five basic products: naphthalene, sulfuric acid, formaldehyde, soda, or lime. The first step of the process involves the sulfonation of the naphthalene rings. Then, the sulfonated naphthalene rings are polymerized by condensation using formaldehyde. When the desired degree of polymerization has been obtained, the polymerized sulfonic acid is neutralized, usually with soda, but sometimes with lime when it is necessary to obtain a superplasticizer free of alkalis and chlorine. (When using lime, it is necessary to add a filtration step to eliminate excess lime.) This process is described in detail in *High Performance Concrete* (Aitcin, 1998).

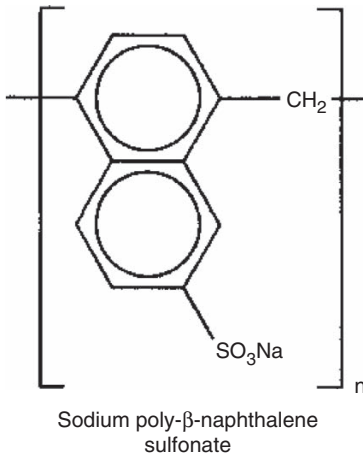


Figure 7.16 Polynaphthalene sulfonate.

The key fabrication parameters are:

- the degree of sulfonation (about 90% in the best case), and the number of β sites sulfonated (about 90% in the best cases);
- the degree of polymerization (about 10 for concrete superplasticizers); and
- the amount of residual sulfates after the neutralization process.

The efficiency of a polynaphthalene superplasticizer depends on the extent to which the producer controls these fabrication parameters. Moreover, some superplasticizer plants use quite pure raw materials, while others use cheaper raw materials that are by-products of other industries to decrease production costs. Consequently, not all commercial polynaphthalene sulfonate bases available on the market possess the same dispersive efficiency. A cheaper polynaphthalene sulfonate is not always the most economical one because its optimum dosage can be significantly higher than that of a more expensive but more efficient one.

Polynaphthalene sulfonate is usually sold as a sodium salt in liquid form having a solid content of about 41% (active polymers and residual sulfates). It is available in powder form, and as stated previously, also exists in the form of its calcium salt. In liquid form, it is very sensitive to low temperatures; below 10°C, it begins to crystallize and rapidly loses its efficiency.

7.7.3 Polymelamine sulfonate

The dispersive properties of polymelamine sulfonate (PMS) were discovered in Germany at the beginning of the 1970s (Figure 7.17). While its patent was

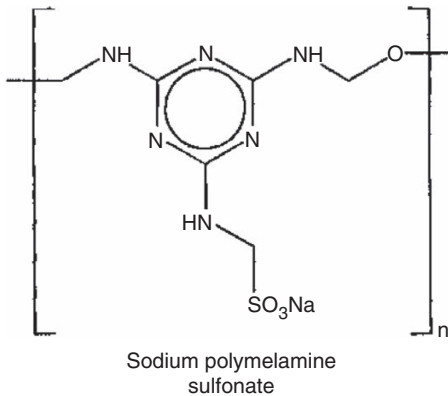


Figure 7.17 Polymelamine sulfonate.

in force, SKW was the only supplier of MelmentTM. Melment was initially a milky solution having a solid content of 21%, but it was later sold at 31% and even 41% solid contents.

Now, polymelamine sulfonate can be produced by any chemical company, and so the quality of commercial products is more variable, depending on the purity of the raw materials used and the degree of control during the polymerization process.

7.7.4 *Compatibility and robustness of polysulfonates*

Polysulfonates are able to disperse some Portland cements very efficiently and maintain a high slump for 1½ hours, while they perform poorly with other Portland cements. Some combinations are compatible, others incompatible; some combinations are robust, others are not. After superplasticizers had been key components of low w/b concretes for approximately 10 years, the compatibility and robustness of polysulfonates was studied in depth. This research effort resulted in the birth of a new science: the science of admixtures.

Polysulfonates disperse cement particles primarily by electrostatic repulsion, but through their SO₃ termination they can also react with C₃A. When a Portland cement is rich in C₃A, in its very reactive (cubic) form, as well as when the calcium sulfate added during grinding does not dissolve rapidly (natural anhydrite, gypsum) and the cement has a low alkali sulfate content (low alkali cement, white cement), a certain amount of polysulfonate is fixed by the C₃A. It is thus diverted from its dispersing function, and so the initial slump can be lost rapidly. Of course, the specific surface area of the cement is a very important factor because the action of polysulfonates

is surficial: the finer the cement, the higher the specific surface area and the larger the surface to be neutralized.

Since the polysulfonate's functional SO_3 group can react with C_3A and thus be diverted from its dispersive function, it is better to introduce polysulfonate as late as possible during mixing. Enough time should be given for the SO_4^{2-} ions released by the alkali sulfates and the different forms of calcium sulfate introduced during final grinding of the cement to react with the C_3A sites present on the surface of cement particles to form ettringite. When the polysulfonate is introduced at a later stage, little of it will react with C_3A , and its dispersive action will be better exploited.

It is not always possible to delay the introduction of the superplasticizer, particularly in low w/b mixtures. In such cases, a “sacrificial” amount of water reducer or superplasticizer can be added to the concrete at the beginning of the mixing process. The dispersive function of this first dosage of polysulfonate does not last very long, because most of it rapidly reacts with the C_3A . When a second amount of polysulfonate is then introduced just before the end of mixing, it will work almost exclusively as a dispersant. In the concrete industry, this is known as the “double introduction” technique.

As a result of the large amount of research carried out in the 1990s on the mode of action of the polysulfonates in Portland cement, it was found by Kim (2000) that the most compatible and robust cement/polysulfonate combinations were obtained with cements having the following characteristics:

- a low C_3A content (6% to 8%);
- sufficient soluble alkali sulfates (0.4% to 0.6%);
- the most rapidly soluble forms of calcium sulfates (hemihydrate or so-called soluble anhydrite); and
- a moderate fineness (lower than $400 \text{ m}^2/\text{kg}$).

At the other end of the spectrum, the worst cements were those with:

- a high C_3A content (8% to 12%);
- a low alkali-equivalent content, below 0.6%;
- the less rapidly soluble forms of calcium sulfate (natural anhydrite, gypsum); and
- a high fineness.

Consequently, the use of polysulfonates is usually not recommended with white cements, except when they can be placed very rapidly, because white cements are rich in C_3A (over 12%) and low in alkalis. In this case, due to its milky colour, the use of polymelamine is recommended because polynaphthalene's brown colour gives a slightly beige colour to concrete.

Polynaphthalenes with a high degree of sulfonation in the β (noon) position are the most efficient. Their optimum degree of polymerization

has been found to be around 10 and their degree of branching should be low (low viscosity).

Polysulfonates are not very expensive: their production cost is not directly linked to the cost of petroleum but rather to that of coal. Their use makes it easy to entrain air and they are robust. However, polynaphthalene's performance is affected by the temperature of the fresh concrete. Polynaphthalenes lose some of their efficiency when the temperature of the fresh concrete is below 10°C, which is not the case for polymelamine. Lignosulfonate and polynaphthalene somewhat retard setting and hardening, but not polymelamine.

7.7.5 *Commercial polysulfonates*

Very often, commercial superplasticizers contain other admixtures that are mixed with a pure base to "improve" their efficiency with certain specific cements or simply to decrease their unit cost. Some commercial superplasticizers are in fact a more or less complex "cocktail" containing some lignosulfonate, some retarder, some accelerator, some air entraining agent, etc. In one case, at least five other admixtures were mixed (in small quantities) with a pure polynaphthalene base.

The use of a specific trade name to designate a superplasticizer or an admixture in general, does not mean that it has a specific chemical composition and that it is always made with the same raw materials. Admixture companies base their branding more on the specific action of their products on concrete rather than on their chemical composition. For instance, during the course of one single year, an air-entraining agent was found to be based on three different chemicals without changing its name, but it remained an excellent air-entraining agent, providing in all three cases a very low spacing factor.

Polysulfonate-based superplasticizers are commonly used by the North American ready-mix industry because there are few incompatible combinations, except perhaps with some low alkali cements. Most American clinkers are so-called Type I/II clinkers containing 6% to 8% C₃A. Moreover, most of the concrete used in the northern United States and in Canada is air-entrained and it is easy to develop a stable network of air bubbles having a low spacing factor with polysulfonates. In addition, the precast industry in North America is fairly small, and has little influence on overall superplasticizer consumption.

The situation is totally different in Europe:

- generally speaking, the European ready-mix industry uses less admixtures than in North America;
- the clinkers produced are richer in C₃A (8% to 12%) so that with polynaphthalene, incompatible and non-robust combinations are more frequent;

- the precast industry, which is quite strong, is the largest user of superplasticizers and its choice influences admixture consumption; and
- entrained air is not as systematically used as in North America, so that it is not an essential selection criterion.

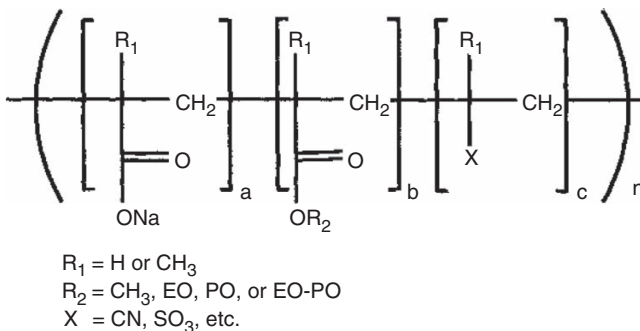
7.8 Polycarboxylates

Polycarboxylates constitute the most recent family of superplasticizers. As mentioned previously, they disperse cement particles essentially by steric repulsion rather than by electrostatic repulsion as is the case with polysulfonates. The functional group of these polymers is their carboxylic termination, COOH^- (Figure 7.18). Polycarboxylates are also broadly used as dispersing agents in detergents and various aqueous-based formulations and processes (Spiratos *et al.*, 2003).

As the configuration of polycarboxylates is more complex than that of polysulfonates, the admixture industry is still trying to determine the key parameters of the polymers' configuration that affect their efficiency in dispersing cement particles.

The first polycarboxylates used as dispersants in concrete were found to be very efficient at a dosage that was often half that of the most efficient polysulfonates. However, some of these early polycarboxylates were found to entrain an excessive amount of air so that an air-detraining agent had to be mixed with them.

From a chemical point of view, a polycarboxylate is composed of a main chain (backbone), on which are grafted two side chains, as represented in Figure 7.19 (Ohta *et al.*, 2000). Because they do not contain a sulfonic termination that could react with active C_3A sites, it was thought that their use would eliminate compatibility problems, which is unfortunately not the case. Some cement/polyacrylate combinations are reported to be



Polyacrylate copolymer

Figure 7.18 Polycarboxylate superplasticizer.

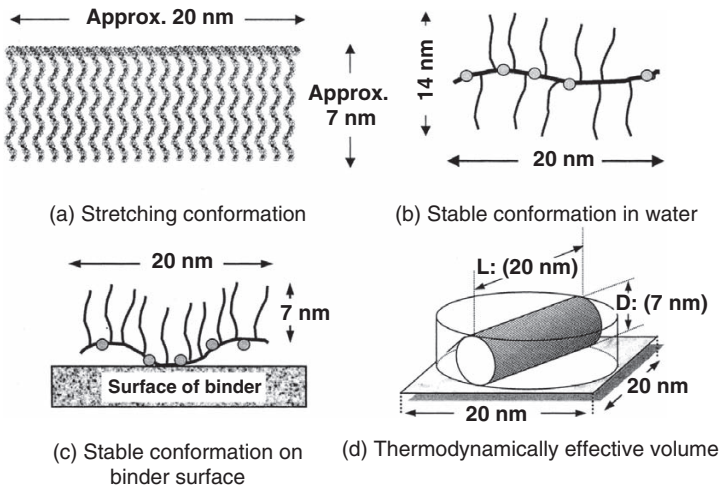


Figure 7.19 Effects of the configuration of polycarboxylates. From Ohta *et al.* (2000). With permission of the American Concrete Institute, 38800 Country Club Drive, Farmington Hills, MI 48331, USA.

non-compatible, because some polyacrylate molecules can still react with C_3A through their carboxylic termination.

For a given cement, the polyacrylate dosage at the saturation point (on a solids basis) is usually one-third to one-half that of a polynaphthalene or polymelamine. This ratio is very different on a liquid basis because the solids content of polyacrylates and polysulfonates are usually different. Commercial polyacrylate superplasticizers are sold with a solids content of 15% to 40%.

On a solids basis, polyacrylates are much more efficient than polysulfonates but as their unit price is much higher, an assessment must be done in each particular case to find the more economical combination. As polyacrylates are less sensitive to C_3A content and reactivity, their use is very common in the European precast industry, which uses fine cements rich in C_3S and C_3A to obtain high early strength. Up to now, there exist some polyacrylates with which it is not easy to develop a stable network of air bubbles having a low spacing factor to protect concrete against freeze-thaw cycles and the action of deicing salts, so their use is not very popular in the North American ready-mix concrete industry.

7.9 Practical use of superplasticizers

7.9.1 Expressing the superplasticizer dosage

The dosage of a superplasticizer can be expressed in different ways. It is often given in litres of commercial solution per cubic metre of concrete,

which is the best way to express it at the batching plant. However, this is not the best way to express it in scientific papers or in a book because not all commercial superplasticizers have the same solids content and specific gravity. It would be a serious mistake to use the same liquid dosage of superplasticizer with a superplasticizer that has a different specific gravity and solids content. For example, melamine superplasticizers can be found as liquid solutions having a solids content of 22%, 33%, or 40% so that their respective dosages vary according to their solids content. Therefore, it is always better to give the superplasticizer dosage as the amount of solids that must be used expressed as a percentage of the mass of cement. This way of expressing the superplasticizer dosage is important when comparing the costs of different commercial superplasticizers. In fact, it is actually the amount of active solids that should be taken into account and not the total amount of solids because, first, not all the solids in a superplasticizer are active dispersing molecules and, second, commercial superplasticizers always contain some residual products. However, for the sake of simplicity, this last distinction will not be made in this book. In order to pass from a dosage expressed in litres per cubic metre to a dosage expressed in solids, it is necessary to know the specific gravity of the liquid superplasticizer and its solids content.

7.9.2 Superplasticizer specific gravity

According to Figure 7.20, the specific gravity, G_{sup} of the liquid superplasticizer is:

$$G_{sup} = M_{liq}/V_{liq} \quad (7.1)$$

if M_{liq} is measured in grams and V_{liq} in cubic centimetres.

7.9.3 Solids content

According to Figure 7.20, the solids content, s , of the superplasticizer is:

$$(M_{sol}/M_{liq}) \times 100 \quad (7.2)$$

Therefore, the total solids content M_{sol} contained in a certain volume of superplasticizer having a specific gravity equal to G_{sup} and a total solids content equal to s is:

$$M_{sol} = \frac{s \times M_{liq}}{100} = \frac{s \times G_{sup} \times V_{liq}}{100} \quad (7.3)$$

For example, 6 litres of a melamine superplasticizer having a specific gravity of 1.10 and a total solids content of 22% contain $0.22 \times 1.1 \times 6 = 1.45$ kg of solids, while 6 litres of a naphthalene superplasticizer having a specific gravity of 1.21 and a total solids content of 42% contain $0.42 \times 1.21 \times 6 = 3.05$ kg of solids.

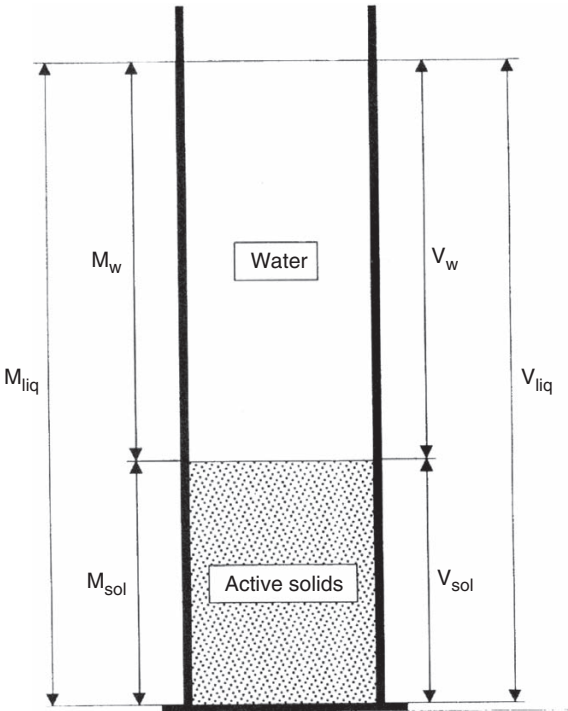


Figure 7.20 Schematic representation of a superplasticizer. Reproduced from *High Performance Concrete*, Aïtcin 1998. (Courtesy of Taylor & Francis).

7.9.4 Mass of water contained in a given volume of superplasticizer

When adding a liquid superplasticizer to a concrete mixture, it is necessary to take into account the amount of water added to the concrete in order to be able to calculate the exact water/binder ratio. This is done as follows. From Figure 7.20:

$$M_{liq} = M_w + M_{sol} \text{ or } M_w = M_{liq} - M_{sol}$$

Since from Equation (7.2):

$$M_{liq} = \frac{M_{sol} \times 100}{s} \quad (7.4)$$

Then:

$$M_w = \frac{M_{sol} \times 100}{s} - M_{sol}$$

This can be written as:

$$M_w = M_{sol} \left(\frac{100}{s} - 1 \right)$$

or:

$$M_w = M_{sol} \left(\frac{100 - s}{s} \right) \quad (7.5)$$

Replacing M_{sol} by its value in Equation (7.3):

$$M_w = \frac{V_{liq} \times s \times G_{sup}}{100} \times \frac{100 - s}{s}$$

and finally:

$$M_w = V_{liq} \times G_{sup} \times \frac{100 - s}{s} \quad (7.6)$$

When using proper units (g and cm³ and/or kg and litres), M_w and V_w are expressed by the same number so:

$$V_w = V_{liq} \times G_{sup} \times \frac{100 - s}{s} \quad (7.7)$$

Sample calculation: 8.25 litres of naphthalene superplasticizer with a specific gravity of 1.21 and a solids content of 40% have been used in a concrete in order to obtain the desired slump. What is the volume of water, V_w , that is added to the concrete when using a solution of a commercial superplasticizer? According to Equation (7.7), the amount of water is:

$$V_w = 8.25 \times 1.21 \times \frac{100 - 40}{100} = 6.0 \text{ l/m}^3$$

7.9.5 Other useful formulae

If d percent is the dosage of the solids of a superplasticizer suggested by the manufacturer to obtain a desirable slump in a concrete containing a mass, C , of cementitious material, the volume of liquid superplasticizer, V_{liq} having a specific gravity G_{sup} and a solids content s can be calculated as follows:

$$M_{sol} = C \times \frac{d}{100} \quad (7.8)$$

but from Equation (7.2):

$$M_{sol} = \frac{s \times M_{liq}}{100} \quad (7.9)$$

therefore:

$$\frac{s \times M_{liq}}{100} = C \times \frac{d}{100} \quad (7.10)$$

and replacing M_{liq} by its value deduced from Equation (7.1):

$$\begin{aligned} \frac{s \times G_{sup} \times V_{liq}}{100} &= C \times \frac{d}{100} \\ V_{liq} &= \frac{C \times d}{s \times G_{sup}} \end{aligned} \quad (7.11)$$

7.9.6 *Mass of solid particles and volumes needed*

If C is the total mass of the cementitious materials used in a particular mix and if d percent is the suggested dosage of solid particles, then the mass M_{sol} of solids needed is:

$$M_{sol} = C \times \frac{d}{100} \quad (7.12)$$

The volume of liquid superplasticizer needed to have M_{sol} of solid particles is calculated as follows. Replacing M_{liq} in Equation (7.1) by its value found from Equation (7.2):

$$V_{liq} = \frac{M_{liq}}{G_{sup}} \quad \text{and} \quad M_{liq} = \frac{M_{sol} \times 100}{s}$$

then:

$$V_{liq} = \frac{M_{sol} \times 100}{s \times G_{sup}} \quad (7.13)$$

7.9.7 *Volume of solid particles contained in V_{liq}*

From Figure 7.1, $V_{sol} = V_{liq} - V_w$. Replacing V_w by its value given by Equation (7.7):

$$V_{sol} = V_{liq} - V_{liq} \times G_{sup} \times \frac{100 - s}{100} \quad (7.14)$$

$$V_{sol} = V_{liq} \left(1 - G_{sup} \times \frac{100 - s}{100} \right) \quad (7.15)$$

7.9.8 Sample calculation

7.9.8.1 Example 1: Expressing a dosage in l/m^3 as a percentage of solids content

A high-performance concrete containing 450 kg of cement per cubic metre of concrete has been made using 7.5 litres of naphthalene superplasticizer. This naphthalene superplasticizer has a specific gravity of 1.21 and a solids content of 41%. What is the superplasticizer dosage expressed as the percentage of its solids content, to the mass of cement?

The mass of 7.5 litres of superplasticizer is:

$$7.5 \times 1.21 = 9.075 \text{ kg}$$

The solids content in this mass of superplasticizer is:

$$9.075 \times \frac{41}{100} = 3.72 \text{ kg}$$

The superplasticizer dosage is:

$$\frac{3.72}{450} \times 100 = 0.8\%$$

of the mass of cement.

7.9.8.2 Example 2: Passing from a dosage expressed as a percentage of solids to a dosage expressed in l/m^3

In a scientific paper, it is stated that a 1.1% superplasticizer dosage was used in a 0.35 water/cement ratio high-performance concrete containing 425 kg of Portland cement per cubic metre of concrete. A melamine superplasticizer having a specific gravity of 1.15 and 33% solids content was used in order to produce the mix. What is the amount of commercial solution that was used?

The amount of superplasticizer solids is:

$$\frac{425 \times 1.1}{100} = 4.675 \text{ kg}$$

This amount of solids is contained in $4.675/0.33 = 14.17$ kg of liquid melamine which represents $14.17/1.15 = 12.31$ of commercial solution.

7.10 Concluding remarks

Superplasticizers are already key components of modern concretes. Their use results in higher strength, higher durability, or higher fluidity. Moreover, their

appropriate use improves concrete sustainability, so that superplasticizer use will continue to increase in the future. The mode of action of polysulfonates and polycarboxylates is now well understood. Polysulfonates are well-established superplasticizers while polycarboxylates are still currently in the late stage of their development. However, the compatibility and robustness of the cement/superplasticizer combinations represents a technical challenge due the great differences observed in the rheological behaviour of cement/superplasticizer combinations.

The new science of admixtures has progressed very rapidly over the last 20 years but research still needs to be done, particularly in the case of polycarboxylates. It is to be hoped that in the near future, cement companies will market their cements with a list of compatible admixtures (or even incorporate them into their cement), as is already being done by a cement company in Pakistan.

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8 Natural aggregates

8.1 Introduction

This is not a very long chapter, not because aggregates are not an important component of concrete, but rather because most of the general rules that have long been in use will continue to apply. Aggregates will have to:

- be clean;
- have a grain size distribution within accepted gradation limits;
- be non-reactive with the cement alkalis. However, if they are potentially reactive, a special low alkali cement or a blended cement containing some fly ash or slag will have to be used.

As all of these issues are well-known, and have been extensively discussed in the literature; they will not be treated in this book. The reader may find in ACI 221 *Guide For Use of Normal Weight and Heavyweight Aggregates in Concrete*, in *Design and Control of Concrete Mixtures* (Kosmatka *et al.*, 2002) and in *Aggregates in Concrete* (Alexander and Mindess, 2005) all of the pertinent information that applies to the use of sand and coarse aggregate in usual concrete.

Only certain aspects of aggregate characteristics will be treated here in detail: first, the saturated surface dry state; second, the influence of the compressive strength and elastic modulus of the coarse aggregate on the corresponding values of concrete; and third, the partial substitution of normal sand by a saturated lightweight sand in low w/b concretes. We again insist on using the saturated surface dry (SSD) state of aggregates as the reference state for aggregates when making concrete.

In all text books, it is stated, first, that the water contained in the aggregate does not influence concrete rheology, which is still true. Second, it is stated that this water does not have any influence on the hydration of cement particles, which is also true except when using saturated lightweight aggregates as a replacement for an equal volume of natural or crushed aggregates (see Section 8.4). Low w/b concretes can rapidly develop high values of autogenous shrinkage at an age when the concrete is still very weak in tension. As a result, a low w/b concrete that does not receive special

water curing cracks immediately. Internal water curing is a very efficient way to fight the adverse effect of autogenous shrinkage in low w/b concretes, and the absorbed water stored within a saturated lightweight aggregate can participate in the cement hydration, thus avoiding the formation of menisci in the hydrating cement paste (see Chapter 13).

8.2 The SSD state: the reference state for aggregates

In Chapter 3, it was stated that the most difficult thing when making concrete is to keep track of all of the “hidden” water introduced into the mixer. The most difficult hidden water to take into account is the water contained in the aggregates, particularly in the sand. We have seen that a change of 2% in the total water content of a sand can represent a variation of about 16 litres of mixing water per m^3 , which represents about 10% of the effective water usually introduced into a mixer. In order to keep track of the variations in the water contained in the aggregates, it is important to define a reference state. By convention, in North America this reference state is called the saturated surface dry state or SSD state. This state is defined in ASTM C127 *Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate* and in ASTM C128 *Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate*. These two standard test methods describe in detail how to measure the SSD state.

8.2.1 *Measuring the characteristics of an aggregate in its SSD state*

Very briefly, for the coarse aggregate, the SSD state is obtained by soaking the coarse aggregate in water for 24 hours. The aggregate is then removed from the water, and the water is dried from its surface using an absorbent cloth. A coarse aggregate in its SSD state is shown schematically in Figure 8.1.

For the fine aggregate, by convention the SSD state is obtained when a small truncated sand cone is no longer held together by the capillary forces between the wet sand particles. Figure 8.2 illustrates the determination of the SSD state for sand. Figure 8.3 represents the determination of the SSD state for a coarse aggregate.

In both cases, the amount of water absorbed in the aggregate when it is in the SSD state, w_{abs} , corresponds to the aggregate absorption. This absorption is expressed as a percentage of the mass of the dry aggregate. In North America, concrete compositions are always expressed with the coarse and fine aggregates in their SSD states.

8.2.2 *Expressing SSD characteristics*

The SSD state of an aggregate is very important when calculating or expressing the composition of a particular concrete because it establishes

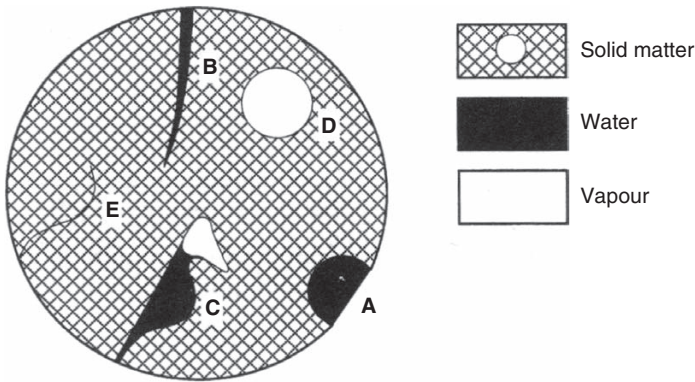


Figure 8.1 Coarse aggregate in its SSD state. Reproduced from *High Performance Concrete*, Aïtcin 1998. (Courtesy of Taylor & Francis).

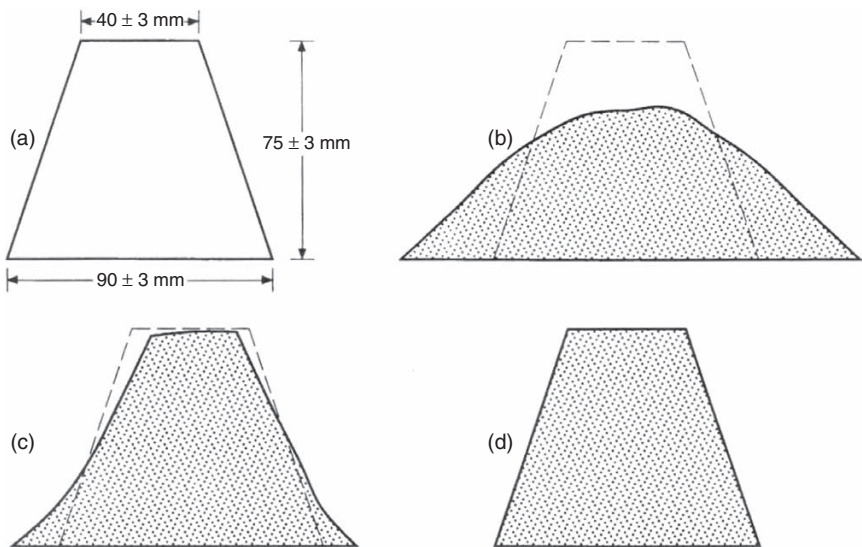


Figure 8.2 Determination of the SSD state for a sand: (a) the standardized minicone used; (b) sand having a water content below its SSD state; (c) sand in a SSD state; (d) sand having a water content above its SSD state. Reproduced from *High Performance Concrete*, Aïtcin 1998. (Courtesy of Taylor & Francis).

a clear differentiation between the two types of water typically found in an aggregate. The water absorbed within the aggregate does not contribute either to the slump of the concrete or to its strength because it does not normally participate in cement hydration. By contrast, the water trapped

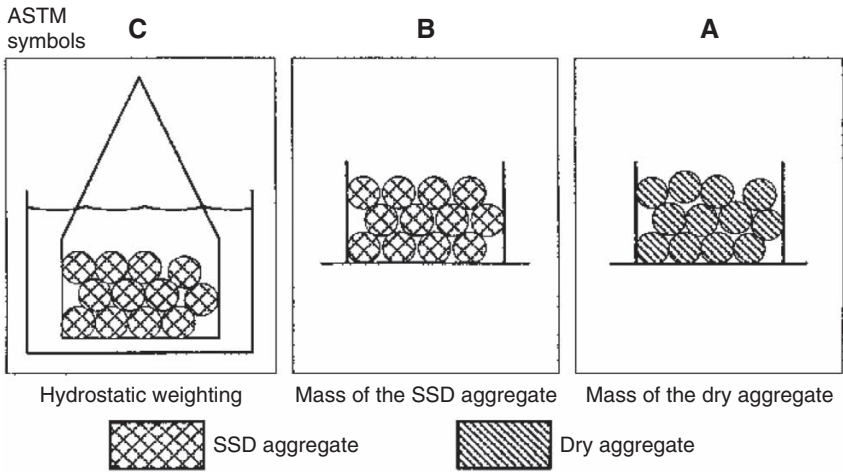


Figure 8.3 Schematic representation of the measurement of the absorption and SSD specific gravity of a coarse aggregate. Reproduced from *High Performance Concrete*, Aitcin 1998. (Courtesy of Taylor & Francis).

between aggregate particles by capillary forces influences both slump and hydration.

When the water content of the aggregate is lower than in its SSD state, the aggregate will absorb some water from the mix. This absorption of water by the aggregate increases the rate of slump loss of the concrete. On the other hand, when the water content of an aggregate is higher than its SSD state, the aggregate will bring water into the mix, as shown in Figure 8.4. If no special correction is made this water will increase the water–binder ratio and the slump. Therefore, the amount of mixing water introduced into the

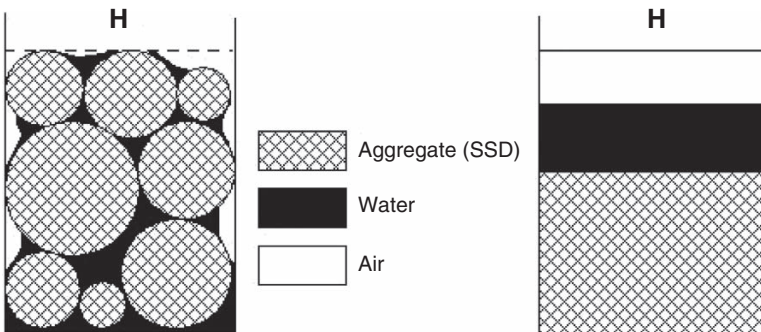


Figure 8.4 Schematic representation of a wet aggregate. Reproduced from *High Performance Concrete*, Aitcin 1998. (Courtesy of Taylor & Francis).

mixer has to be adjusted in order to keep the water–binder ratio and the slump constant.

The difference between the total water content of an aggregate, w_{tot} , and its water content in the SSD state, w_{abs} , is called the moisture content of the aggregate and is denoted by w_b . The moisture content of an aggregate can be negative if the total water content is lower than the water absorption. This occurs frequently in summer for coarse aggregates. For example, if 1000 kg of coarse aggregate having a water absorption, w_{abs} , of 0.8% is absolutely dry ($w_{tot} = 0$), this means that 8 litres of water can be absorbed by the coarse aggregate in the fresh concrete after mixing. This amount of water will undoubtedly have a significant effect on the slump loss rate because the absorption of these 8 litres of water is not instantaneous. On the other hand, when the same coarse aggregate has a total water content of 1.8% after a rain shower, then 10 litres of extra water are brought to the mix by the coarse aggregate. This represents a drastic increase of the amount of mixing water. If no correction is made in the mix composition, this can have a detrimental effect on the slump, the compressive strength, and the permeability of the concrete.

Therefore, in this book, the following definitions will be used. The total water content of an aggregate is defined as:

$$w_{tot} = \frac{\text{mass of the wet aggregate} - \text{mass of the dry aggregate}}{\text{mass of the dry aggregate}} \times 100 \quad (8.1)$$

With the ASTM conventions shown in Figures 8.3 and 8.4:

$$w_{tot} = \frac{H - A}{A} \times 100 \quad (8.2)$$

The absorption of an aggregate, w_{abs} , will correspond to:

$$w_{abs} = \frac{\text{mass of the SSD aggregate} - \text{mass of the dry aggregate}}{\text{mass of the dry aggregate}} \times 100 \quad (8.3)$$

or with the ASTM conventions shown in Figure 8.3:

$$w_{abs} = \frac{B - A}{A} \times 100 \quad (8.4)$$

The specific gravity of an aggregate in the SSD state is called the SSD specific gravity. Figure 8.3 illustrates schematically how to measure the SSD specific gravity of either coarse or fine aggregate. With ASTM notations, the SSD specific gravity of an aggregate is equal to:

$$G_{SSD} = \frac{B}{B - C} \quad (8.5)$$

The SSD specific gravity expresses how much denser than water an SSD aggregate is. The application of Archimedes' principle shows that G_{SSD} is the specific gravity that has to be used to calculate exactly the volume occupied by the aggregates in a concrete mix (Aïtcin, 1971).

For Portland cement or any supplementary cementitious material or dry powder, the specific gravity, G_c is equal to the mass of the dry material divided by its volume. The ASTM C128 standard test method explains how to measure this value practically.

$$G_c = \frac{A}{A - C} \quad (8.6)$$

8.3 Influence of the mechanical properties of the coarse aggregate on the corresponding concrete properties

It is wrong to believe that the mechanical properties of low w/c ratio concrete are simply those of a stronger concrete. It is just as wrong to consider that the mechanical properties of low w/c ratio concrete can be deduced by extrapolating those of usual concretes. Conversely, it would also be wrong to consider that none of these are related. Finally, it is also wrong to apply blindly to low w/c concretes the same relationships that were developed over the years linking the mechanical properties of a usual concrete to its compressive strength. It is better to examine the influence of the fundamental mechanisms linking concrete microstructure to the macro-structural property under evaluation.

Certainly, there are cases when low w/c ratio concrete behaves simply as a stronger concrete, but there are other instances when low w/c ratio concrete behaves quite differently. The differences observed in the mechanical behaviour of low w/c ratio concrete and usual concrete result from the fact that their microstructures are totally different, particularly in the transition zone between the coarse aggregates and the cement paste. When an external load is applied to a low w/c ratio concrete it does not develop the same stress field and the material does not behave in the same way.

The high water–binder ratio of usual concretes is manifested in micro-structural terms by a porous microstructure, especially around the coarse aggregates where a more or less thick interfacial transition zone (ITZ) with a high porosity can be observed. The higher the water–binder ratio, the more porous the cement paste microstructure and the thicker the transition zone. Therefore, in a usual concrete there is a limited degree of stress transfer between the hydrated cement paste and the aggregate, particularly at the coarse aggregate level. In these concretes, the mechanical properties of the coarse aggregate do not influence significantly the mechanical properties of concrete, because it is the hydrated cement paste that constitutes the weakest link. Therefore, most of the mechanical properties of a usual concrete can be closely related to the mechanical properties of the hydrated cement paste

(or its water–binder ratio) and to its compressive strength. This explains why, in usual concrete, it is easy to develop simple relationships between compressive strength and most other mechanical properties.

On the contrary, the microstructure of low w/b concrete is more compact, particularly in the transition zone. Therefore, the mechanical properties of the coarse aggregate have much more influence on the mechanical properties of low w/b concrete. Even the water–binder ratio law no longer holds in the case of some low w/c ratio concretes made with “weak” coarse aggregates. For any coarse aggregate, there is a critical value of the water–binder ratio below which any further decrease of the water–binder ratio does not result in a significant increase of compressive strength. This critical value depends not only on the strength of the rock from which the coarse aggregate is made but also on the maximum size of the coarse aggregate because, when crushing a piece of rock, the smallest fragments are usually stronger than the coarsest ones because they contain fewer defects.

In broad terms, it can be said that usual concretes act essentially as homogeneous and isotropic materials in which the weakest link is the hydrated cement paste and/or the transition zone. On the other hand, low w/b concretes essentially act as non-isotropic composite materials made of hydrated cement paste and aggregates that can each have quite different mechanical properties. The properties of this composite material are influenced by the properties of each of its constituents as well as the water–binder ratio (Asselanis, *et al.*, 1989; Baalbaki *et al.*, 1991).

It is easy from a mechanical point of view to make a clear distinction between a usual concrete having a water–binder ratio of 0.50 and a low w/c ratio concrete having a water–binder ratio of 0.30 but it is more difficult to make such a distinction when the water–binder ratio gradually changes within this range. In fact, there is no sharp discontinuity in the behaviour of concretes having an intermediate water–binder ratio, but rather a continuous evolution from one behaviour to the other. This is another reason why it is not safe to believe that the mechanical properties of low w/c ratio concretes are simply those of a stronger concrete.

It is not our intention here to make an extensive review of all of the recent results published in the literature, because too often the precise conditions under which these results were obtained are not known with enough certainty and therefore it is sometimes difficult to interpret them correctly. The next sections instead mainly present results obtained mostly at the Université de Sherbrooke, focusing on general trends rather than on specific issues.

8.3.1 Compressive strength

Obviously, the compressive strength of low w/b concrete is higher than that of usual concrete. As is the case for usual concretes, the compressive strength of low w/c ratio concrete increases as the water–binder ratio

decreases. However, the water–binder “law” is only valid until the “crushing strength” of the coarse aggregate becomes the weakest link within the high-performance concrete. When coarse aggregates are no longer strong enough in comparison with the strength of the hydrated cement paste, the compressive strength of a low w/c ratio concrete does not increase significantly as the water–binder ratio decreases. The only way to increase the compressive strength of such a low w/c ratio concrete is therefore to use a “stronger” coarse aggregate. In some places, such a situation can result in a significant price gap between one particular low w/c ratio concrete and another having a 10 MPa higher strength, because the stronger coarse aggregate might have to be hauled over a long distance. Designers should be aware of this price gap when selecting the compressive design strength for a particular project.

Even when a coarse aggregate is strong enough, it is still impossible to state a general relationship between the water–binder ratio and the low w/b concrete compressive strength, because of the multiplicity of factors influencing the relationship between f'_c and the water–binder ratio. Based on our personal experience, the following broad guidelines can be used to predict the **maximum** compressive strength (not the **design strength**) that can be achieved for different water–binder ratios, as shown in Table 8.1. In this table, it is assumed that the coarse aggregates are stronger than the resulting concrete. The proposed values might appear to pertain to overly broad ranges, but considering the great number of material combinations and material properties used to make low w/b concrete, it is difficult to be more specific. Only the testing of specimens obtained from trial batches can provide the actual values that can be achieved in a particular location.

There are also other issues related to compressive strength that are important and need to receive particular attention. Some of these are:

- the early compressive strength of low w/b concrete;
- the influence of the maximum temperature reached at early age on the compressive strength of the concrete;

Table 8.1 Maximum compressive strength as a function of the w/b

w/b	f'_c (MPa)
0.40	50
0.35	75*
0.30	100*
0.25	150*

* Coarse aggregate must be stronger than this value.

- the long-term development of the compressive strength of low w/b concrete; and
- the strength of cores compared to cast specimens.

However, these issues will not be treated here.

8.3.2 Elastic modulus

The elastic modulus of low w/c ratio concrete becomes a key factor when designing tall buildings because it helps to determine the rigidity of the structure, especially when it has to face strong winds. For example, the 216 m high (58 storeys) Two Union Square skyscraper in Seattle was designed with a 130 MPa concrete having an elastic modulus of 50 GPa, in spite of the fact that from a purely static point of view a 90 MPa concrete would have been sufficient. It was necessary to increase the design compressive strength to 130 MPa to achieve a design elastic modulus of 50 GPa. The concrete producer used a very strong glacial pea gravel ($\phi_{\max}$ 10 mm) in his 0.22 w/b concrete. In order to maintain a rapid and smooth delivery of this concrete, the contractor opted for night placement. To keep peace with the neighbourhood around the concrete plant, the contractor and concrete producer offered to build, *gratis*, a playground for the children of the community (Aïtcin, 1998).

More recently, the Freedom Tower built in New York at the site of the World Trade Center was designed with a particular specification: a design elastic modulus greater than 43 GPa. In this case, the contractor was obliged to import (by boat, which was not costly) a granite coarse aggregate from Nova Scotia, Canada. In Japan, Watanabe *et al.* (2008) have reported that the construction of a 49 storey high-rise residential building, the Kobugi Tower in Kawasaki required a concrete having a compressive strength of 150 MPa. The elastic modulus of this concrete varied from 47 to 57 GPa. It was made with a coarse aggregate having an average compressive strength of 175 MPa and an elastic modulus of 60 GPa.

The Burj Khalifa Tower in Dubai, the highest building in the world in 2008, was built with a low w/b concrete having a design strength of 80 MPa and a design elastic modulus of 43.8 GPa (average value 47.9 GPa). To make a concrete with such characteristics, it was necessary to reduce the design w/b ratio to 0.27. The binder content was 484 kg/m³, with 12% fly ash and 9% silica fume (Aldred, 2010).

Nilsen and Aïtcin (1992) have shown that it is possible to make a 0.27 w/b concrete with the elastic modulus ranging between 26 and 60 GPa by changing the nature of the coarse aggregate. The lowest value of the elastic modulus was, of course, obtained with a lightweight aggregate and the highest with a heavyweight ilmenite aggregate. Empirical relationships

were proposed for lightweight and normal weight concrete:

$$E'_c = 0.31\rho^{1.29} f_c^{0.35} \text{ (GPa)}$$

and for heavyweight concrete:

$$E'_c = 0.00845\rho^{1.80} f_c^{0.29} \text{ (GPa)}$$

where ρ is the density, in kg/m^3 ; and f_c is the compressive strength, in MPa.

Baalbaki (1997) proposed an empirical formula linking some types of rocks with the elastic modulus of low w/b concrete. Based on results obtained from similar low w/b concretes made with crushed aggregates of different origins: limestone, sandstone, and granite, the main mechanical properties of which are given in Table 8.2, Baalbaki proposed a simple relationship:

$$E'_c = K_o + 0.2f'_c \text{ (GPa)}$$

where K_o is a factor depending on the type of aggregate.

Based on the experimental results, he proposed that $K_o = 9.5$ GPa for sandstone, $K_o = 19$ GPa for granite, and $K_o = 22$ GPa for limestone. In order to fit experimental results with such a very simple relationship (Figure 8.5), it may be seen that the K_o value has to vary over a wide range. Baalbaki (1997) was able to express K_o as a function of the elastic modulus of the coarse aggregate, so that the previous relationship can be expressed more generally as:

$$E'_c = -52 + 41.6\log(E_a) + 0.2f'_c,$$

where E_a is the elastic modulus of the coarse aggregate.

A nomograph (Figure 8.6) predicting the elastic modulus of any type of concrete can be deduced from the knowledge of the elastic modulus of the coarse aggregate and the compressive strength of the concrete. Baalbaki (1997) also found that the Poisson's ratio of the aggregate

Table 8.2 Mechanical properties and characteristics of the aggregates used by Baalbaki (1997)

	<i>Limestone</i>	<i>Granite</i>	<i>Sandstone</i>
Compressive strength, C_0 (MPa)	95	130	155
Modulus of elasticity, E_0 (GPa)	60	50	30
Poisson's ratio, ν_0	0.14	0.13	0.07
Splitting strength, T_0 (MPa)	7.5	12.0	7.0
Porosity (%)	2.9	3.0	6.4
Specific gravity	2.68	2.72	2.53
Absorption (%)	1.2	1.1	3.7

Courtesy of Walid Baalbaki.

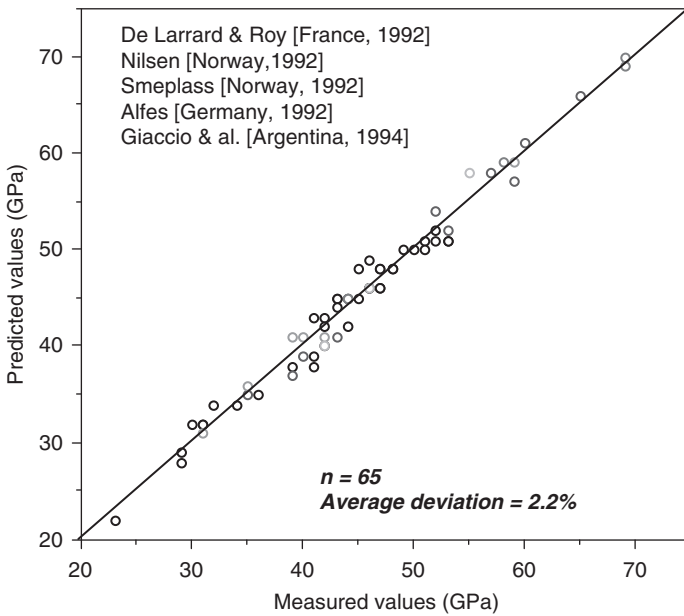


Figure 8.5 Correlation between predicted and measured values of the elastic modulus using the Baalbaki model when the characteristics of the paste and the coarse aggregate are known. (Courtesy of W. Baalbaki).

influences the elastic modulus of concrete and proposed the following empirical formula:

$$E'_c = 5.5(E_m)^{0.53}(E_a)^{0.22}(\nu_a)^{0.38}$$

where E_m is the elastic modulus of the mortar, E_a the elastic modulus of the aggregate, and ν_a is the Poisson ratio of the coarse aggregate. This formula is interesting in that it shows the relative influence of these different parameters on the value of the elastic modulus of a low w/b concrete.

However, in spite of the merits of these empirical formulas, the authors strongly believe that, rather than relying on these theoretical or empirical models to predict the elastic modulus of a high-performance concrete, it is better to measure it directly on specimens made under real field conditions or from trial batches, as suggested by Khayat *et al.* (1995):

Rather than relying on a generic formula, it would be better for important projects to determine the modulus (of elasticity) directly for each high-strength concrete proposed for use. Even for a given aggregate, different moduli can result from changes in mixture proportions, so aggregate-specific and mixture-specific tests are desirable.

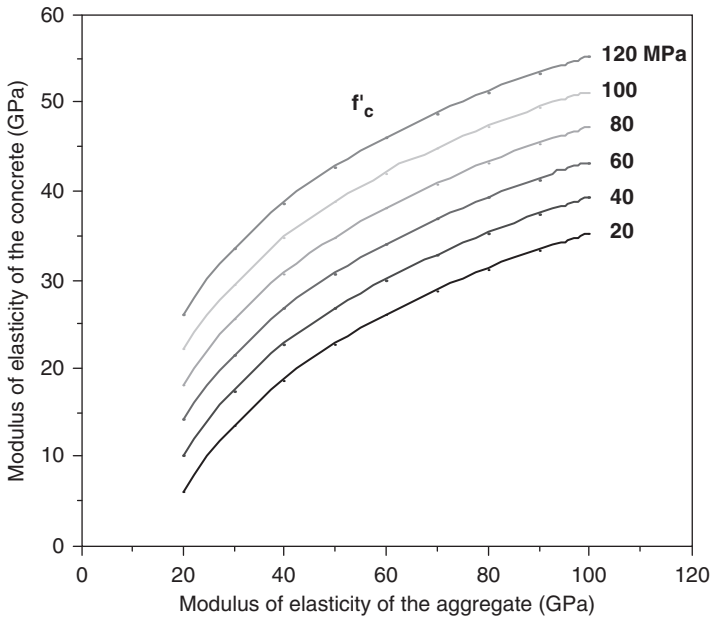


Figure 8.6 Nomograph for predicting the value of the elastic modulus of a concrete according to the value of the elastic modulus of the coarse aggregate and concrete compressive strength. (Courtesy of W. Baalbaki).

Concrete producers interested in developing a market for low w/b concrete should start by making three experimental batches having, for example, water–binder ratios of 0.35, 0.30, and 0.25 for each type of promising aggregate (hard, clean, and of a mostly cubic shape). They should measure the compressive strength, the modulus of rupture, the elastic modulus, and Poisson’s ratio of these different concretes in order to be able to provide a data sheet to designers, so that appropriate values can be used in the various calculations involved in designing low w/b concrete structures. Based on these experimental values, it should be possible to fit the parameters required for the different models to obtain a good prediction of the actual mechanical properties of the low w/b concrete. Further, a specific price can then be set for a certain level of compressive strength or a certain value of the modulus of elasticity.

8.3.3 *Stress–strain curves*

Many different equations representing the stress–strain curves of usual concrete have been proposed over the years. The existence of so many equations suggests only that the problem of finding a simple equation to

fit experimental data is not easy, because all of the parameters that influence the shape of the stress–strain curve are related both to the properties of the concrete and to the experimental conditions. The ascending branch of the stress–strain curve is not always linear and depends on the quality of the matrix/aggregate interface, the rate of strain, the composition of the matrix, and the nature of the aggregate. Therefore, a sensible equation should incorporate the following parameters: the peak value of f'_c , the strain value at this peak, the secant modulus, the tangent modulus, and the strain at which the rupture criteria are defined.

In reality, a low w/b concrete behaves more like an artificial rock than a usual concrete. The experience available in the domain of rock mechanics is very valuable and can reduce the need to start from scratch when considering the stress–strain curve. From a stress–strain curve perspective, rocks can be broadly classified into three categories according to the shape of the hysteresis curve obtained when performing a loading–unloading test (Figure 8.7). Similar hysteresis shapes have also been found with low w/b concrete specimens (Aïtcin and Mehta, 1990).

Houpert (1979) studied the influence of the characteristics of rocks on the shape of the stress–strain curve and found that, in fact, most of stress–strain curves consisted of segments that could be related to the three ideal curves shown in Figure 8.7. If we look closely at the general stress–strain curve shown in Figure 8.8, we see that it is composed of four main segments identified by the letters A, B, C, D. From the origin to A, the behaviour is non-linear viscoelastic corresponding to the closing of pre-existing cracks, especially those perpendicular to the direction in which the axial load is applied. Between A and B, the behaviour is linear elastic; the strain is elastic and reversible; there are few changes in the microstructure of the rock except perhaps under repeated loading and unloading cycles. The B–C part of the curve corresponds to a viscoelastic linear behaviour; cracks are steadily developing, but they remain stable. If the sample is unloaded, a permanent strain remains. The C–D portion of the curve corresponds to

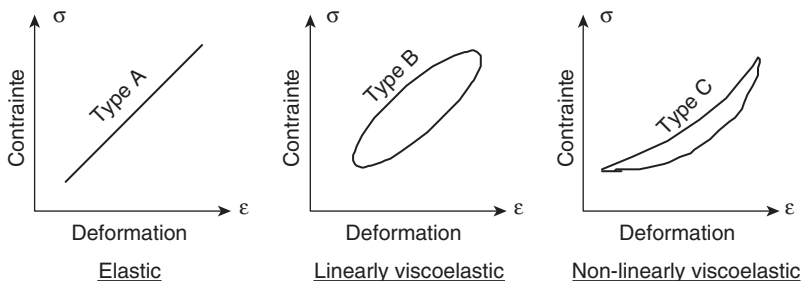


Figure 8.7 Schematic representation of the response of a rock to its loading and unloading (hysteresis curve). Reproduced from *High Performance Concrete*, Aïtcin 1998. (Courtesy of Taylor & Francis).

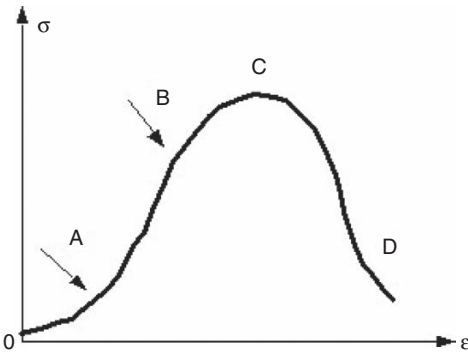


Figure 8.8 Schematic stress–strain curve for rock. From Houpert (1979). (Courtesy of Taylor & Francis).

the development of unstable cracks beginning close to point C at which the maximum stress was reached. By point D, the fracture of the rock is well advanced and the remaining strength is essentially due to the friction between the cracked parts.

This same scenario also applies to high-performance concrete. Therefore, designers should be aware that the simplified equations that appear in the various codes are only crude approximations of the behaviour of the low w/b concrete they are intended to represent.

The most widely used equations appearing in the codes are:

- CEB/FIB:

$$\varepsilon_0 = \frac{1}{1000} [2.0 + 0.005 (f'_c - 50)]$$

$$\varepsilon_u = \frac{1}{1000} \left[2.5 + 2 \left(1 - \frac{f'_c}{100} \right) \right]$$

- Norway:

$$\varepsilon_0 = \frac{1}{1000} [0.004f'_c + 1.9]$$

$$\varepsilon_u = \frac{f'_c}{E_c} \times \frac{2.5\varepsilon_0 E_c}{f'_c - 1.5}$$

The significance of f'_c and E_c can be seen in Figure 8.9. In most cases, the authors prefer to obtain the actual stress–strain curve experimentally rather than to rely on such equations.

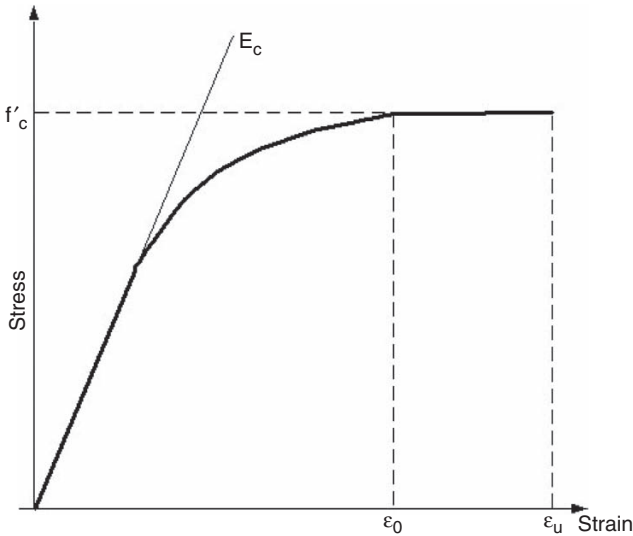


Figure 8.9 Typical stress-strain curve used in codes. Reproduced from *High Performance Concrete*, Aïtcin 1998. (Courtesy of Taylor & Francis).

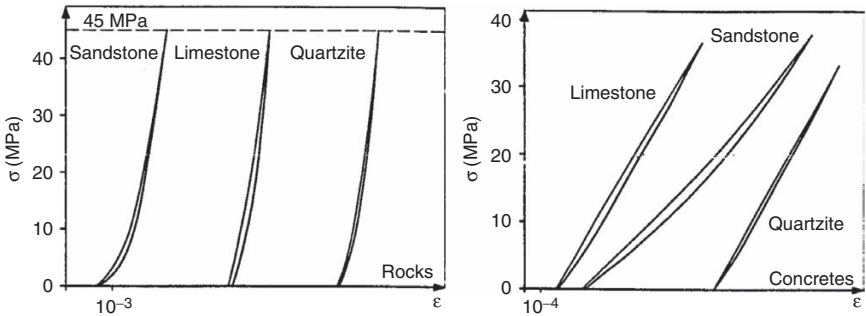


Figure 8.10 Different shapes of stress-strain curves. (Courtesy of Walid Baalbaki).

In order to illustrate how different the shapes of stress-strain curves can be, Figure 8.10 shows how the nature of the aggregate strongly influences the shape of the stress-strain curve of the concrete. This last point emphasizes once again the importance of selecting “good” coarse aggregates when making low w/b concrete, and how the properties of a particular low w/b concrete can be tailored to the designer’s needs by selecting the appropriate coarse aggregate.

8.4 Partial substitution of a normal weight aggregate by a saturated lightweight aggregate

Generally, lightweight aggregates are used to build lighter structures, with concretes having densities ranging from 1350 to 1850 kg/m³. Expanded shale, clay, and slate aggregates are usually used in such concretes. These lightweight aggregates are marketed both as sand and as coarse aggregate. In North America, they must conform to ASTM C 330. They are used essentially to reduce the dead weight of a structure, for example, when building additional floors on top of an existing building, or to improve the buoyancy of offshore platforms to facilitate their transportation to the offshore site, and so on. Since the total substitution of a normal weight aggregate by a lightweight aggregate results in a decrease of compressive strength and elastic modulus, in some cases the substitution is only partial and involves only the coarse aggregate. However, partial substitution of both fine and coarse aggregates is possible, as a compromise between density and compressive strength, in order to satisfy the requirements of a particular design.

Over the years, the use of saturated lightweight aggregate has also been promoted to provide an internal source of water for cement hydration for normal strength concrete by Klieger (1957) and Roberts (2004); and for low w/b concrete by Weber and Reinhardt (1997). However, until recently, this has not been done very often in practice (Villareal and Crockner, 2007), in spite of the fact that the use of internal curing provides three advantages:

- more complete hydration of the Portland cement by providing some later curing in normal strength concrete;
- the hydration of cementitious materials that have a slow rate of hydration. It is all too often forgotten that the pozzolanic reaction needs water to develop. Consequently, when normal strength concrete containing supplementary cementitious materials is exposed to dry conditions, it is always possible that the cementitious materials in the end act only as fillers because, through lack of water, these cementitious materials will not be able to react with the lime liberated by the hydration of Portland cement; and
- better control of autogenous shrinkage in low w/b concrete.

Recent studies at the Université de Sherbrooke could make internal curing even more attractive particularly in the case of low w/b concrete. When part of a normal sand (about 20%) is substituted by a saturated lightweight sand (Figure 8.11) and the concrete is then cast in insulated forms so that the initial hydration occurs in quasi-adiabatic conditions, it is possible to eliminate practically all of the concrete shrinkage without the use of any additional chemical admixtures (Duran-Herrera *et al.*, 2008). This is a very significant advantage because it eliminates one serious handicap of low w/b concrete: its tendency to develop early cracking. Low w/b concrete is much more sustainable than normal strength concrete, that is, its use results in

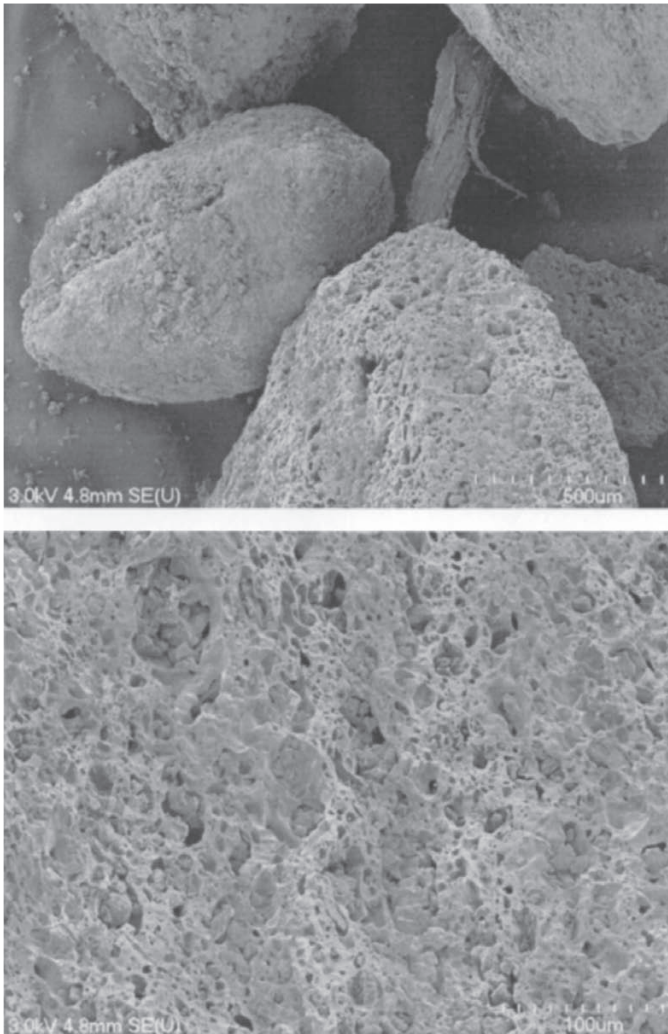


Figure 8.11 Lightweight sand (expanded shale).

a significant decrease of CO₂ emissions per unit load supported. It also results in a significant saving in aggregates. A concrete having practically no shrinkage has long been the “Holy Grail” of designers. Such a use of internal curing is developed in more detail in Chapter 12.

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9 Aggregates derived from industrial wastes

9.1 Introduction

One major component of concrete sustainability is the use of recycled or waste materials. There are three principal classes of such materials:

- supplementary cementitious materials, such as blast furnace slag, fly ash, and silica fume, that can be used to replace a portion of the Portland cement, as discussed in detail in Chapter 5;
- used oils, spent solvents, rubber tires, and other wastes that can be used as fuels in the manufacture of Portland cement, as mentioned in Chapter 1;
- some construction and demolition wastes, including old concrete, that can be recycled to serve as coarse aggregate in concrete. Since the coarse aggregate generally makes up about 40% of the mass of a typical concrete, reducing the amount of natural aggregate required can have a significant effect on preserving our natural resources.

In Europe and in North America, the amount of construction and demolition wastes created is a little more than 1 ton per person per year (of the same order of magnitude as the per capita consumption of concrete). Much of this material is used for road base or sub-base material, and some is disposed of in landfills. However, at least some of this material can be treated so that it becomes suitable for use as coarse aggregate, and can thus replace some of the natural aggregate. This topic will be the focus of the current chapter.

Some of the solid wastes that have been considered for use as concrete aggregates are listed in Table 9.1.

It must be emphasized here that we are limiting the discussion primarily to *coarse* aggregates. The fine aggregate that is produced when construction and demolition wastes are processed for use as aggregate generally contains a certain amount of old cement paste and mortar; this tends to lead to problems with strength and mix stability, and increases the magnitude of drying shrinkage and creep (Alexander and Mindess, 2005). Thus, a RILEM report (Hansen, 1990) recommends that all material smaller than

Table 9.1 Some solid wastes that have been considered as concrete aggregates

<i>Material</i>	<i>Industry</i>	<i>Composition</i>
Mineral wastes	Mining and mineral processing	Natural rocks
Blast furnace slags	Iron and steel	Silicates or aluminosilicates of calcium and magnesium, silicate glasses
Building rubble	Demolition	Concrete, brick, masonry
Metallurgical slags	Metal refining	Silicates, aluminosilicates, glasses
Bottom ash	Electric power	Silica glasses
Municipal wastes	Commercial and household wastes	Glass, plastic, metals
Incinerator residues	Municipal and industrial	Container glass, metals, silica glass
Granulated rubber	Automotive (used tires)	Rubber

2 mm (passing the #8 sieve) not be used. Similarly, in the United Kingdom, BS 8500-2: 2002 (British Standards Association, 2002) prohibits the use of fine recycled concrete in new concrete mixes. Other jurisdictions, however, do permit the use of limited amounts of fine recycled aggregate. This will be discussed separately in Section 9.2.1.

9.2 Recycled concrete

Concrete is one of the major components of construction and demolition (C&D) wastes; it has been estimated that concrete represents about half of such wastes in North America and in the European Union (Meyer, 2008). Recycling concrete is relatively straightforward. Its processing is similar to that used with many natural aggregates: crushing, removal of contaminant materials, washing, and screening into the appropriate size fractions.

Concrete from a demolition site will, of course, be intermixed with the myriad of other materials found in modern construction, such as wood, brick, glass, metals, tile, gypsum, plastics, asphalt, dirt, and so on, as shown in Figure 9.1 (Alexander and Mindess, 2005). Thus, inevitably, even properly processed recycled concrete aggregate will contain traces of some of these materials. There is currently (2011) no ASTM standard dealing specifically with the requirements for recycled concrete aggregates. However, Sakai (2007) has proposed limits on the amounts of deleterious substances in recycled concrete aggregates; these are shown in Table 9.2. More specific compositional requirements are specified in the British standard BS 8500-2: 2002. These are shown in Table 9.3. However, these values may be on the conservative side; Poon and Chan (2005) found that for some lower level applications, as much as 10% contaminant material could be tolerated.

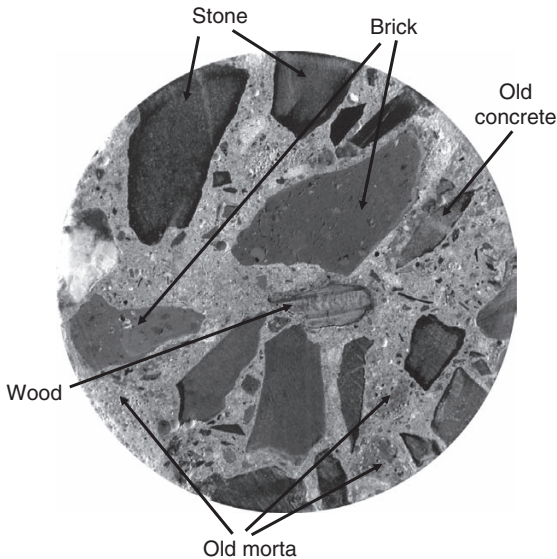


Figure 9.1 Cross-section through 68-mm core containing recycled concrete and rubble as coarse aggregate. Reproduced from *Aggregates in Concrete*, Alexander and Mindess 2005. (Courtesy of Taylor & Francis).

Table 9.2 Maximum amounts of deleterious materials in recycled concrete aggregate

<i>Deleterious substance</i>	<i>Maximum amount (mass %)</i>
Tile, brick, ceramics, asphalt	2.0
Glass	0.5
Plaster	0.1
Inorganic substances other than plaster	0.5
Plastics	0.5
Wood, paper	0.1
Total deleterious materials	3.0

After Sakai (2007).

This shows the necessity of evaluating each source of recycled aggregate on its own for any particular application.

It has generally been found that the *strength* of the source of the recycled aggregate does not have much effect on the strength of the resulting concrete. While the strength of the recycled aggregate concrete may be as much as 8 MPa lower than that of concrete made with natural aggregate at the same w/b ratio, this difference can be made up easily with a slight reduction in w/b ratio (Alexander and Mindess, 2005). The other engineering properties

Table 9.3 Compositional requirements for coarse recycled concrete aggregate in BS 8500-2: 2002

<i>Deleterious substance</i>	<i>Maximum content (mass %)</i>
Masonry	5.0
Fines	5.0
Lightweight material	0.5
Asphalt	5.0
Other foreign materials (e.g. glass, plastics, metals)	1.0
Acid-soluble sulfates, SO ₃	1.0

Table 9.4 Properties of natural aggregate (NA) and recycled concrete aggregate (RCA) concretes

<i>Property</i>	<i>NA</i>	<i>RCA (% coarse aggregate)</i>		
		<i>30</i>	<i>100</i>	<i>100 (equal strength)</i>
28-day cube strength (MPa)	41.5	40.5	37.0	41.5
Flexural strength (MPa)	4.9	4.8	4.6	4.9
Elastic modulus (GPa)	27.5	28.0	25.5	27.0
Shrinkage ($\mu\epsilon$)	565	570	630	639
Initial surface absorption ($\text{ml/m}^2/\text{s} \times 10^{-2}$)	29	31	47	35
Air permeability ($\text{m}^2 \times 10^{-17}$)	2.7	3.8	14.3	6.6
Carbonation depth (mm)	13.5	13.5	16.5	12.5
Abrasion depth (mm)	0.61	0.65	1.02	0.72
Freeze-thaw durability factor (%)	97	98	96	97
Coefficient of chloride diffusion ($\text{cm}^2/\text{s} \times 10^{-6}$)	1.16	1.17	—	1.05

After Dhir *et al.* (2004).

of recycled aggregate concrete are not much affected, as shown in Table 9.4 (after Dhir *et al.*, 2004).

In general, it has been found that concrete made with recycled aggregate has a somewhat higher absorption, and a somewhat lower relative density, than concrete made with natural aggregates. As well, with any other source of relatively unknown aggregate, it would be prudent to have a proper petrographic analysis carried out. This would serve to identify any contaminants which might cause durability problems.

In addition to aggregates derived from the demolition of concrete structures, some of the concrete that is batched is returned to the plant in the ready-mix truck, where it may be discharged and allowed to harden. This material may then also be crushed for use as concrete aggregate in new concrete, as described in Chapter 16. It has the advantage of being

very “clean”, since it was never used in a structure, and is thus free of the contaminants mentioned earlier. It has been estimated (Obla *et al.*, 2007) that about 5% of the estimated 455 million cubic yards of concrete produced annually in the United States (2006 data) is returned to the plant, and so this represents a significant source of recycled aggregate.

9.2.1 *Fine recycled aggregate*

The discussion above has dealt specifically with *coarse* recycled aggregate. Many jurisdictions, however, also permit the use of the *fine* fraction as well. The fine fraction tends to include larger amounts of hydrated cement and mortar. This leads to mixes that are harsh and sometimes unworkable. It tends to increase the drying shrinkage and creep properties of the new concrete. Most of the strength loss is also attributable to the portion of recycled aggregate finer than 2 mm (Hansen, 1990). Thus, the use of fine recycled aggregate should be limited to between 10% and 20% of the fine aggregate.

9.2.2 *Practical considerations*

It must be noted that there can be considerable variability amongst different sources of recycled aggregate, leading to correspondingly large variations in the properties of the resulting concrete. Zega *et al.* (2010) showed clearly that the properties of the recycled concrete were much more affected by the type of natural aggregate used in the source concrete than by its w/b ratio. This must be taken into account when using recycled aggregates. For instance, Deshpande *et al.* (2009) found that some concretes made with 100% recycled coarse aggregate were of poor quality compared to concrete made with natural aggregates, in terms of compressive and flexural strength, elastic modulus, and shrinkage. This suggests that for some recycled aggregates, a blend of recycled and natural aggregates might be required.

Recycled concrete aggregate has had the (ill-deserved) reputation of leading to inferior concrete. This may be because of the way in which concrete mixes containing this material have been designed. If recycled aggregate merely replaces natural aggregate at the same volume, the amount of *mortar* will be increased, since the crushed concrete contains a considerable amount of old mortar. For proper mix design, Fathifazl *et al.* (2008) have suggested that the recycled aggregate be considered as a two-phase material: natural rock and mortar, with this mortar being considered as part of the overall mortar content of the new concrete. Concrete designed in this way was shown to be similar in all respects to conventional concrete.

Currently, relatively little recycled concrete aggregate is used to produce new concrete in North America. This is largely because of economic considerations (though the extreme conservatism of the concrete industry should not be discounted in this regard). The concrete rubble must be

transported to a central site, separated from other construction debris, and then crushed and graded. This is generally more expensive than quarrying “virgin” aggregate. However, as nearby sources of natural aggregates are depleted, necessitating higher transportation costs, the economics may change. The cost of disposing of construction debris in landfills is also becoming more expensive. As well, driven by the necessity of making the concrete industry more sustainable, some government agencies are beginning to require the use of recycled materials in construction supported by public funds. It is this that is most likely to accelerate the use of recycled concrete aggregates.

9.3 Other industrial wastes

While recycled concrete is the major source of aggregate from industrial wastes, a number of other industrial wastes have also been investigated for their use as concrete aggregate.

9.3.1 *Recycled tires*

According to Xi *et al.* (2004), about 2–3 billion scrap tires are stockpiled in the United States alone, with almost 250 million more generated each year. This poses considerable environmental problems, since they often cannot be disposed of in ordinary landfills; they are unsightly and subject to fire. They are already widely used as an alternative fuel in cement kilns, but this hardly puts a dent in the stockpiles of tyres. There is thus now increasing interest in incorporating some of this rubber into concrete as a replacement for some of the fine and coarse aggregate. For this purpose, it may be shredded, chipped, ground, or crumbed.

Of course, rubber has a much lower strength and elastic modulus than cement. Therefore, the compressive and flexural strengths, as well as the elastic modulus, will be much lower with the use of rubber aggregates; the amount of the strength and stiffness loss increases with increasing rubber content. According to El-Dieb *et al.* (2001) and Eldin and Senouci (1993), this loss in strength can be as high as 80%. This is due to the fact that the rubber particles represent weak inclusions in the matrix; as well, under load, as the rubber deforms it induces large tensile stresses in the matrix, leading to premature cracking and failure. Xi *et al.* (2004) also found that the use of proper coupling agents to improve the rubber-cement bond, such as PVA or silane, serves to enhance the mechanical properties of the concrete.

However, the rubber does impart some flexibility to the system (Scripiunus *et al.*, 2007), thereby reducing crack propagation, and this leads to an increase in strain capacity and toughness (energy absorption) of the system (Xi *et al.*, 2004; Taha *et al.*, 2005). The use of rubber aggregates also increases the free shrinkage of the concrete considerably (Turatsinze *et al.*,

2006, 2007). They argued, however, that despite the increase in shrinkage, these concretes still displayed a much enhanced strain capacity; the addition of fibres was found to further enhance the performance of the rubberized concrete.

Also, it has been suggested that rubber aggregate improves the sound absorption and the thermal properties of the concrete. However, while there are some interesting possibilities with the use of rubber aggregates, this technology has yet to be exploited to any significant degree in practice.

9.3.2 Glass

Glass is a very common household and industrial waste. Currently, it is primarily only clear glass which is recycled by industry. The coloured glass, which is generally not colour sorted, is mostly landfilled. However, it has long been considered a potential source of concrete aggregate (Phillips and Chan, 1972; Johnson, 1974; Meyer, 2003). Waste glass cannot be used as coarse aggregate, because the brittle and flaky glass particles are likely to break down during the mixing process. Moreover, since they tend to have sharp or jagged edges, they pose a safety hazard during handling. Thus, in most potential applications, the glass is envisaged as fine aggregate.

The factor that most militates against the use of glass in concrete is that it is highly susceptible to alkali–aggregate reactivity (ASR), even when low alkali cements are used (Moulinier *et al.*, 2006). The most common waste glass is soda lime glass, which is particularly susceptible to ASR. However, as with many natural aggregates, ASR is a highly complex phenomenon, and it is not always easy to predict how a particular glass will behave in concrete. For instance, Figure 9.2 shows the behaviour of mortar bars containing 10% glass aggregates of different sizes and colours (Jin *et al.*, 2000). It may be seen that the expansion depends on both the colour of the glass and its fineness. It may also be seen that the coloured glasses were less reactive than the clear glass; indeed, the green glass was no different from the reference aggregate. This was explained as being due to the fact that the green glass contained chromium oxide (to give it its green colour). More significantly, it may be seen that there is a “pessimum” particle size, at the #16 mesh size. If the glass is ground to be much finer than this, at least passing the #50 mesh, then its reactivity again becomes essentially the same as that of the reference aggregate.

In addition to the ASR problem, there are practical difficulties in using glass as aggregate. The workability of the concrete is reduced because of the angular shape of the crushed glass, and the air content is increased because of the involvement of the many small-sized particles (Park *et al.*, 2004). Thus, as with other unusual aggregates, any particular source of glass aggregate must be studied carefully before it is used in concrete.

One novel application of glass aggregate is its use in decorative or architectural concrete (Liang *et al.*, 2007). Glass comes in a wide variety

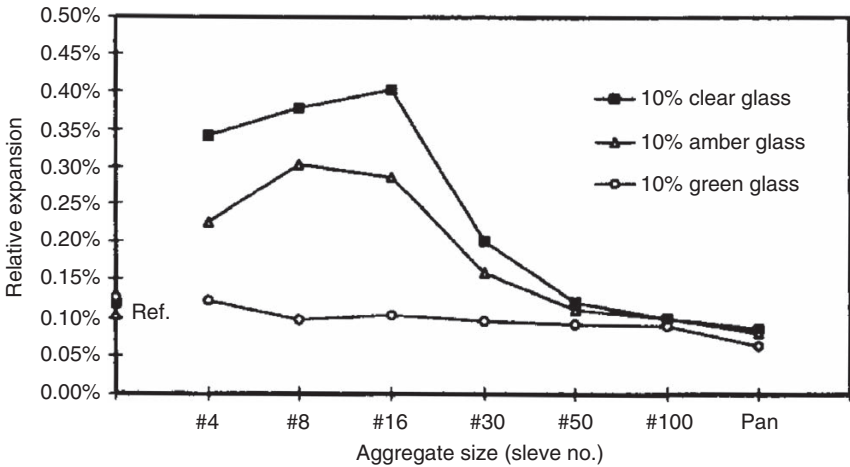


Figure 9.2 Expansion of mortar bars with 10% glass aggregates of different size and colour. From Jin *et al.* (2000). With permission of the American Concrete Institute, 38800 Country Club Drive, Farmington Hills, MI 48331, USA.

of colours, and can both reflect and refract light. It is particularly effective when used with white cement.

9.3.3 Incinerator bottom ash

Many municipalities try to dispose of solid household and other wastes through incineration. Though this reduces the solid mass by about 70% (Pera *et al.*, 1997), about 90% of the remaining incinerator residue consists of *bottom ash*, a slag-like material remaining on the grate of the incinerator. Another major source of bottom ash is the coarser material found at the bottom of the furnace in coal-burning power plants. Although not as reactive as fly ash, it does have some cementitious properties.

Bottom ash from municipal incinerators generally contains various metals, including zinc and aluminium, which may react chemically with the cement, leading to the formation of products that are deleterious, causing swelling and cracking. Though it may be possible to beneficiate such ashes, this has not been done on a commercial scale.

Bottom ash from coal combustion is somewhat more promising. According to Aggarwal *et al.* (2007) and Andrade *et al.* (2007) the bottom ash has a high water demand, necessitating the use of superplasticizers. In general, the strength of concrete incorporating bottom ash as fine aggregate is decreased. However, it may still be adequate for use in structural applications, particularly for lower strength grades of concrete. A recent

study by Topcu and Bilir (2010) suggested that a bottom ash content of 40% to 50% of the fine aggregate was optimal in terms of strength.

9.4 Other waste materials

A number of other waste materials have been examined as possible concrete aggregates, such as plastics, wood chips, foundry sands, and so on. All of these tend to compromise the strength or durability of the concrete, and require considerable beneficiation if they are to be used. No doubt other waste materials with useful properties for concrete will emerge in the future, but these are unlikely to be in sufficient quantity to permit a significant reduction in the use of natural aggregates.

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10 Entrained air

10.1 Introduction

The accidental discovery of the benefits obtained for both fresh and hardened concretes when they are stabilized with 3.5% to 6% of air (35 to 60 litres per m^3) in the form of a network of very tiny bubbles (10 to 100 micrometres in diameter) was a significant step forward in the improvement of concrete durability. In this chapter, we will emphasize that some air should be entrained in all concretes, not only to improve their durability against freeze–thaw cycles, but also to improve their workability, a key factor when considering the durability and sustainability of concrete structures. We are convinced that entrained air is a key component of good concrete everywhere, not only in northern countries such as Canada. We are not alone in holding such a conviction. The Japanese also share this belief: systematically, they entrain 3.5% to 6% of air in all of their concrete in spite of the fact that resistance to freeze–thaw cycles is not a serious problem in Japan, except in the northern part of the Japanese archipelago, Hokaido Island.

10.2 Myths of entrained air

10.2.1 *Entrapped and entrained air*

When ordinary non-air entrained concrete is cast in forms, large and irregular air bubbles are always trapped in the hardened concrete, in spite of the vibration applied during its placement. The air in these large bubbles is called *entrapped* air. Usually, ordinary concrete that has been placed with care contains 1% to 2% (10 to 20 litres per m^3) of entrapped air. This volume depends on the viscosity of the binder paste, on the amount of coarse aggregate, on the thickness of the concrete layer, on the intensity of the vibration, and on many other factors. Each of these large air bubbles creates a point of weakness within the concrete and decreases its mechanical properties.

In order to obtain a well dispersed network of very fine air bubbles within hardened concrete, it is necessary to use an air entraining agent (Dodson, 1990; Rixom and Mailvaganam, 1999). (It should be noted that the expression “air entraining agent” is misleading: this type of admixture does not entrain any air by itself, it only stabilize the air entrained during mixing in the form of millions of tiny bubbles. This type of admixture would better be referred to as an air bubble stabilizer.) In the fresh concrete, this admixture is concentrated at the surface of the air bubbles, where it forms a thin envelope strong enough to resist both bubble destruction by the mixing action and fusion with other bubbles (coalescence) . The addition of an air entraining agent thus results in a system of millions of well distributed tiny bubbles in both the fresh and the hardened concrete.

In order to significantly improve the workability of fresh concrete, and to decrease bleeding and segregation, 3.5% to 4.5% of air can be entrained. This means increasing the paste volume by 35 to 45 litres per m^3 . In order to improve the freeze–thaw resistance in the presence (or not) of deicing salts, it is necessary to entrain more air, 5% to 6% (50 to 60 litres per m^3). In this case, it is also very important that the air bubbles be close enough to each other to provide good protection. The average distance between the small bubbles is a very important factor called the “spacing factor, $\bar{L}$ ”; this will be discussed in Section 10.7.

10.2.2 Beneficial effects of air entrainment

Unfortunately, for too many people in the concrete industry, entrained air does only two things: it improves concrete resistance against freeze–thaw cycles, and it decreases concrete strength. This is highly misleading. In fact, the most beneficial actions of entrained air are:

- fluidification of the paste volume;
- improvement of concrete rheology;
- decrease of bleeding;
- decrease of the sorptivity and permeability of hardened concrete;
- dissipation of the energy concentrated at the cracks tips; and
- free volume available for expansive reaction products.

It is true that a concrete that contains 50 to 60 litres per m^3 of tiny bubbles is not as strong as a concrete of the *same water/cement ratio* that contains 10 to 20 litres of entrapped air. But, what is not taken into account in such simplistic reasoning, is that entrained air improves the concrete workability, so that the same workability can be obtained with less mixing water. Less mixing water means a lower water–binder ratio, which in turn means higher strength. Consequently, the 5% strength decrease rule for each 1% additional air content, which is true for entrapped air, is not true for entrained air. Experience shows that in the case of low strength mixes

(20 MPa or less) it is the contrary that is observed. Thus, when comparing the strength of air entrained and non-air entrained concretes, it is important to compare concretes having both the same workability and w/b ratio. Indeed, due to their lubricating action in the fresh concrete, air entraining agents could be considered as water reducers!

10.2.3 Air entrainment and sustainability

Since concrete durability is essentially a function of its w/b ratio rather than of its strength, a concrete containing 5% to 6% of entrained air is more durable and sustainable than a non-air entrained concrete of the same workability, even though its compressive strength is lower. Thus, in order to improve the sustainability of concrete, it is crucial to stabilize a small volume (3.5%–4.5%) of air in the concrete in the form of a network of very well dispersed, small bubbles, since this leads to a significant improvement in the properties of the fresh concrete. The resulting small loss in compressive strength can easily be overcome by slightly reducing the w/b ratio with a water reducer or superplasticizer. This improves concrete durability without adding a gram of cement to the mix, which is excellent from an environmental point of view. Only in northern countries with very severe climatic conditions will it be necessary to increase the amount of entrained air to obtain a low enough spacing factor to protect concrete against freezing and thawing cycles (Whiting and Nagi, 1998).

10.3 Beneficial action on the workability of fresh concrete

As stated previously, entraining 35 to 60 litres of air in fresh concrete corresponds to a decrease of an equivalent volume of sand, and the mix becomes more “creamy”. This modification of the composition of the paste improves several properties of the fresh concrete, in particular its workability. The usual explanation for this beneficial action is that the millions of very small air bubbles act like ball bearings within the paste. In fact, it is more complicated than this, because the entrained air also affects the viscosity and cohesiveness of the paste. Experience shows that the presence of entrained air decreases the risks of external bleeding and segregation because the air bubbles create stronger links between the cement particles and the water molecules, that serve to oppose gravity forces within the paste. This beneficial action is also seen in the transition zone between the paste and the aggregates because internal bleeding is also reduced for the same reasons.

A small volume of entrained air improves the workability of concretes made with manufactured sands or sands from the recycling of waste concrete, where the shape and the absorptivity of the sand particles have a strong negative affect on the workability of concrete. Entrained air can also be used to improve the workability of concretes made with a very

coarse sand. The senior author had to recommend the use of entrained air in the Canadian Arctic because the only sand available had a fineness modulus of 4.5 and was producing very harsh mixes. The freeze–thaw resistance of the concrete was not at all a concern in this particular case: the Canadian Arctic enjoys a dry climate with only a very few freeze–thaw cycles each year!

Finally, entrained air improves drastically the workability of very rich mixes containing more than 400 kg of binder (Aïtcin, 1998). It is very easy to demonstrate this effect by a simple experiment. First make a batch of a non-air entrained low w/b concrete having a w/b ratio of 0.35. It will be seen that the mix is very cohesive and viscous, and difficult to shear with a scoop. When a small amount of air entraining agent is added, it will be seen that as the air bubble network develops within the paste, the mix becomes more workable and less viscous so that it is easier to shear. This improvement in the workability of high-performance concrete by a small amount of entrained air has been used in many field applications because it facilitates placing and pumpability, and it improves the visual appearance of concrete elements when the forms are stripped.

10.4 Beneficial action against damage

When cracks develop in the cement paste, most of the fracture energy is concentrated at the crack tips. When the growing crack hits a bubble, all of this energy is released onto the surface of the bubble; quite often, the crack stops there. This helps to decrease crack growth that otherwise would decrease the durability of the concrete.

10.5 Beneficial action on permeability and sorptivity

The effect of entrained air on permeability is controversial. For instance, Neville (1995) has stated that air entrainment *reduces* the permeability of the paste while Kosmatka *et al.* (2002) have claimed that air entrainment has no effect on permeability. It is our current view that the presence of a network of air bubbles should reduce the migration of water through the capillaries due to the formation of menisci when a capillary pore terminates in a bubble. For the same reason, the sorptivity of air entrained concrete should be lower than that of a non-air entrained concrete having the same w/b ratio.

10.6 Beneficial action against expansive reactions

The millions of well dispersed air bubbles provide an empty volume into which expansive products can be deposited without any harmful effect on concrete. In damaged field concretes, as well as in specimens exposed to freezing and thawing cycles, some air bubbles filled with ettringite crystals

are regularly seen. The ions necessary to form ettringite inside the bubbles were transported there by water during the freezing and thawing cycles.

Raphaël *et al.* (1989) had the opportunity to observe (using an electron microscope) the concrete cores taken from seven dams built by Hydro-Québec with seven different granite aggregates. These granites contained quartz crystals having an undulatory extinction due to some internal stresses. They are known to be slightly reactive with the alkalies contained in the cement. In the case of these seven dams, the air bubbles and the weak transition zone provided enough space to accept the expansive gel developed during the alkali–aggregate reaction. The result was that instead of a weakening of the concrete, it was observed that the compressive strength and the elastic modulus of the concrete cores were much higher than the design strength. The permeability of these concretes also had decreased drastically. In this case, the slight reactivity of the aggregate did not disrupt the paste microstructure but rather improved it, because there was enough space to accept the expansive gel in the bubble network which was initially introduced in the concrete to counteract freeze–thaw cycles. In the case of the other three dams where the aggregates used were very reactive, the presence of even 50 to 60 litres of entrained air per cubic metre of concrete was not sufficient to counteract the expansive gel; these three concretes were severely damaged.

10.7 Beneficial action on freeze–thaw durability

In North America, the freeze–thaw durability of concrete is tested according to the very severe ASTM C666 standard. Two procedures are proposed in this standard:

- *Procedure A* with freeze–thaw cycles in water,
- *Procedure B* where the freezing is carried out in air.

Usually, the freeze–thaw durability is tested with Procedure A. The temperature at the centre of the specimen goes from -15°C to $+5^{\circ}\text{C}$ in 6 hours.

In Canada, for a concrete to be considered freeze–thaw resistant, it must successfully sustain 300 freeze–thaw cycles. After the two weeks of initial curing, it takes at least 75 days of testing (for a total of at least 13 weeks), to determine whether a concrete is freeze–thaw resistant. As this test takes very long, another more rapid evaluation of the freeze–thaw durability has been developed. From his pioneering work on entrained air, Powers found that an average spacing of 200 micrometres between air bubbles could efficiently protect concrete against freeze–thaw cycles. This average spacing is called “the spacing factor, $\bar{L}$ ”. The spacing factor is measured according to ASTM standard C 457–98, *Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete*.

According to the Canadian Standard A23.1, the upper limit of the spacing factor is 220 micrometres for a normal strength concrete and 250 micrometres for a low w/b concrete. However, the standard contains a waiver: when a concrete fails the spacing factor limit, it can be exposed to 300 freeze–thaw cycles to verify freeze–thaw durability.

In the case of the Confederation Bridge, for which the Canadian government specified a minimum 100 year life cycle, the low w/b concrete had to be able to sustain 500 cycles (Procedure A) . As it was impossible to meet the 220 micrometres spacing factor required at that time for any type of concrete, it was necessary to carry out a special research programme on the freeze–thaw durability of the selected mix (Aïtcin, 1998). After 500 cycles of Procedure A, the study showed that the critical spacing factor in that particular case was equal to 350 micrometres, a value much greater than the 220 micrometres then required. In the same study, the freeze–thaw cycling was continued after 500 cycles. The different mixes under study failed in the same order as the decreasing spacing factor. The last concrete that failed after 1956 freeze–thaw cycles of Procedure A had a spacing factor of 180 micrometres. Of course, a low water–binder ratio and a low spacing factor do not provide eternal protection for concrete against the action of freeze–thaw cycles; they only delay its destruction. In nature, even the hardest rocks in the mountains are eventually destroyed by freeze–thaw cycles.

The Canadian standard also specifies the maximum values of the water–binder ratio according to different classes of exposure because, as is too often forgotten, the spacing factor is a necessary, but not sufficient, condition to make concrete freeze–thaw durable. Freeze–thaw durability is also greatly affected by the w/b ratio (Pigeon et Pleau, 1995; Aïtcin *et al.*, 1998).

The very stringent Canadian specifications influence the way air entraining agents are used in Canada. Due to the great diversity of the mixing equipment, the variation in the ability of sands to trap the entrained air within the mortar, the influence of the mixing time, of the temperature, of the type of placing used, etc., it is necessary in every particular field case to adjust the dosage of air entraining agent to obtain an entrained air content of 5% to 6% with the right spacing factor.

10.8 Entrained air and supplementary cementitious materials

The effects of entrained air in concrete made with Portland cement are well documented in the literature. The various factors affecting the total volume of entrained air and the spacing factor have been studied in depth, but this is not always the case for all of the supplementary cementitious materials presently used by the cement industry. The presence of a supplementary cementitious material in a blended cement can either facilitate or complicate the entrainment of air for a given spacing factor. Presently, in the literature,

it is possible to find words of caution concerning the use of certain types of fly ash (Jolicoeur *et al.*, 2009). Generally speaking, the difficulty of entraining (stabilizing) an air bubble network in the case of some blended cement containing fly ash is attributed to the presence of a high carbon content in the fly ash. As seen earlier (Chapter 5), carbon can be present in two distinct forms in a fly ash: as rather coarse particles of unburned carbon and in the form of soot that coats some fly ash particles. Air entraining agents seems to be preferentially absorbed by the carbon so they are no longer available to stabilize the air bubbles generated during mixing. Usually, it is necessary to double or triple the regular dosage of the air entraining agent to be able to stabilize the right percentage of air. Moreover, in a few cases, it has been found that even increasing the dosage of the air entraining agent was not sufficient to entrain enough air.

Another problem comes from the variability in the carbon content of any particular fly ash, which can be a function of the power delivered by the power plant. When a power plant is operating at a reduced capacity at night, the amount of unburned carbon is usually higher; when dealing with such a fly ash, it is necessary to homogenize it if the blended cement is to be used in an air entrained concrete. It is possible to improve the quality of such a fly ash by using a cyclone separator to eliminate the coarsest particles of the fly ash (Chapter 5) but this process does not solve the problem caused by the presence of soot on the surface of the cement particles. This is a very interesting area of research from a sustainable development perspective. Unfortunately, at present, very few researchers are active in this area, which requires a strong knowledge of physical chemistry, organic chemistry, and concrete science.

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11 Hydration reactions

11.1 Introduction

It is not possible to specify or use concrete properly if the basis of hydration reactions is not well understood. As stated by Jorge Schlaich (1987):

One cannot design with and work with a material which one does not understand thoroughly.

Therefore, sustainability must start with education.

Not many specifiers and designers have taken during their studies a materials course devoted entirely to concrete; for them the hydration reaction is at the same time both simple and mysterious. It is known that hydration is the chemical reaction between water and the anhydrous minerals present in Portland cement that makes concrete harden. The water–cement ratio law is well known, but its true meaning is generally ignored (Bentz and Aïtcin, 2008). It is known that the hydration reaction is accompanied by the liberation of heat, but it is not so well known that it also produces a volumetric contraction known as chemical contraction. It is even less well known that autogenous shrinkage is a consequence of this chemical contraction. Therefore, we have decided to devote a whole chapter to hydration in order to demystify the subject. The hope is to better understand the consequences of hydration not only on concrete properties but also on the way in which concrete must be used in the field to build durable, sustainable, and economical structures. We will not write any complex chemical reactions. Rather we will concentrate on the description and explanation of the physical and thermodynamic consequences of the hydration reaction. However, before explaining the hydration reaction in detail, it is very important and useful to report as an “entrée” some basic work done by Le Chatelier as early as 1904, by Powers in the 1940s and 1950s, and the more recent schematic representation of hydration by Jensen and Hansen (2001).

11.2 The paradoxical experiment of Le Chatelier

More than 100 years ago, Henri Le Chatelier (1904) became interested in Portland cement hydration and reported the results of a simple experiment. He was one of the first researchers to take a scientific look at this particular phenomenon. He was a great experimentalist, and used the few scientific instruments available to him at that time; but he also used his eyes and his logic. His experiment is represented schematically in Figure 11.1.

In this experiment, Le Chatelier filled two long-necked glass containers with the same cement paste up to the base of the neck. In one container, he added some water up to the middle of the neck so that hydration occurred under water. In the second flask, hydration occurred in air. As a very cautious experimentalist, Le Chatelier placed a glass cork with a small hole in both containers to prevent any evaporation that could modify the hydration reaction. In the flask in which the paste was covered by some water, he observed that the level of water decreased significantly during the first 2 or 3 days, and then less rapidly. That is, in this flask, during hydration the cement paste absorbed some water (evaporation was prevented by the cork). In the second container in which the hydration reaction occurred in air, he observed that within a matter of a week, the volume of the paste

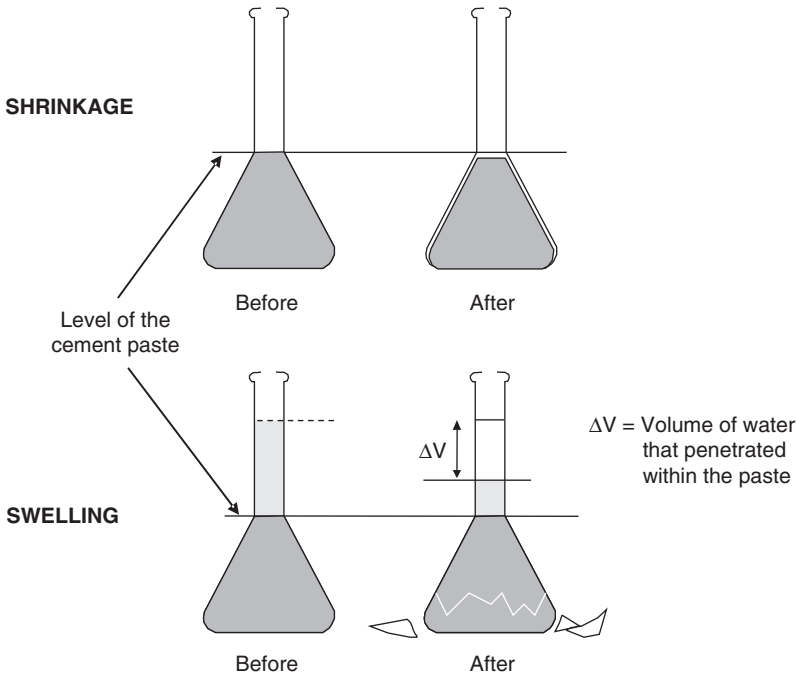


Figure 11.1 Le Chatelier's experiment. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

shrank so that it no longer occupied the entire volume of the glass container. In this case, he noted that the reduction in the apparent volume increased with time. After some time, Le Chatelier further observed that the glass container in which the cement paste had hydrated under water broke due to the expansion of the hydrated paste.

His conclusions were that a change in curing conditions can result in two totally different behaviours (Aitcin, 1999):

- when cured in air, a cement paste shrinks
- when cured in water it expands.

When curing the cement paste under water, the apparent volume expansion was accompanied by an intake of water, due to the contraction of the absolute volume of the hydrating cement paste. He explained this apparently paradoxical behaviour of the volume of the cement paste by the “physical” role of water during cement hydration that is concomitant with its chemical role.

When the cement paste is hydrating, its absolute volume (the volume of the solids) decreases because the volume of the newly formed hydrates is smaller than the sum of the absolute volumes of the anhydrous particles and the water that have reacted. As long as the cement paste behaves as a “soft” solid, it contracts but when the hydrated paste starts to become rigid due to the first links created by the hydrates, porosity is created within the cement paste. This volumetric contraction is now known as *chemical contraction* (or *Le Chatelier contraction* in the French scientific literature).

When the hydration reaction occurs in air, in the absence of an external source of water, the chemical contraction generates porosity, and menisci are developed within the hydrating cement paste. These menisci generate tensile forces that decrease the apparent volume of the paste because its internal “strength” is not sufficient to oppose these tensile forces. As a result, the apparent volume of the hydrating paste decreases and the paste shrinks. When the same paste hydrates under water, the water provided by this external source fills the porosity created by chemical contraction so that no menisci are formed. If there are no menisci, there are no tensile forces and consequently the apparent volume of the hydrating cement paste is not reduced, that is, the cement paste does not shrink.

Candidly, Le Chatelier admitted that he was unable to explain why, when curing was carried out under water in-quasi isothermal conditions, the apparent volume of the hydrated cement paste increased to such a point that it eventually broke the glass container.

This phenomenon can only be linked to a phenomenon other than the chemical contraction that occurs whenever Portland cement reacts with water. An experiment at Sherbrooke University shows that this expansion phenomenon is linked to water, because when the external source of liquid is an oil it does not result in the breaking of the container. Before retiring,

the senior author (Aïtcin) asked Mladenka Saric, one of his PhD students, to reproduce this experiment with different modern Portland cements and various water–cement ratios. He also added a new experiment: all of these cement pastes were cured under a very penetrating hydraulic oil. He observed that modern cement gave exactly the same results as those observed by Le Chatelier with the cement he used over 100 years ago (Figure 11.2; Bentz and Aïtcin, 2008).

Until recently, it was difficult to explain the expansion of the apparent volume of the hydrating paste when it is cured under water. This phenomenon did not interest many people because the swelling was not significant *at room temperature* and because, most of the time, concrete in the field hydrates in air and not under water. In those cases in which the concrete was hydrating under water, nobody took note of this hidden and insignificant swelling.

However, in a more recent experiment (Duran-Herrera *et al.*, 2008) it was observed that when a concrete hydrates in the presence of an *internal* source of water (partial substitution of sand by a saturated lightweight sand) in quasi-adiabatic conditions in insulated forms (and thus no longer at room temperature) the initial swelling could be multiplied by 5 or 6 compared to the swelling observed in quasi-isothermal conditions (Figure 11.3). In 2007, Vernet was asked to explain the 300 microstrains swelling observed under such curing conditions; his explanation was that in quasi-adiabatic conditions, the curing conditions favour the growth of crystals having a rapid growth, essentially Portlandite and ettringite, and that it is the forces generated by these “micro-jacks” that results in the swelling of the apparent volume of the paste.

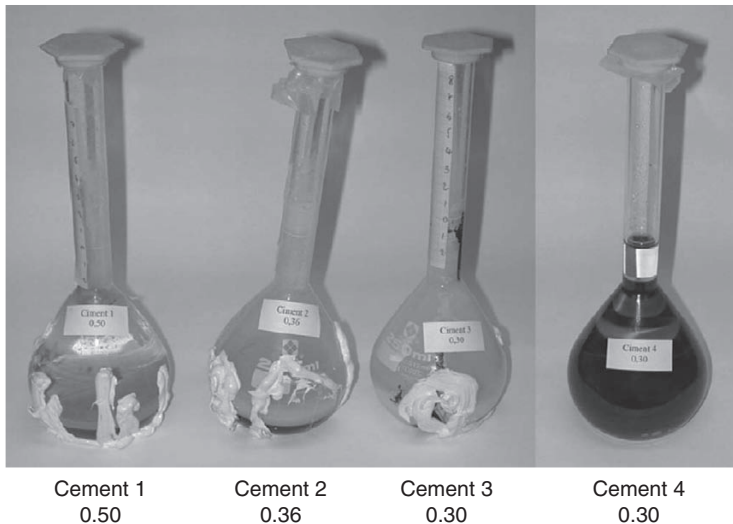


Figure 11.2 Reproduction of the Le Chatelier experiment with modern cement.

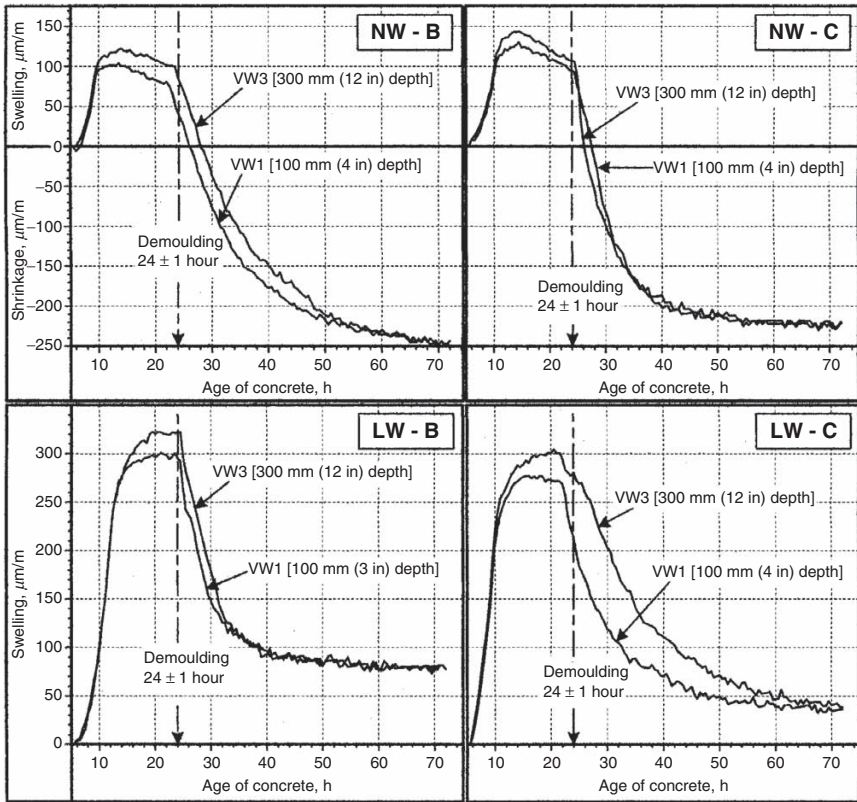


Figure 11.3 Hydration with internal curing in quasi-adiabatic conditions.

The technological consequences of Le Chatelier's experiment are still very important, because they show how concrete reacts to its curing conditions:

- in air, it shrinks;
- under water at room temperature (isothermal conditions), it swells slightly;
- under water in adiabatic conditions, it swells significantly.

Le Chatelier was able to evaluate the absolute volumetric contraction as about 8% of the apparent initial volume of the paste when it starts its hydration process. In 1934, Lynam referred to "autogenous shrinkage" as the reduction of the apparent volume of the cement paste when it hydrates in isothermal conditions, in the absence of any evaporation or source of external water. Six years later, H.E. Davis (1940) defined autogenous shrinkage in this manner:

Autogenous volume changes of concrete are defined as those which result from alteration in physical and chemical structure within the mass itself, due to causes other than: (1) movement of moisture to or from the surrounding atmosphere (2) rise or fall in temperature and (3) stresses caused by external load or restraint.

Autogenous shrinkage did not attract very much the attention from the scientific community for a long time because it was considered as a marginal phenomenon without any practical influence on the properties of the hardened concrete. This is easily explained by the fact that until recently, usual concretes had a high w/b ratio, generally higher than 0.50. In concretes with such a high w/b ratio, autogenous shrinkage is negligible when compared to drying shrinkage. The real problem of concrete from a durability point of view was not autogenous shrinkage but rather drying shrinkage. Davis wrote:

Moreover, it would ordinarily be neither practical nor desirable to attempt to differentiate between the autogenous movements which are believed usually to be of relatively small magnitude and the direct effects of drying and temperature change.

This last statement was valid for the high w/b ratio concretes produced at that time but it is no longer true for the low w/b ratio concretes that are presently used.

When, in the 1990s, concrete with low w/b began to be used more commonly in applications other than construction of very strong columns in high rise buildings, researchers and practitioners were faced with the catastrophic consequences of uncontrolled autogenous shrinkage in non-water cured low w/b concrete structures. In such concretes, autogenous shrinkage develops very rapidly during the first hours following the casting of the concrete, at a time when the hydrated cement paste is not very strong, so that large cracks develop very rapidly, severely impairing the durability of the concrete structures. Fortunately, we now know several different ways of counteracting the rapid development of autogenous shrinkage in low w/b concretes as described in Chapter 12 on shrinkage.

11.3 Powers' work on hydration

It is rather pretentious to attempt to summarize Powers' work on hydration (Powers, 1947) in a single paragraph, but it must be admitted that reading Powers in his original text is not an easy task for a civil engineer. The text is so dense that it is difficult to read more than a few pages at a time. Fortunately, others have already summarized the essentials of Powers' work on hydration (Neville, 1995; Jensen and Hansen, 2001), and we can borrow from them the points of importance for a civil engineer.

Powers found that the amount of water necessary to form hydrates (stoichiometric water) corresponds to a w/c ratio of about 0.22. He also found that when a cement paste actually hydrates in a closed system, it is necessary to have a w/c ratio of about 0.42 to reach full hydration, because during hydration a certain amount of water is strongly bound to the newly formed hydrates. Subsequently, this water is no longer available to hydrate the remaining anhydrous particles, so that to reach full hydration it is necessary to increase the w/c ratio from 0.22 to 0.42. He called the water tightly bound to the hydrates “gel water” and the hydrated cement paste “cement gel”. These terms are quite vague, but it must be admitted that, 50 years later, our knowledge of the cement paste micro- and macro-structure is not much better. He also confirmed the value of the chemical contraction previously found by Le Chatelier.

11.4 Schematic representation of the hydration reaction (after Jensen and Hansen)

In 2001, Jensen and Hansen proposed a very simple representation of the hydration reaction in accordance with Powers’ findings (Figure 11.4). On the x-axis, they show the degree of hydration of the cement paste, represented by the ratio of the mass of anhydrous particles that have reacted to the initial mass of these anhydrous particles. At time 0, the degree of hydration is 0; when all the cement particles have reacted, the degree of hydration is 1. The time taken to reach full hydration is not considered. On the y-axis, the relative volume occupied by the materials that react is given. At time $t = 0$, point I divides the segment (0, 1) in two parts: the relative volume occupied by the anhydrous cement particles and the relative volume

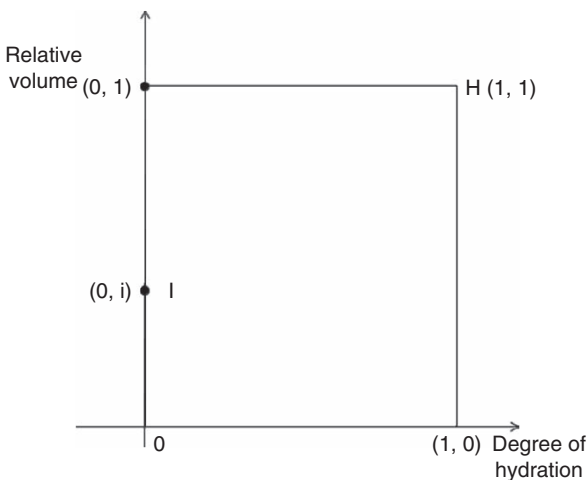


Figure 11.4 Schematic representation of Jensen and Hansen (2001).

occupied by water. In this representation, the cement paste does not include any entrapped air.

11.4.1 Hydration of a 0.60 w/c paste in a closed system

Let us examine, for example, a cement paste having a w/c ratio of 0.60 that is hydrating in a closed system, that is, in the absence of any drying or of any source of external water (Figure 11.5). According to Powers, water reacts in two ways when it comes in contact with cement particles:

- some water reacts chemically with the cement to form hydrates. As stated previously, Powers found that the w/c ratio necessary to stoichiometrically react with cement particles was about 0.22; this corresponds to the amount of water consumed chemically by the hydration reaction;
- some water is physically fixed to these hydrates as gel water. This gel water is no longer available to hydrate the unhydrated anhydrous particles. Hence, the w/c ratio necessary to fully hydrate the cement particles is about 0.42.

Using the Jensen and Hansen representation, it is possible to make the following observations as hydration progresses:

- the volume of the anhydrous cement particles decreases from point I (0, i) to point E (1, 0);

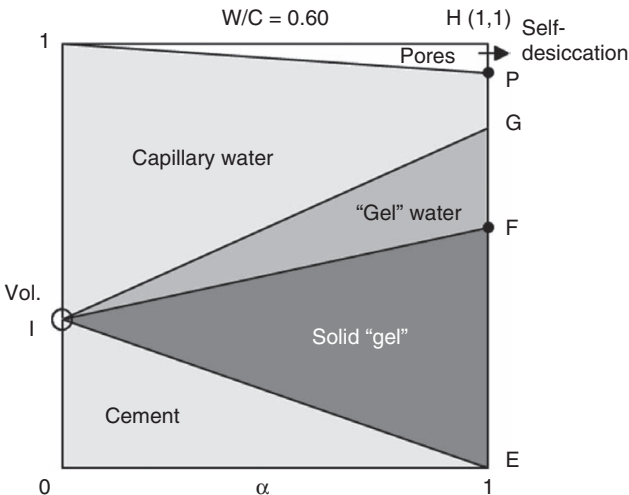


Figure 11.5 Hydration of a 0.60 w/c paste in a closed system. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

- the volume of cement gel increases from I (0, i) to F (1, f);
- the volume of the gel water increases from I (0, i) to G (f, p);
- when all of the cement particles have hydrated, a certain amount of capillary water remains;
- a certain porosity appears in the closed system. At full hydration, this porosity is equal to the segment P (1, p) H (1, 1). This porosity corresponds to the chemical contraction of the hydrated cement paste.

It should be noted that in this schematic representation, the unit volume of the cement paste does not change; the volumetric contraction occurring in the soft hydrated cement paste before it is structurally strong enough to create some porosity is not taken into account; in fact, it is negligible.

At the end of the hydration process, the hydrated cement paste is composed of four parts:

- the hydrates,
- the gel water,
- some capillary water, and
- a porosity filled with water vapour (since we are in a closed system).

Of course, the greater the w/c, the greater the amount of water remaining as capillary water in the final system. The larger the capillaries, the larger the volume occupied by the unused water. Therefore, from a durability point of view, the worse the concrete, because this large connected capillary network will offer easy avenues for aggressive ions to invade the concrete. This large network will also favour the rapid evaporation of the capillary water and subsequently increase drying shrinkage.

11.4.2 Hydration of a 0.42 w/c paste in a closed system

Let us now examine what happens in a 0.42 w/c paste hydrating in a closed system (Figure 11.6). According to Powers, at the end of the hydration process, all of the cement particles are fully hydrated and no capillary water remains in the system. However, the chemical contraction of the hydrated paste has created some porosity. The only difference between this figure and the preceding one is that points P and G are the same at the end of the hydration process. There is no longer any capillary water in the system.

11.4.3 Hydration of a 0.42 w/c paste exposed to an external source of water

What happens when, as in the experiment of Le Chatelier, the hydration of the 0.42 w/c paste occurs in the presence of a source of external water (Figure 11.7)? The graph is essentially the same, except that now the porosity

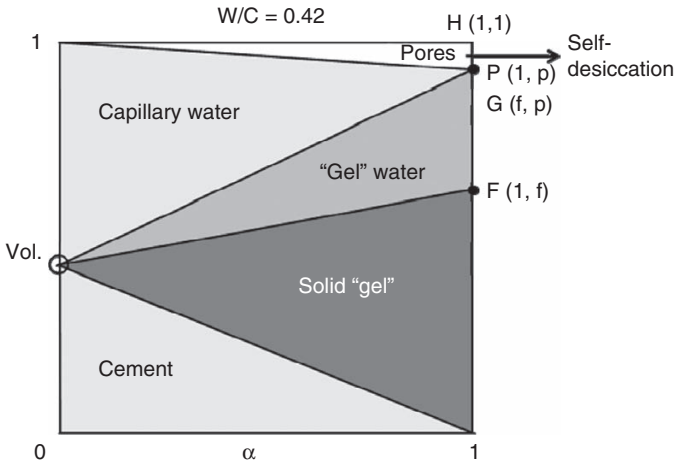


Figure 11.6 Hydration of a Portland cement paste having a 0.42 w/c in a closed system. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

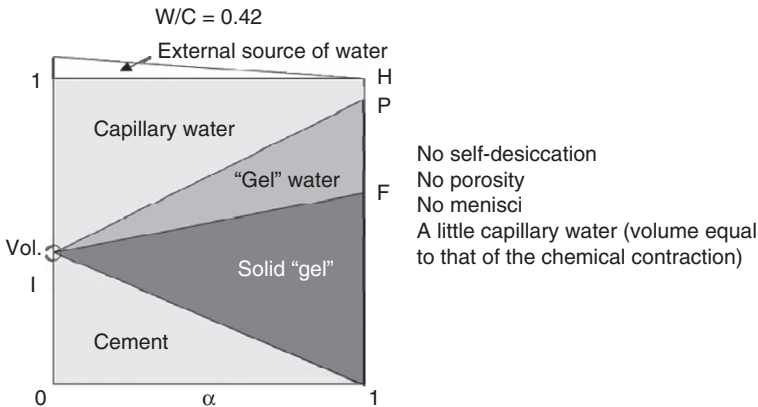


Figure 11.7 Hydration of a Portland cement paste having a w/c of 0.42 in the presence of an external source of water. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

due to the chemical contraction is filled with water, instead of air and water vapour. Unfortunately, even in the fully hydrated system, there is some water left. Using Powers' results, Jensen and Hansen showed that this water, which fills the porosity created by the chemical contraction, can be used to fully hydrate a cement paste having a w/c of 0.36.

11.4.4 Hydration of a 0.36 w/c paste exposed to an external source of water

Powers was not able to make a 0.36 w/c paste having the same fluidity as a 0.42 paste, because superplasticizers had not yet been discovered. In Figure 11.8, the initial point I is somewhat higher on the y-axis because there is more cement and less water in the paste. At the end of the hydration process, the hardened cement paste is composed of cement gel and gel water; it does not contain any capillary water or any porosity. From a theoretical point of view, it is a perfect solid that does not have any porosity. This is the type of cement paste that should be used to make durable and sustainable concrete!

11.4.5 Hydration of a 0.30 w/c paste in a closed system

What happens when the w/c of the paste is lower than 0.36, for instance equal to 0.30 (Figure 11.9)? This is the type of concrete used for the construction of very strong columns in high rise buildings. In such a case, the hydration reaction stops when all the water has reacted. At that time only a fraction of the cement has reacted (the fraction corresponding to a w/c ratio of 0.42). Consequently, some anhydrous particles remain unhydrated in the hardened cement paste. The porosity that appears due to the chemical contraction corresponds to 8% of the volume of the cement that has been hydrated.

However, as explained earlier, in spite of only the partial hydration of the cement particles, the compressive strength of the concrete still increases because compressive strength is determined not only by the amount of hydrates formed but also by how close together the anhydrous particles were in the initial cement paste (Bentz and Aïtcin, 2008).

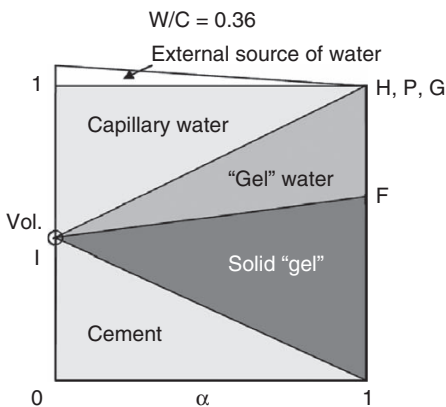


Figure 11.8 Hydration of a cement paste having a w/c of 0.36 in the presence of an external source of water.

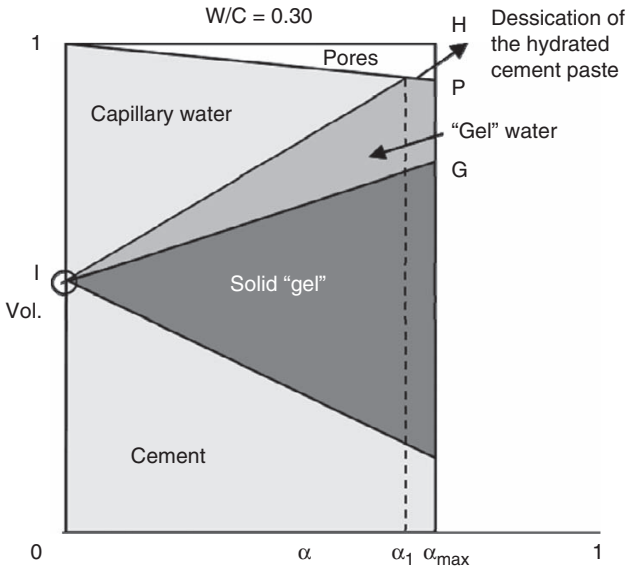


Figure 11.9 Hydration of a Portland cement paste having a w/c of 0.30 in a closed system. Reproduced from *Binders for Durable and Sustainable Concrete*, Aitcin 2008. (Courtesy of Taylor & Francis).

In fact, it has been observed that even in a 0.30 w/c paste, the remaining anhydrous particles are still able to extract some of the gel water so that the actual amount of hydrated cement is slightly higher. The calculation can be found in Jensen and Hansen (2001).

11.4.6 Practical consequences

A very important practical conclusion can be drawn from Le Chatelier's experiment and Powers' work, using the schematic representation of Jensen and Hansen (2001). Theoretically, in a closed system, full hydration (no evaporation or external source of water) is reached for a w/c ratio of 0.42.

Above a w/c ratio of 0.42 some of the water introduced during mixing is not used to hydrate the cement paste and remains in the hardened paste as capillary water. The greater the w/c, the greater the remaining capillary water, and the greater the volume of the capillary network. This leads to a lower concrete strength and reduced concrete durability, that is, the worse the concrete from a sustainability point of view. In essence, there is a considerable waste of cement, water, and aggregates.

In spite of the presence of capillary water, some porosity filled with water vapour also appears in the hardened concrete due to chemical contraction. The higher the w/c, the lower the chemical contraction because there is

less cement to hydrate. The menisci at the interface of the vapour and the capillary water create tensile forces responsible for autogenous shrinkage. The higher the w/c, the lower the autogenous shrinkage because menisci are formed in larger capillaries (Bentz and Stutzman, 2006).

Theoretically, when there is an external source of water, full hydration can be reached at a 0.36 w/c ratio. This water can be internal to the concrete (internal curing) or external to the concrete (external water curing). Theoretically when a concrete having a w/c ratio equal to 0.36 is water cured (internal or external), when full hydration is reached it no longer contains either capillary water or porosity: it is a compact solid composed of cement gel and gel water. Moreover, in the absence of menisci such a concrete does not develop any autogenous shrinkage. This is the perfect concrete we are looking for in our quest to make concrete durable and sustainable.

Internal curing is far superior to external curing to achieve such an ideal concrete because the source of the “external” water is well dispersed throughout the whole mass of concrete. Indeed, it is observed that external (to the concrete) curing is effective only for the first few centimetres below the water cured surface. *External curing is however very important* because it reinforces the microstructure of the surface cement paste and consequently very efficiently protects the reinforcing steel from corrosion. The lower the w/c ratio, the lower the penetration of water when using external curing.

Below the critical value of 0.36 that ensures full hydration, concrete compressive strength continues to increase in spite of the fact that it is always the same amount of cement that hydrates (that corresponding to the 0.36 w/c ratio). This compressive strength increase is due to the closeness of the cement particles in the initial cement paste. **The closer the cement particles, the more rapid the compressive strength gain, and the higher the ultimate strength, but also the more rapid and the larger the development of autogenous shrinkage in the absence of any water curing.** This decreases the durability and the sustainability of concrete structures made with low w/c concretes when they are not properly cured.

Therefore, from a practical point of view:

- The most durable, sustainable, and economical concrete is a 0.36 w/c ratio concrete in which some internal curing has been incorporated (saturated lightweight sand, for example).
- A 0.36 w/c ratio concrete cured with an external source of water develops a dense and durable “skin” that improves its surface durability and protects the reinforcing steel from corrosion. However, in the interior of massive concrete elements the external curing has little effect.
- The lower the w/c ratio and the worse the curing, the greater the risk of rapid cracking, and the poorer the durability and sustainability of the structure.

It is primarily in columns carrying large service loads that concrete having a w/c lower than 0.36 should be used. These concretes do not crack except perhaps when they are deformed while the concrete is still hot from the heat of hydration. However, external curing can fill the microcracks resulting from the thermal shock with new hydrates. In this case, as the water is external to the system, the volume of the new hydrates formed is larger than the volume of the anhydrous cement particles so that the newly formed hydrates can quickly fill these microcracks. In very low w/c concrete, some cement will never hydrate: usually, it is the inner portions of the coarser cement particles that do not hydrate. These unhydrated portions of the cement particles act as a filler (albeit a very expensive one), but at the present state of the art, we do not know how to eliminate this “waste” material.

We would therefore always recommend the use of internally cured 0.36 w/c ratio concrete except for columns, where a lower w/c can be used to increase both concrete compressive strength and elastic modulus.

11.5 Composition of the cement gel

11.5.1 Hydration products

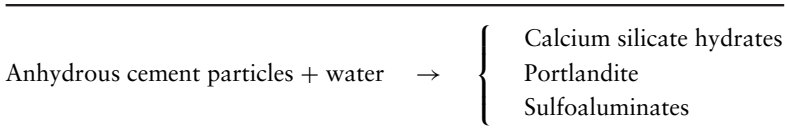
Using a scanning electron microscope, it may be seen that the cement gel is essentially composed of:

- calcium silicate hydrates that can have two types of morphology depending on the w/c ratio;
- hexagonal Portlandite ($\text{Ca}(\text{OH})_2$) crystals; and
- sulfoaluminate crystals that can be needle-like (ettringite) or in the form of platelets (monosulfoaluminate).

Therefore, for a civil engineer, the hydration reaction can be written as in Scheme 11.1.

From a more “chemical” point of view, the two anhydrous calcium silicates found in Portland cement, tricalcium silicate (C_3S) and dicalcium silicate (C_2S) hydrate to form calcium silicate hydrate (C–S–H) (Figure 11.10) and Portlandite (CH) (Figure 11.11). The calcium silicate hydrate formed through the reaction of C_3S and C_2S with water does not have a fixed chemical composition; its Ca/Si ratio can vary significantly between 1 and 2 so that it has become common practice to write it simply as C–S–H.

Scheme 11.1



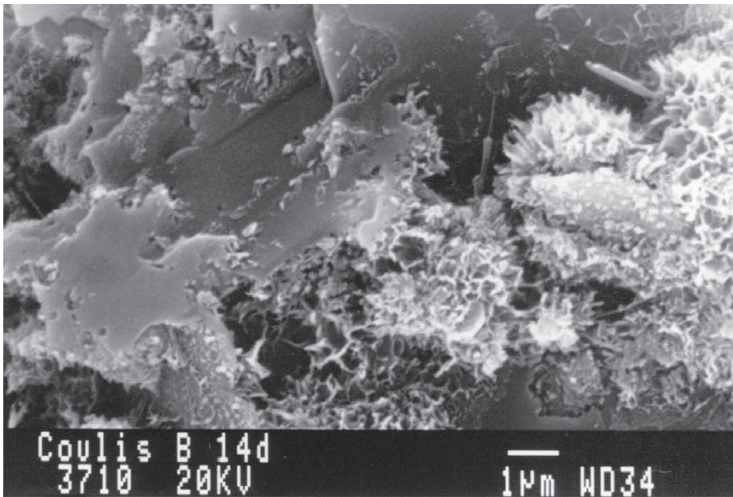


Figure 11.10 Calcium silicate hydrate (external product).

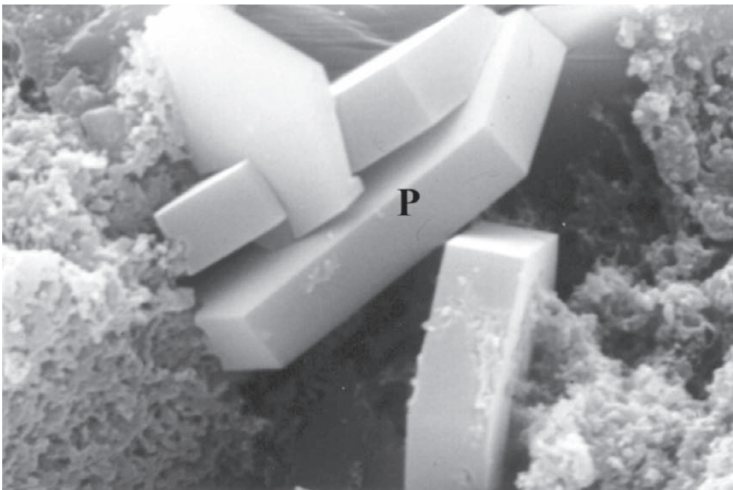


Figure 11.11 Portlandite crystals. (Courtesy of I. Kelsey-Lévesque).

The calcium aluminate present in Portland cement (C_3A) reacts with the calcium sulfate added to control the setting to form, initially, a needle-like mineral called ettringite (Figure 11.12). When all of the gypsum has reacted, the ettringite is partially decomposed by the C_3A to form a compound less rich in sulfate called *monosulfoaluminate* which crystallizes in the form of platelets (Figure 11.13). The tetracalciumaluminoferrite (C_4AF) forms compounds morphologically similar to the two previous ones.

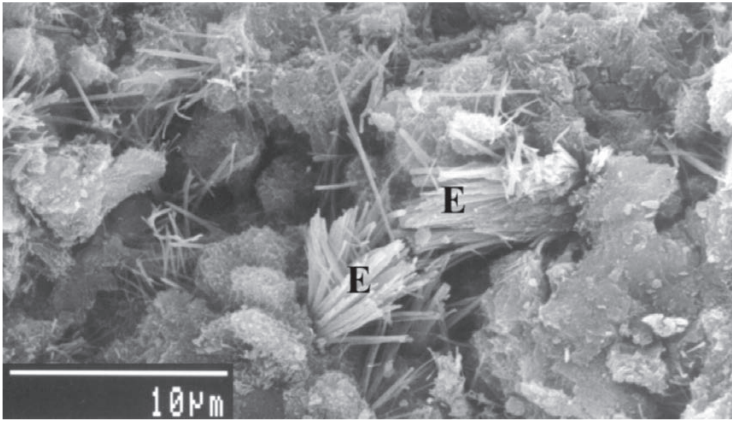


Figure 11.12 Ettringite crystals. (Courtesy of I. Kelsey-Lévesque).

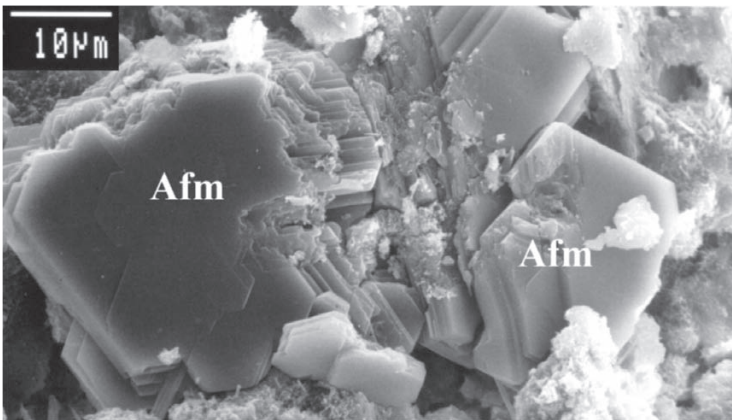
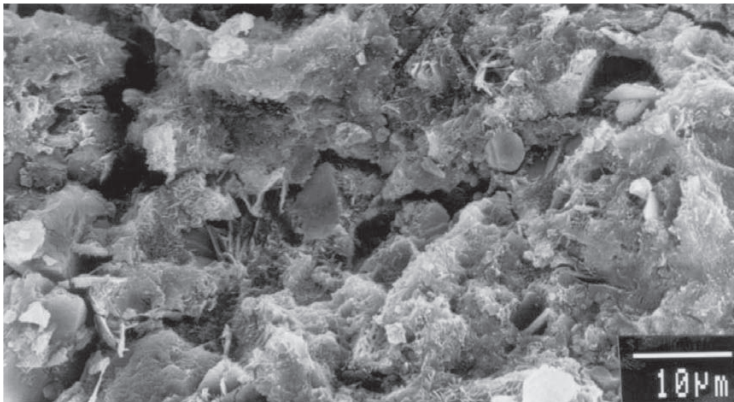


Figure 11.13 Monosulfoaluminate crystals. (Courtesy of I. Kelsey-Lévesque).

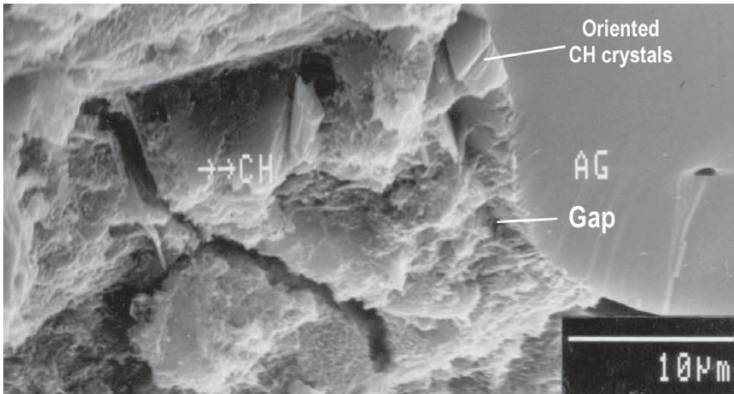
Figures 11.14 and 11.15 show the general aspects of high and low w/c pastes. The actual chemical reactions occurring in a cement paste have been described in detail by Gartner *et al.* (2002) and by Bensted (2001). The most advanced knowledge on the composition and morphology of C-S-H can be found in Nonat (2005).

11.5.2 Why is it necessary to add gypsum when producing Portland cement?

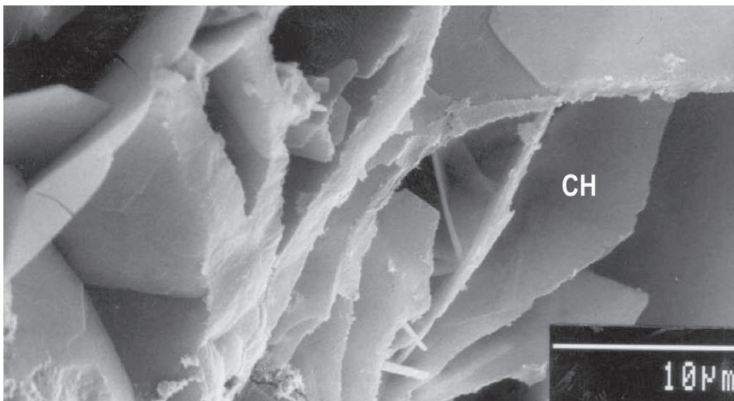
It is necessary to add some calcium sulfate to the clinker when making Portland cement, usually around 5% of the mass of Portland cement clinker



(a)



(b)



(c)

Figure 11.14 Microstructure of high w/c ratio concrete: (a) high porosity and heterogeneity of the matrix; (b) oriented crystals of Portlandite (CH); (c) CH crystals. (Courtesy of Arezky Tagnit-Hamou).

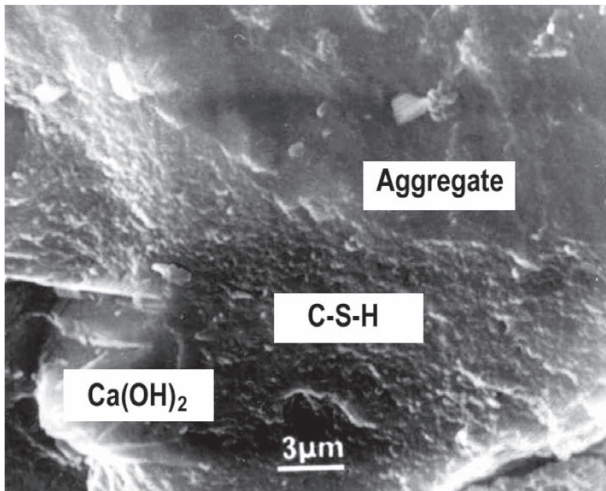


Figure 11.15 Microstructure of a low w/c concrete. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

(Bensted, 2005). It is added during the final grinding in order to control C_3A hydration. In the absence of calcium sulfate, C_3A reacts very strongly and rapidly with water to form aluminous hydrates (hydrogarnets) that stiffen the hydrating cement paste, leading to so-called “flash set”. Without gypsum, it would be practically impossible to use Portland cement as we now do. When C_3A is in the presence of $CaSO_4$, it is transformed into the sulfoaluminous mineral ettringite, that coats the C_3A surface with a semi-imperious layer that prevents the formation of aluminous hydrates. This is the mechanism by which calcium sulfate is used to control the setting of Portland cement.

For many years, calcium sulfate was added in the form of gypsum ($CaSO_4 \cdot 2H_2O$). As a result cement chemists in the industry still use the word “gypsum” as synonymous with calcium sulfate, in spite of the fact that, from a mineralogical point of view, their “gypsum” is now a cocktail of different mineralogical forms of calcium sulfate: gypsum, hemihydrate ($CaSO_4 \cdot \frac{1}{2}H_2O$), anhydrite ($CaSO_4$), and synthetic calcium sulfate ($CaSO_4$). Cement chemists use such a cocktail to match the solubility rate of their “gypsum” to the reactivity of the C_3A present in their Portland cement.

The C_3A reactivity depends on:

- the solubility rate of the C_3A that in turn depends on its morphological form (cubic or orthorhombic or a mixture of both);
- the amount of C_3A ;

- the fineness of the cement, that determines the number of active C_3A sites present on the surface of the cement particles; and
- the amount of alkali sulfates.

For example, hemihydrate is more rapidly soluble than gypsum, and synthetic calcium sulfate is more rapidly soluble than natural anhydrite. Natural anhydrite is the least rapidly soluble form.

Usually, cement chemists use impure gypsum that can contain some natural anhydrite and some calcium carbonate, because it is cheaper than “pure” gypsum. In a gypsum quarry, “pure” gypsum (i.e. less contaminated gypsum) is sold to the gypsum industry because in a gypsum plant it is crucial to use as pure a form as possible to increase the efficiency of the automated plant. The gypsum board fabrication process is not very robust, so that it requires pure gypsum. Moreover, in an effort to reduce their production costs, some cement plants are “helping” various industries that generate gypsum wastes to eliminate them (moulds from the ceramic industry, rejects of gypsum board plants, calcium sulfate from desulfurization plants, etc.). There is at least one cement plant that is very advanced in this type of recycling; it receives calcium sulfate wastes from 15(!) different plants. In order to feed the final grinder with a constant “gypsum”, this cement plant must use a homogenization hall for its 15 sources of gypsum.

Two types of problems occur when the gypsum content is too low or its solubility is not appropriate for the particular cement clinker with which it is to be interground. When there is no, or not enough, calcium sulfate in the Portland cement or when it is not rapidly soluble, C_3A reacts very rapidly. The concrete quickly loses its workability and starts to harden in the mixer (*flash set*). If this happens, it is essential to react very rapidly by adding as much water as possible to the mixer and emptying it as soon as possible; otherwise, it will be necessary to manually empty the mixer. This type of accident is now quite rare but it does happen from time to time.

Another setting problem occurs when Portland cement contains too much hemihydrate after grinding. The amount of gypsum added to the Portland cement may have been correct but, during the final grinding, too much of the gypsum was decomposed into hemihydrate due to the rise in temperature in the ball mill. Such partial dehydration of the gypsum is likely to occur when producing very fine cements; that is, the residence time of the cement particles in the ball mill can be long enough to partially dehydrate some of the gypsum. In this case, it is the rehydration of the hemihydrate in the mixer in the form of gypsum crystals that reduces the workability of the concrete (*false set*). However, if the mixing is continued, the concrete will partially recover its workability because some of the precipitated gypsum starts to dissolve.

Both *flash set* and *false set* have the same effect on concrete rheology: a rapid stiffening. However, in the case of *false set*, continued mixing makes the phenomenon disappear, while in the case of *flash set*, it worsens

the problem. As it is impossible to discriminate between these cases when they occur, it is always more prudent to add as much water as possible to the mixer and to discharge it as soon as possible. Later, a small mortar batch made in a mortar mixer can determine if it is a false set or a flash set problem.

If it is *false set*, it will be necessary to lengthen the mixing time to recover the desired slump with the defective cement. If it is *flash set*, there are two solutions:

- stop the construction and ask the cement producer to empty the cement silo and start with a new cement; or
- add 3% to 5% gypsum (or even better hemihydrate) to the mixer to provide the “missing” gypsum that caused the problem.

False set situations are rare because cement plants now use very efficient cyclones to separate the fine particles produced during grinding so that the time of residence of the fine particles is much shorter than before. Some cement chemists call this “*cold grinding*”.

11.5.3 Why are there alkalis in Portland cement?

It is well known that some aggregates can react with the alkalis (Na^+ , K^+) present in the cement to produce swelling compounds that can destroy concrete structures more or less rapidly. This swelling of the concrete depends on:

- the reactivity of the aggregate to the alkalis in the cement;
- the amount of soluble alkalis present in the cement; and
- the presence of water.

We are amongst the few who believe that danger of the alkali–aggregate reaction is overestimated in the minds of many engineers, perhaps because the great number of papers and the many conferences concerning this subject. According to Aitcin’s personal experience, less than 1% of the bad concretes that he examined over the course of his career had been deteriorated by an alkali–aggregate reaction. Even in the case of the 10 dams owned by Hydro-Quebec that were discussed in Chapter 8, the small amount of alkali–aggregate reaction observed in seven of them was due to quartz particles having an undulatory extinction (weak reactivity). This reaction was in fact beneficial to the concrete; it reinforced the transition zone around these quartz particles. The compressive strength and elastic modulus of the concrete in these dams were significantly higher than specified. Moreover, the 28-day values obtained during construction were more than adequate, and the water permeability of these concretes was particularly low. In the case of the three other dams, however, the alkali–aggregate reaction was catastrophic not only from a structural point of view but also from an

economic point of view. In one case, two turbines out of 24 were blocked due to the swelling of the concrete, and Hydro-Quebec was losing more than \$100 000 per day in the year 2000.

Clays and shales, the raw materials usually used to make clinker, generally contain less than 1% of alkalis. During the manufacturing process, these alkalis are volatilized and precipitated on the Portland cement clinker in the form of alkali sulfates of different forms, or are trapped in the C_3A . Pure C_3A crystallizes in the cubic form but as soon as it traps more than 3.7% of Na_2O , the C_3A crystallizes in the orthorhombic form which is less reactive. Usually, the C_3A found in Portland cement clinker is a mixture of the cubic and orthorhombic forms. The lower the alkali content of the cement, the greater the amount of C_3A crystallizing in the cubic form: the higher the alkali content, the greater the amount of orthorhombic C_3A .

A cement is said to be low in alkalis if its Na_2O equivalent is less than 0.60. The Na_2O equivalent is calculated as follows:

$$Na_2O \text{ equiv} = (Na_2O) + 0.685(K_2O)$$

where (Na_2O) and (K_2O) are the contents in percent of Na_2O and K_2O . In this formula, the K_2O content is transformed into an equivalent molecular amount of Na_2O .

Some cement plants use raw materials that have a very low alkali content and can produce, without any difficulty, clinker having an Na_2O equiv content lower than 0.30% or sometimes even lower than 0.20%. However, despite the claims of their marketing departments, such low alkali cements are not particularly better than those of their competitors. As long as the alkali content is less than 0.60% Na_2O equiv, a cement is properly qualified as a low alkali cement.

One great disadvantage of low alkali cements is that they do not contain enough rapidly soluble alkalis to control C_3A hydration, especially when using polysulfonate or polyacrylate dispersing agents (water reducers, superplasticizers). For most purposes, a “good” Portland cement is one that has an Na_2O equiv between 0.60% and 0.80%. Moreover, now that it is easy to find blended cements containing some fly ash or slag, it is as safe to use such blended cements when faced with potentially reactive aggregates as it is to use low alkali cements.

11.6 Heat of hydration

Le Chatelier and Powers carried out their experiments on very small laboratory samples of cement paste, in quasi-isothermal conditions. However, in large concrete elements, the temperature increases significantly before it cools down. The concrete temperature increases because the hydration reactions of the four mineral phases in Portland cement are all exothermic. The phase that liberates the highest amount of heat per unit of volume or

mass is the C_3A , followed by the C_3S , then the C_2S , and finally the C_4AF . But, as the C_3A content in Portland cement is only about 8%, it is actually its C_3S content (50% to 60%) that is responsible for most of the heat developed in a concrete. Therefore, when making Portland cement clinker with a low heat of hydration, it is important to form as little C_3S and C_3A , and as much C_2S and C_4AF , as possible. Further, as the hydration rate depends on the fineness of the cement, fine cements hydrate more rapidly than coarse cements; a Portland cement having a low heat of hydration must have a low specific surface area.

When considering the increase in temperature of a concrete placed in the forms it is important to destroy a myth solidly anchored in the concrete industry: that the maximum temperature reached by the concrete is primarily a function of the cement content. While this was true for a long time when the w/c ratios used were high (above 0.50), it is no longer true in low w/c concretes having w/c ratio lower than 0.40. In fact, it is the amount of cement *that is hydrating at the same time* that governs the concrete temperature. In a very low w/c concrete, the hydration reaction slows down rapidly because: (1) water becomes less and less accessible for hydrating more cement particles; and (2) because the hydration process passes from a dissolution/precipitation mode (outer product) to a diffusion mode (inner product), which is a much slower process. Therefore, the maximum temperature observed at the centre of a large structural element made with a high-performance concrete is not much greater than that of the same structural element made with a normal strength concrete. In a joint research project carried out in 1991 by McGill University and Sherbrooke University (Cook *et al.*, 1992), it was shown that the maximum temperature reached at the centre of three large columns ($1 \times 1 \times 2$ m) was almost the same when using 35, 90, and 120 MPa concretes having water–cement ratios equal to 0.45, 0.31, and 0.25, respectively, and that contained, respectively, 353, 470, and 540 kg of cement per cubic metre (Aïtcin, 1998). It was explained in Chapter 3 that the difference in the strength of these different concretes can be related to the distance between the cement particles in the fresh cement paste. The closer the cement particles, the stronger the links created by the cement hydration.

Structural designers do not like this increase in temperature because when it is too high it can create large thermal gradients within the structural element, not only when the temperature increases but also during the subsequent cooling, depending on the size and shape of the element. In practice, the maximum temperature reached by the concrete is a function of the heat liberated during cement hydration and the heat losses through the forms. During cooling concrete contracts, and if there are any restraints it will crack. When the temperature gradients become too large, and if there are too many restraints to thermal contraction, the concrete cracks because it has not achieved sufficient tensile strength. To avoid this cracking when it is potentially dangerous, designers should specify Portland cement

having a low heat of hydration, or a blended cement containing a high amount of fly ash or slag for large structural elements. In order to have a significant decrease of the maximum temperature, the percent of substitution of Portland cement must usually be of the order of 50% or higher.

Insulated forms can be used to limit the development of thermal gradients because they limit the heat losses. Of course, the maximum temperature reached at the centre of the concrete element will be slightly higher but not by much because fresh concrete is not a good heat conductor. As insulated forms limit the development of large thermal gradients within the concrete during its hydration, the concrete hydrates in homogeneous and isotropic conditions everywhere within the forms, which is much better than when concrete is subjected to external heating to accelerate its hardening.

In a *slipforming* operation, the use of insulated forms is also very advantageous because it isolates the concrete within the forms from the influence of external temperature. When slipforming concrete, it is very important that all of the concrete hardens at the same rate, in order for it to leave the forms with the same consistency (Lachemi and Elimov, 2007). As a slipform operation is a 360° operation, it may happen that the sides of the slipform exposed to shade and sunshine experience significantly different temperatures, so that the concrete does not harden uniformly.

When concrete hardens in insulated forms, the temperature rise is homogeneous and isotropic; all of the concrete within the forms benefits equally from this acceleration of hydration. When the internal temperature increases, it does not result in the development of thermal gradients. It is only when the forms are removed that the surface of the element is subjected to a thermal shock and can crack. However, external water curing can rapidly seal the microcracks generated by the thermal shock (Chapter 13). With the increasing use of blended cements, it can be very advantageous to use insulated forms to keep the heat of hydration within the concrete element. Since the hydration reaction is self-activating, any temperature increase accelerates the rate of hydration and results in an increased early strength.

Finally, the use of insulated forms presents another advantage: it reduces and in some cases eradicates autogenous shrinkage because when concrete is cured in quasi-adiabatic conditions, it does not shrink but rather swells enough to compensate for the chemical contraction of the cement paste.

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12 Shrinkage

12.1 Introduction

“Volumetric changes” would be a more appropriate title for this chapter because, depending on the curing conditions, concrete may shrink or swell. However, the common usage is the term “shrinkage” rather than volumetric changes to describe the variations in the apparent volume of concrete. In any event, concrete shrinks much more often than it swells.

In most text books, *creep* is associated with shrinkage, creep being the volumetric contraction associated with the application of a constant load, while shrinkage is the volumetric contraction associated with a non-loaded specimen of concrete. We have deliberately excluded creep from this chapter, in spite of its great importance in practical applications in pre-stressed and post-tensioned structural elements because:

- This book is essentially a “materials” book and not a “structures” book.
- The physico-chemical phenomena that explain creep are still the subject of considerable scientific debate. However, nano-indentation tests (Acker *et al.*, 2004) have clearly shown that the movement of water in C–S–H under the application of a constant load is somehow involved in creep.
- The formulae used to predict creep in structural elements are essentially empirical and their predictive value is in some cases of the order of $\pm 10\%$, 20% or even 30% .
- Creep is a research area in which much more effort should be invested.

Shrinkage is the Achilles’ heel of concrete because if it gets out of control it can result in severe cracking that facilitates the penetration of aggressive ions, and renders the reinforcing steel more vulnerable to rusting. Severe rusting generates spalling which in turns exposes new surfaces to corrosion. Consequently, the durability of concrete structures can be severely compromised and their life cycle shortened drastically when shrinkage results in severe cracking. This premature aging impairs the sustainability of concrete structures because it is then necessary to demolish them, to dispose

of the old materials, and to use new materials to rebuild them. Therefore, it is important to learn how to control the cracking due to shrinkage. To do this, it is important to understand its origin, or rather, as we will see, *their* origin because concrete undergoes several types of shrinkage. Once the phenomena that generate shrinkage are well understood, it is easy to develop technical strategies to mitigate the effects of shrinkage.

For the great majority of civil engineers, concrete only shrinks. This is almost true, but when concrete is cured under water, it swells (Aïtcin, 1999a). This phenomenon was observed more than 100 years ago by Le Chatelier (Aïtcin, 2008). At that time Le Chatelier was not able to explain it, and it must be admitted that 100 years later, we have not yet found a simple and clear explanation.

12.2 Types of shrinkage

For most engineers, shrinkage refers to the contraction of either fresh or hardened concrete upon a loss of water (Aïtcin *et al.*, 1997). When this loss of water occurs in fresh concrete, the resulting shrinkage is called *plastic shrinkage*; when it occurs in hardened concrete, it is called *drying shrinkage*. In both cases, the water is usually lost by evaporation to the atmosphere but the loss can also result from the suction of an underlying dry concrete or soil, or from dry forms. These two types of shrinkage and their resulting deformations are well known and well covered in the literature. They have the same physical origin: when water evaporates from concrete menisci are created in the capillary pore system and it is the tensile stresses generated at the level of the menisci that result in a contraction of the paste. Depending on the severity and the rapidity of this loss of water, the size distribution of the capillary pores and their degree of connectivity, the concrete surface can crack more or less severely. Of course, any restraint to concrete contraction concentrates the cracking around this restraint.

The third type of shrinkage that has received a great attention and which is familiar to civil engineers is *thermal shrinkage*. The hydration reactions of cement are exothermic. The concrete temperature first increases until the heat lost through the forms and the bottom and top surfaces equals the heat generated inside the concrete by hydration; then, the concrete temperature decreases. As for the great majority of materials, a temperature decrease generates a contraction which is called “thermal shrinkage”. *Thermal contraction* would be a better expression to define this type of volumetric change, but for the sake of uniformity of the language applying to the volumetric changes of concrete, the expression thermal shrinkage is most commonly used.

The last two types of shrinkage, *autogenous shrinkage* and *carbonation shrinkage*, are not so well known by civil engineers. Autogenous shrinkage, which has not received a great deal of attention until recently is even considered by many civil engineers as a “new” type of shrinkage developed

only in low w/c concretes. Carbonation shrinkage which, from a practical point of view, is negligible in comparison to drying and autogenous shrinkages will not be treated in this chapter.

As stated earlier, autogenous shrinkage was noted in 1934 by Lynam, and was studied by Davis (1930) at a time when it was impossible to make workable concretes having a low w/c ratio. Autogenous shrinkage is a physical consequence of cement hydration, so that all concretes experience some autogenous shrinkage whatever their w/c or w/b is. For many years it was possible to ignore autogenous shrinkage because it was negligible in comparison to drying shrinkage in the high w/c concretes then used to build concrete structures. These concretes usually had a w/c ratio greater than 0.50 and thus contained more water than necessary to hydrate the Portland cement. They had a relatively large capillary porosity composed of large pores in which large menisci developed upon self-desiccation. Large menisci mean low tensile stresses and low tensile stresses mean small contractions.

Autogeneous shrinkage can no longer be ignored because more and more concretes are now cast with w/c or w/b ratios lower than 0.40. In such concretes, it is not possible to neglect autogenous shrinkage because, it can be of a greater magnitude than drying shrinkage and it starts to develop as soon as hydration begins, at a time when the tensile strength of the paste is very low. In concretes having w/c or w/b ratios lower than 0.35, uncontrolled autogenous shrinkage can result in very rapid and severe cracking. Fortunately, various different technical solutions exist to mitigate this problem.

12.3 Plastic shrinkage

Water evaporates from the surface of any fresh concrete that is exposed to hot weather or windy conditions, with the result that the surface cracks more or less severely depending on the evaporation rate. As previously stated, it is the menisci developed in the capillary pore system of the fresh concrete by the evaporation of water that creates the tensile stresses that cause the concrete surface to crack. The prevention of plastic shrinkage is therefore simple: it is only necessary to eliminate or minimize water evaporation. Text books and building codes list the various strategies to minimize plastic shrinkage, such as the installation of windbreaks or the use of temporary sunshades. Unfortunately, these are not as commonly used in practice as one would like.

12.3.1 *Why is plastic shrinkage now becoming more critical?*

Concretes having a high w/b ratio (greater than 0.50) contain more water than the binder can hold so that after their vibration they tend to *bleed*. The concrete surface becomes covered by a more or less thick layer of water, depending on the w/b used: the higher the w/b, the thicker the layer of

bleed water. Of course, it is this layer of water that evaporates first and that prevents the formation of menisci within the paste. Usually, when the evaporation conditions are not too severe, the presence of a layer of bleed water protects the surface of usual concretes from cracking. But, as the w/b of the concrete decreases, the mix contains more cement and less water, so that low w/b concretes bleed very little or not at all: the lower the w/b ratio, the less the bleeding and the greater the risk of cracking. The situation is exacerbated when a low w/b concrete also contains a very fine material such as silica fume. As a result, for all practical purposes, below a w/b of 0.35 concrete no longer bleeds, and if the evaporation conditions are severe, the surface of the fresh concrete cracks rapidly.

12.3.2 *How can we avoid plastic shrinkage cracking?*

There are several ways of preventing plastic shrinkage cracking. The easiest (and best) way is simply to cure the concrete properly using fogging, evaporation retarders, or curing membranes. These are described in detail in Chapter 13. In addition, there are one or two other techniques that may be used.

12.3.2.1 *Shrinkage reducing admixtures*

Shrinkage-reducing admixtures can be used to decrease the surface tension and angle of contact of the interstitial solution in the fresh concrete. They reduce the tensile stresses within the menisci, and consequently the risks of cracking. However, as will be seen later, they are mostly used to mitigate autogenous shrinkage.

12.3.2.2 *Synthetic fibres*

The addition of synthetic fibres reduces plastic shrinkage crack formation, because the fibres increase somewhat the tensile strength of the plastic concrete and, more significantly, promote a uniform distribution of very fine cracks that are much less damaging to concrete durability than the formation of a few large cracks.

12.4 Autogenous shrinkage

As stated previously, any cement paste, whatever its w/c, develops some autogenous shrinkage. It is an unavoidable consequence of the hydration reaction when this hydration occurs in the absence of an external source of water (Aïtcin, 1999b). In low w/b concretes, the autogenous shrinkage can be of a considerable magnitude, and it becomes more severe as the w/b ratio decreases. It also starts at a time when the concrete is still weak in tension. It is therefore a serious issue that must be addressed properly to

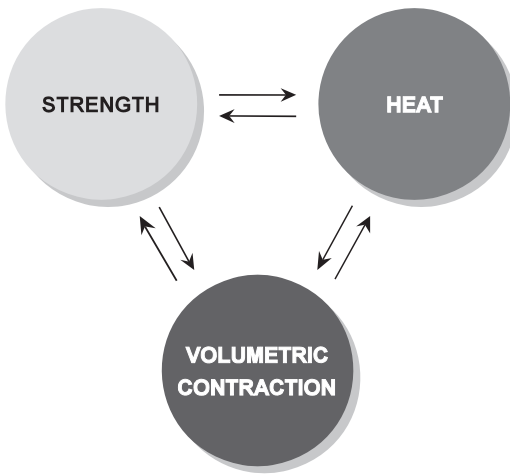


Figure 12.1 Portland cement hydration. Reproduced from *Binders for Durable and Sustainable Concrete*, Aïtcin 2008. (Courtesy of Taylor & Francis).

improve the durability and sustainability of low w/b ratio concrete, and to avoid the possibility that a low w/b concrete becomes a very impervious concrete only between the cracks (Bentz and Peltz, 2008). Indeed, many of the first structures built with low w/b concrete were found to crack severely two or three days after their casting, necessitating costly repairs. However, now that the underlying phenomena that generate autogenous shrinkage are well understood, several strategies can be implemented to counteract it and thus to avoid the development of early cracking in structures built with low w/b concretes.

12.4.1 *Origin of autogenous shrinkage*

Autogenous shrinkage is a consequence of the chemical and physical transformations that occur in a cement paste during its hydration. As shown schematically in Figure 12.1, the hydration reaction creates at the same time strength, heat, and an absolute volume reduction. Le Chatelier and Powers have shown that when Portland cement hydrates, the absolute volume of the hydrated cement paste is about 8% to 10% smaller than the sum of the absolute volumes of the cement and water that have reacted (Aïtcin *et al.*, 1997). This phenomenon is called “chemical contraction”.

As long as cement paste behaves like a soft material, it contracts, but when the newly formed hydrates generate the first physical links between cement particles, the cement paste starts to behave like a solid that restrains the chemical contraction. Consequently, the absolute volume reduction is physically transformed into empty capillary pores distributed throughout

the hydrating cement paste. In the scientific literature, this phenomenon is called “self-desiccation”. Self-desiccation results in the formation of menisci within the hydrating cement paste and menisci generate tensile stresses. It is these tensile stresses that generate the contraction of the apparent volume of concrete referred to as “autogenous shrinkage”.

When there is an external source of water that can fill the porosity developed by self-desiccation as soon as it is created, menisci are no longer formed and tensile forces no longer develop within the hydrated cement paste, and so the cement paste does not contract. The concrete no longer shrinks. **The source of water is external to the cement paste but it can be either external to the concrete (usual water curing) or internal to the concrete (internal curing).**

Another strategy that can be used to decrease the consequences of autogenous shrinkage is to introduce a chemical admixture during mixing that decreases the surface tension and angle of contact of the interstitial solution within the hydrating cement paste. This decrease of the surface tension decreases the stresses generated by the menisci so that overall autogenous shrinkage is reduced.

Still another strategy to counteract autogenous shrinkage is to add a material to the mix that will expand during the first 2 or 3 days by a volume equal to the reduction of the apparent volume that autogenous shrinkage would have generated (Nagataki and Goni, 1998; Maltese *et al.*, 2005; Collepardi *et al.*, 2005). These three strategies are developed in more detail below.

Note: It must be realized that this explanation of the origin of autogenous shrinkage is a considerable simplification of a much more complex phenomenon that develops at a nanoscale level within the cement paste during its hydration. Those who would like to delve more deeply into the physico-chemical phenomena involved in autogenous shrinkage are directed to: Tazawa (2000), Barcelo *et al.* (2001), Lura *et al.* (2002), Mihashi and de B. Leite (2004), and Ollivier and Vichot (2008).

12.4.2 External water curing

Until recently, external water curing was carried out primarily to improve early hydration by avoiding too rapid a desiccation of the cement paste. It is assumed that at the end of the initial curing period enough cement has been hydrated to provide sufficient strength. By the end of proper water curing, the concrete should withstand drying shrinkage without cracking, because its tensile strength is large enough to resist the tensile stresses generated by the menisci accompanying the desiccation of concrete. Of course, it is the water contained in the large pores that evaporates first and, as the capillary pores are large in concrete having a high w/b ratio, so are the menisci. Large menisci generate low tensile stresses, which results in a low rate of drying shrinkage development. The water still remaining in the

finest pores continues to hydrate the cement particles as long as it does not evaporate.

In addition, external curing provides another significant advantage in the case of low w/b concretes: it decreases the development of autogenous shrinkage in all of the parts of the concrete that can be reached by this external water. Experience has shown that normal external curing significantly decreases autogenous shrinkage in the outer 50 to 100 millimetres of concrete. This improvement of the concrete “skin” is very important because it dramatically lowers, or even eliminates, the risk of surface cracking, so that the outer layer of reinforcing steel remains well protected by its concrete cover (Morin *et al.*, 2002).

Finally, while the penetration of the external water is easy at the beginning of water curing of low w/c concretes, as soon as some of this water starts to hydrate the cement particles in the concrete skin, the hydration products start to fill the open capillary porosity. It is important to remember that when the water that reacts with a cement particle comes from an external source, the solid volume of the hydrated products is greater than the volume that the unhydrated cement particles had occupied in the cement paste. Consequently, the concrete skin becomes increasingly impervious, so the penetration of the external water slows down and eventually stops after some time.

External water curing is thus effective primarily in decreasing autogenous shrinkage only at the level of the concrete skin. However, this is still very important because it involves the part of the concrete that is most susceptible to the penetration of deleterious ions. In order to decrease or eliminate the autogenous shrinkage occurring deeper in the concrete, it is necessary to implement internal curing.

12.4.3 *Internal curing*

Internal curing involves the introduction of some “hidden” water during mixing, that is, water that does *not* interact with the mixing water and admixtures used to provide the desired slump and workability. Later, when any form of desiccation occurs within the concrete, this hidden water can be sucked up by the hydrating cement paste either to fill the porosity created by self-desiccation and/or to continue to hydrate the cement particles (Bentz *et al.*, 2006). Internal curing is also very important when dealing with concretes made with blended cements which hydrate more slowly than Portland cement because it provides a source of water very close to the cementitious particles that can enter into the hydration reaction when the capillary water evaporates.

We must again emphasize that while this water is internal to the concrete (hence the name “internal curing”), it is still external to the initial cement paste. When this water is sucked up to hydrate some still anhydrous cement particles, it also tends to fill the capillary porosity and the porosity created by

self-desiccation. Consequently, internal curing also leads in an improvement of the impermeability of the cement paste which is beneficial for strength development and durability.

Internal curing has been implemented in three different ways:

- through a partial or a total substitution of the coarse aggregate by a saturated coarse lightweight aggregate (Klieger, 1957; Weber and Reinhardt, 1997);
- through a partial substitution of the fine aggregate by a saturated lightweight sand (Bentz *et al.*, 2006; Villarreal and Crocker, 2007; Duran-Herrera *et al.*, 2007, 2008); and
- through the introduction of superabsorbent polymers (SAP) during mixing (Jensen and Hansen, 2001, 2002; Lura *et al.*, 2002; Kovler and Jensen, 2005; Mechtcherine *et al.*, 2008). In this case, it is necessary to increase the volume of mixing water by an amount equal to the volume of water that will be absorbed by the superabsorbent polymers during mixing.

Internal curing is described in greater detail in Chapter 13.

12.5 Thermal shrinkage

It is well known that the hydration reaction releases heat (Figure 12.1). The heat released depends on the phase composition and fineness of the cement, on the amount of cement that reacts with water, and on the initial temperature of the fresh concrete, since the hydration rate is a function of temperature. At the same time, however, some heat is also lost to the environment through the forms and the top and bottom surfaces. The heat loss depends on the difference between the ambient temperature and the temperature of the hydrating concrete, the nature of the surface through which heat is lost, and the nature of the forms. Other things being equal, heat losses are greater through steel forms than through wood forms.

Because of this contradictory situation, the concrete temperature first increases and then decreases, eventually reaching equilibrium with the ambient temperature. This release and eventual loss of heat during hydration has several technological consequences:

- The initial homogeneity of concrete is quickly lost, because very rapidly the temperature of the hardening concrete varies according to its location within the structural element.
- Close to the forms and to the top surface, the heat losses are greater than in the centre of the concrete element; therefore, temperature differences are quickly developed within the mass of concrete (*thermal gradients*).

In the warmer parts, cement hydrates more rapidly than in the colder ones, which means that the microstructure of the hardened cement paste changes according to its location within a concrete element. The only way to mitigate the development of thermal gradients during hardening is to use insulated forms. The subsequent stripping of these forms may generate a surface thermal shock and the occurrence of thermal gradients during cooling, but by then the concrete has gained a fair portion of its final strength.

12.6 Limiting the risk of cracking due to thermal gradients

The existence of excessive thermal gradients within hardening concrete can generate cracking, depending on the level of tensile stresses reached by the concrete. Therefore, when casting large structural elements, it is important to limit as much as possible the temperature reached by the hardening concrete, in order to decrease as much as possible the thermal gradients. Usually, this is achieved by:

- decreasing the temperature of the fresh concrete;
- using a cement clinker having a low heat of hydration;
- using a blended cement containing preferably 50% or more of supplementary cementitious material; and/or
- using a high fly ash content concrete (Malhotra and Mehta, 2008).

Currently, there exist several mathematical models that permit the evaluation of the risk of cracking in massive structural elements due to large thermal gradients. The weakest part of these models is the proper evaluation of thermal expansion of the hardening concrete, since it varies during hardening from almost that of water just after mixing to that of the hardened concrete. It is, however, easy to measure properly the coefficient of expansion of the hardening concrete with acceptable precision just after setting, as shown by Kada *et al.* (2002).

12.7 Aggregates and shrinkage

A simple and efficient way to decrease the apparent volumetric variation (shrinkage and creep) of a particular concrete element is to increase its aggregate content. Pickett (as cited by Pons and Torrenti, 2008) estimated that when a paste is mixed with an aggregate that represents 50% of the total volume, its shrinkage is reduced by a factor of three. Similarly, Neville (1995) estimated that an aggregate volume of 30% reduces by half the shrinkage of the mixture.

What must be emphasized is that whatever the aggregate content, the shrinkage of the *cement paste* stays the same; it is the shrinkage of the *concrete* that is reduced. The aggregate skeleton only restrains the shrinkage

of the paste. Therefore, if the shrinkage of concrete is reduced by the presence of the aggregates, this means that the cement paste itself develops a more extensive but also more uniformly distributed network of microcracks. From a durability and sustainability point of view, a well-distributed network of very fine microcracks is much safer than the presence of very few macrocracks through which aggressive agents can easily penetrate concrete and attack the reinforcing steel. Aggregate content remains a key factor in the control of concrete shrinkage. Its optimum content remains a trade-off between the necessary rheological characteristics of the fresh mixture and the shrinkage and creep characteristics of the hardened concrete.

12.8 Conclusion

The most important types of shrinkage for low w/b concretes are plastic shrinkage and autogenous shrinkage. They develop very rapidly in the first 24 hours, as soon as hydration begins. The lower the w/b, the greater the plastic and autogenous shrinkage, and the greater the risks of early cracking if the concrete is not properly water cured.

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13 Curing

13.1 Introduction

While everybody agrees that concrete must be cured properly, and this is required by all concrete building codes, it is a pity to see how poorly concrete is still cured in the field. This may be because until recently, people did not realize how poor curing practices would drastically decrease the durability and sustainability of concrete structures. The effects of bad curing were observed only in the long term, when those involved in the initial construction process were no longer active in the field. As early as 1930, Gonnerman wrote:

Studies of numerous investigations have conclusively demonstrated that adequate curing of concrete is essential in order to develop to a high degree the desirable properties of concrete. ... Curing becomes of particular importance where water-tightness and durability under severe conditions of exposure are desired.

Since then, how many concrete specialists, including ourselves, have preached in the wilderness on the subject of concrete curing? But, as sustainability has become a global preoccupation and has forced the concrete industry to take a fresh look at concrete, it is time to take this opportunity to have another kick at this particular can!

A more serious reason to try to enforce good curing practice in the field comes from the fact that more and more blended cements are now being used to improve the sustainability of concrete structures. Since blended cements contain different amounts of various supplementary cementitious materials that react more slowly than Portland cement, concrete curing has become more critical than ever before. When concretes made with a blended cement are not cured properly, the cementitious materials substituted for Portland cement act only as fillers. This severely impairs the durability and sustainability of the concrete structure. We have always been in favour of a greater use of supplementary cementitious materials by the concrete industry, *as long as they are properly cured*. However, if the perception in

the concrete industry of the importance of curing does not change rapidly, the use of supplementary cementitious materials should be discouraged because it will lead to disaster in terms of durability and sustainability. The enforcement of proper curing practice is as important to sustainability as is the substitution of some Portland cement by some cementitious materials.

We are beginning to see some encouraging signs in the concrete community of taking curing seriously, because in matters of durability things have changed. Due to their outstanding properties and characteristics (when they are properly cured), low w/b ratio concretes are more and more commonly being prescribed by architects and designers. But low w/b ratio concretes are very sensitive to bad early curing practice, and the effect of bad curing can be observed immediately while all of the principal actors participating in the construction process are still present in the field to observe them. Therefore, it is now more important than ever to cure concrete properly because:

- Low w/b ratio concretes do not contain enough mixing water to fully hydrate the Portland cement and supplementary cementitious materials they contain.
- Water curing mitigates autogenous shrinkage development in low w/b ratio concretes and the concomitant risk of early cracking.
- More and more concretes are made with blended cements having a lower initial reactivity than Portland cement, so they need a longer curing period.

There is no single way to cure concrete: it is the responsibility of the engineers to enforce the most appropriate technique, taking into account the characteristics of the concrete mixture, the ambient conditions, and the jobsite conditions. In what follows, the advantages and limitations of some of the different ways of curing concrete will be reviewed in order, we hope, to facilitate the decision-making process and ensure that the most appropriate curing procedure is used in any particular case.

13.2 Curing concrete as a function of its w/c ratio

When choosing the best curing procedures for any particular project, the w/c ratio must be taken into account, as follows.

13.2.1 Concretes having a w/c ratio greater than 0.42

In Chapter 11, it was shown that, from a theoretical point of view, 0.42 is a critical w/c ratio. Concretes made with Portland cement having a w/c ratio greater than 0.42 contain enough water to fully hydrate all of the Portland cement (if full hydration is possible). Therefore, in order to benefit from all of the binding potential of the Portland cement, it is necessary to keep this water inside the concrete as long as possible. Preventing the evaporation of

this water is the best means of providing good curing conditions for such concretes. For example, spraying an impervious membrane on the concrete surface can provide adequate protection against evaporation, as long as the curing membrane is not torn.

It is, however, important to remember that in such concretes when the Portland cement is fully hydrated, the hardened cement paste contains a capillary porosity filled not only with water, but also with some air or water vapour due to the development of autogenous shrinkage. The greater the w/c ratio, the greater the capillary porosity, the larger the pores, and the easier the evaporation of this water. Easy drying means high drying shrinkage and high drying shrinkage means potential cracking. Moreover, a large and open interconnected capillary porosity also means that the penetration of aggressive ions into the concrete by osmotic pressure will be easy. If the water surrounding the concrete is rich in a particular ion that can have a detrimental effect on concrete durability, the ions will move within the water to equilibrate their concentration in the whole mass of water, without any water flow. Therefore, the use of concrete having a w/c ratio greater than 0.42 means an increased vulnerability, *even when it has been properly cured*. The greater the w/c ratio, the greater the vulnerability of concrete.

Thus when the w/c ratio is greater than 0.42, only concretes cast under water can be considered to be truly durable as long as the water is not too pure because, in that case, the ion migration will be from the inside of the concrete to the outside. For instance, in the Canadian great north, the water is so pure that hydrated lime (Portlandite) is leached from the concrete surface, which then becomes porous and more fragile. Such leaching of hydrated lime can also be observed in concrete dams built in the mountains where the water is very pure. The leaching stops only when there is no hydrated lime left inside the concrete. The mass loss can be as great as 20% to 30% of the mass of concrete over the long term.

13.2.2 *Concretes having a w/c ratio between 0.36 and 0.42*

Jensen and Hansen (2001) have demonstrated that if some additional water is introduced into a hardening cement paste having a w/c ratio between 0.36 and 0.42, full hydration can still be reached. In the case of a w/c ratio of 0.36, from a theoretical point of view the fully hydrated Portland cement paste ends up as a **non-porous solid**. From a practical perspective, this is particularly important because the absence of any porosity represents a great advantage for making concrete durable; the penetration of aggressive ions will be severely limited and possible only through cracks of mechanical origin.

To properly cure concrete having a w/c ratio between 0.36 and 0.42, it is necessary to provide some additional water within the hardening paste to fully hydrate the Portland cement and to avoid the development of self-dessication and autogenous shrinkage. This can really only be done

through internal curing, which will be described in detail later in this chapter.

13.2.3 *Concretes having a w/c ratio less than 0.36*

Jensen and Hansen (2001) have also shown that, in such concretes ($w/c < 0.36$), it is impossible to fully hydrate all of the cement particles, so some portion of Portland cement remains unhydrated. If such concretes are not water cured, at the end of the hydration process they contain a very fine porosity filled with air and water vapour due to the chemical contraction of the paste. As stated previously, it is the appearance of menisci within this porosity that results in the development of autogenous shrinkage and the concomitant risk of early cracking, because it occurs when the cement paste is still very weak in tension. The lower the w/c ratio, the greater the autogenous shrinkage and the higher the risk of cracking. But when some external water (external to the paste) is provided to fill this porosity, no menisci are formed; there is then no autogenous shrinkage and no risk of early cracking. Therefore, concretes having a w/c ratio below 0.36 **must** be water cured, not to improve the hydration conditions but rather to counteract and mitigate the effect of high autogenous shrinkage (Meeks and Carino, 1999; Bentz, 2007).

If it is so risky to use low w/c concrete from a durability point of view, then why are they prescribed? Low w/c concretes are prescribed because at present that is the only way to achieve very high concrete strength and elastic modulus. As discussed in Chapter 11, for these concretes the strength gains are not due to the complete hydration of the Portland cement but rather due to the proximity to each other of the cement particles in the hardening cement paste. The lower the w/c ratio, the smaller the distance between the cement particles; less “glue” is necessary to bridge these cement particles, leading to stronger mechanical links (Bentz and Aïtcin, 2008). For instance, the w/c ratio of reactive powder concretes that have compressive strengths of about 200 MPa is about 0.20. The lower the w/c ratio, the greater the amount of unhydrated cement that acts as a filler.

Indeed, if cracks of mechanical origin develop in such concretes, the unhydrated cement can be hydrated by any external water that penetrates through these cracks, providing a self-healing potential. It would be a pity not to use low w/c ratio concretes just because they are sensitive to bad curing practice; it is better to learn how to cure them properly, which is in fact not too difficult.

13.2.4 *Developing an appropriate field curing strategy according to the w/c ratio*

We have now seen that the “best” way to cure concrete in any particular application depends upon its w/c ratio. Consequently, it is necessary to

implement different strategies in the field to minimize the risks of cracking due to shrinkage and to increase the durability and sustainability of the concrete:

- *For concretes having a w/c ratio greater than 0.42, it is important to keep the mixing water inside the concrete as long as possible.*
- *For concretes having a lower w/c ratio, it is important to provide some additional water as soon as possible to avoid the development of autogenous shrinkage.*

13.3 Curing concrete to avoid plastic shrinkage

Plastic shrinkage occurs due to the evaporation of the water contained in the fresh concrete. There is no evaporation when the ambient air is saturated with water or when evaporation is prevented by covering the concrete surface with an impervious layer. There are several means to achieve one or other of these goals.

13.3.1 Fog nozzles

Fog nozzles similar to those used in nurseries to cultivate flowers can be used to saturate the ambient air above the concrete surface so that the necessary condition for evaporation does not exist (Figure 13.1). This technique is simple and not costly to implement. It is commonly used in the summer in the city of Montreal, Canada (Morin *et al.*, 2002).

Fog nozzles can be used to prevent plastic shrinkage with any concrete, whatever its w/c.

13.3.2 Impervious layer or membrane

There are two ways to protect the surface of fresh concrete against evaporation with an impervious layer. The first one is to cover the concrete surface with an **evaporation retarder**. The second one is the use of a **curing membrane**.

13.3.2.1 Evaporation retarders

Evaporation retarders are aliphatic alcohols that cover the concrete (i.e. the layer of bleed water) with a monomolecular film that prevents water evaporation. (Evaporation retarders are also commonly used to prevent the evaporation of water in domestic swimming pools in summer.) An evaporation retarder can be sprayed over the surface of concrete as soon as it has been placed and finished. Usually, the protection last long enough. Evaporation retarders can be used with any concrete, whatever its w/c ratio.



Figure 13.1 Fogging to prevent plastic shrinkage.

13.3.2.2 Curing membranes

When sprayed on the surface, curing membranes form an impervious layer that prevents water evaporation and eliminates the risk of cracking. This technique is well known and has been commonly used for many years (Figure 13.2). When used with high w/b concretes that contain more water than necessary to fully hydrate the binder ($w/b > 0.42$), they eliminate the necessity of water curing. However, if the membrane is torn water can evaporate. The use of curing membranes on pavements made with binders containing supplementary cementing materials may not provide protection that lasts long enough to permit the later hydration of the cementitious materials. In such a case, it is better in terms of durability to combine its use with some internal curing (Villarreal and Crocker, 2007).

But, it is important to insist that curing membranes must not be used with concrete having a w/c ratio lower than 0.42, because later on this membrane will prevent the penetration of additional water to mitigate autogenous shrinkage and early cracking risks, except when some form of internal curing is provided. In this particular case, it is the internal curing that will mitigate the development of early autogenous shrinkage and the risk of cracking associated with it.



Figure 13.2 Application of a curing membrane just after concrete casting.

Curing membranes can be used with concretes having a w/c ratio greater than 0.42. In the case of concretes having a w/c ratio lower than 0.42, the use of a curing membrane *must be accompanied* by internal curing.

13.4 Curing concrete to avoid autogenous shrinkage

As stated earlier, autogenous shrinkage is not a serious problem with concretes having a w/c ratio greater than 0.42. However, it is important to water cure concretes having a w/c ratio lower than 0.42 to control autogenous shrinkage. This means that it is necessary to provide additional water to the paste as soon as it starts its hydration.

13.4.1 External curing

Water spraying or the use of water saturated blankets or geotextiles can be used to avoid the development of autogenous shrinkage of any concrete surface. Experience has shown that the penetration of this additional water is limited to the top surface of the concrete. For a concrete having a w/c ratio of 0.35, this external water can penetrate down to about 50 mm. This external water not only avoids the formation of menisci in the porosity created by the hydration reaction in this zone, but also hydrates some unhydrated

cement particles and fills the porosity. The lower the w/c ratio, the lower the penetration rate and the total penetration of this additional water. *However, it is very important to water cure the concrete skin in order to increase the protection of the outer layer of reinforcing steel.*

The concrete skin is an essential part of concrete from a durability point of view, because it is the first line of defence against the ingress of any aggressive agents. However, few papers have been written on this subject; the two best are those by Kreijger (1987) and Bentur (2006). Due to the so-called wall effect, the composition of the surface concrete is quite different from that of the interior concrete. Kreijger actually recognized different layers in the concrete skin: a first layer richer in cement followed by a second one richer in mortar. Usually, in both layers the w/c is greater than in the mass of concrete. The use of draining form linings has been proposed to improve the tightness of the concrete skin, but this is an expensive solution that works best with concretes that have a high w/c ratio and so are intrinsically not particularly durable. In our opinion, to provide a durable concrete skin to *any* concrete structure, one should use a concrete having a w/c lower than 0.42, and require external water curing for 7 days.

13.4.2 Internal curing

As external water curing only affects the concrete skin, the best way to mitigate autogenous shrinkage is to provide some internal curing. Internal curing involves dispersing tiny water reservoirs within the entire mass of concrete. These small water reservoirs must be able to release their water when the paste starts its self-desiccation process when the hydration reaction begins. If these water reservoirs are well dispersed and well distributed within the concrete, this water will be very close to the hydrating cement particles so that it can fill the porosity created by the chemical contraction. No menisci are formed, no tensile forces are created, and consequently the paste does not shrink.

It is important to point out that while this type of curing is internal to the concrete, it is external to the cement paste. When this external water starts to fill the porosity due to the chemical contraction, it can also hydrate some unhydrated cement particles. Since the volume of hydration products is greater than the volume of the unhydrated cement particles, these new products of hydration reduce the porosity created by chemical contraction (Bentz *et al.*, 2006).

Internal curing can be achieved in three different ways, as in the following sections.

13.4.2.1 Partial or total substitution of the coarse aggregate by an equal volume of saturated lightweight coarse aggregate

This method was used by Hoff and Elimov (1995) during the construction of the Hibernia Offshore Platform (Newfoundland) and was proposed for

high-performance concrete by Weber and Reinhardt (1997). It is easy to implement: it is only necessary to saturate the coarse lightweight aggregate using sprinklers. This method has, however, some slight disadvantages:

- The open porosity of coarse lightweight aggregates is not very large, usually 5% to 6%, so that their water retention potential is not as high as that of a fine lightweight aggregate.
- Coarse lightweight aggregate represents coarse inclusions in the hardening mix, so that the elastic modulus of the substituted concrete is decreased.
- In some cases, the compressive strength is also decreased.

In the case of the Hibernia Offshore Platform, the 50% substitution of the saturated lightweight coarse aggregate was done primarily to lighten the concrete and increase the buoyancy of the platform. It was found that this substitution did not decrease the compressive strength. The slight reduction of the elastic modulus was within acceptable limits.

13.4.2.2 *Partial substitution of the fine aggregate by an equal volume of saturated lightweight sand*

This method is more interesting than the preceding one because:

- The absorption of a fine lightweight aggregate is much greater than that of a coarse lightweight aggregate. It may be of the order of 10% to 20%, so that much more water can be stored in a given volume of lightweight aggregate. Therefore, less lightweight aggregate has to be purchased and transported to modify the original mix.
- Saturated fine lightweight aggregates represent fine inclusions that are well distributed within the mass of concrete, so that the extra water they bring to the mix is closer to the cement particles.
- Water can be sucked up easily by the hydrating cement paste.
- The elastic modulus and compressive strength of the concrete do not decrease; rather they increase somewhat due to better hydration conditions.

It has been found that fine lightweight aggregates produced from expanded slate or shale are more efficient than those produced from expanded clay.

In addition, a partial substitution of the fine aggregate by an equal volume of saturated lightweight sand can be used to promote later hydration when using blended cements containing supplementary cementitious materials (Villarreal and Crocker, 2007), or in low w/b concrete to mitigate autogenous shrinkage (Duran-Herrera *et al.*, 2007; Cusson and Hoogeven, 2008).

13.4.2.3 Use of super-absorbent polymers (SAPs)

Super-absorbent polymers (such as those used in baby diapers) can store up to 50% to 200% of their volume of water, depending on the purity of the water. When used in concrete, their absorption capacity is in the lower range: 50% to 100%, because of the different ions present in the interstitial solution. This method has been described by Jensen and Hansen (2001) and Kovler and Jensen (2005) and has been used by Metchtcherine *et al.* (2006). According to Jensen and Hansen (2001), when the water they contain has been sucked up by the hydrating paste, the SAP leaves tiny empty bubbles that can protect the concrete against freeze–thaw cycles. However, SAPs are costly. They also tend to segregate during mixing (“floating”) and it is necessary to correct the amount of mixing water to take into account the volume of water that will be absorbed by the SAPs. However, these are not insurmountable difficulties.

13.4.2.4 Internal curing in insulated forms

Duran-Herrera *et al.* (2008) have shown that by substituting 20% of the fine aggregate by an equal volume of saturated lightweight sand in a 0.35 w/b ratio concrete in large concrete elements ($0.6 \times 0.6 \times 0.6$ m) cast in insulated forms, autogenous shrinkage can be eliminated because of the significant swelling of the concrete during the first 24 hours. This technology should receive more attention in the future, particularly in precast plants. It is not expensive to implement, and it corresponds to a very ecological curing of concrete that does not involve the emission of CO₂.

13.4.3 Use of an expansive additive

Instead of using shrinkage compensating cements that are not generally available, and that are costly and tricky to use from a rheological point of view, the addition of a small amount of an expansive compound has been proposed to mitigate shrinkage. Nagataki and Goni (1998) are using expansive sulfocalcic compounds and Collepardi *et al.* (2005) dead burned lime particles, having a particular grain size distribution, that hydrate during the first 48 hours and lead to an expansion equal to what would have been the autogenous shrinkage. This method is simple to implement, not very expensive, and efficient.

13.5 Curing concrete to mitigate drying shrinkage

Drying shrinkage cracking is only a concern with concretes having a w/b ratio greater than 0.42. As previously described, these concretes are batched with more water than that necessary to fully hydrate the Portland

cement, and they have a well-connected capillary porosity; the greater the w/c, the larger and the better connected this capillary porosity is. When such concretes dry, water evaporates easily and menisci are formed. The larger capillaries empty first, followed by progressively finer capillaries as evaporation proceeds. This means that, as evaporation proceeds, the tensile forces created by these menisci increase. When there is a restraint, concrete starts to crack when the tensile forces exceed the tensile strength of the cement paste. When the crack propagates inside the concrete it opens new zones to drying, and so on. External or internal water curing only delays the time at which a w/b > 0.42 concrete will begin to shrink due to drying. However, because of this period of water curing, this shrinkage will begin when the concrete has achieved a greater tensile strength. As long as curing membranes are continuous, they too considerably reduce drying shrinkage.

Drying shrinkage can be mitigated using shrinkage reducing admixtures that decrease the surface tension in the menisci and the angle of contact. Drying shrinkage of concrete can also be reduced by increasing the coarse aggregate content as described in Chapter 12. The only way to eradicate drying shrinkage is to put a very strong sealer on the concrete surface. Tar can be used in a dry underground location, and silanes on exposed surfaces.

13.6 Implementing concrete curing in the field

As stated in the introduction, it is a pity that concrete is still so poorly cured in the field, in spite of the fact that concrete curing is always specified. Why is this? The reasons are quite straightforward: the contractor is not paid specifically to do it, but it costs money. However, if the contractor is specifically paid to cure the concrete, he will do so (Figure 13.3) – it then becomes profitable. This is the implacable economic law that governs work in the field.

Make curing concrete a profitable item in the contract and it will be cured. Therefore, the way to motivate contractors to cure concrete properly is to:

- write very clear specifications describing in detail the type of curing desired;
- ask the contractor to price each of the curing steps; and
- check carefully that the contractor then follows the specifications.

Curing concrete has a cost that has been estimated at 0.5% to 1.5% of the cost of the project (Morin *et al.*, 2002) but since proper curing has been enforced by the City of Montreal, it has been efficient. In some cases, the people involved in the monitoring of curing were obliged to ask the contractor to stop curing because he was too zealous! Curing concrete is a long-term investment that does not cost very much. It will certainly increase significantly the active life of concrete structures.



Figure 13.3 Yes, they are paid to water-cure concrete and they do it diligently.

13.7 Conclusion

This chapter on concrete curing is one of the shortest in this book, but it is also one of the most important. The concrete industry has to drastically change its culture regarding curing. Concrete curing is as important as the w/c ratio for durable and sustainable concrete. Curing specifications:

- must be written in detail, taking into account the w/b ratio;
- contractors must be paid specifically to implement curing; and
- the control of this curing must be vigilant and strict.

The modest cost of curing concrete is a long-term investment: it lengthens the active life of concrete structure, and is intimately associated with sustainability.

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14 Specifying durable and sustainable concrete

14.1 Introduction

Low w/c ratio concrete is much more than simply stronger concrete (Aïtcin, 1998). It cannot be specified in the same way as usual concrete because some of the consequences of the hydration reaction that do not significantly affect the properties of usual concrete can no longer be ignored. For example, low w/c ratio concretes are very sensitive to:

- external temperature, as well as their initial temperature after batching;
- the selection of the cement–superplasticizer combination (Aïtcin, 1998);
- drying shrinkage (Aïtcin, 1998);
- the development of autogenous shrinkage (Aïtcin *et al.*, 1997);
- the mechanical characteristics of the coarse aggregate when making a very strong concrete or a concrete with a high modulus of elasticity (Aïtcin and Mehta, 1990; Nielsen and Aïtcin, 1992).

If any one of these issues is not addressed properly in the specifications, the use of low w/c ratio concrete may result in a total failure: the concrete structure can be severely cracked, exposing the reinforcing bars to easy penetration of external aggressive ions or gas. In the following, these points will each be addressed, to help specifiers in understanding why it is necessary to write very precise and stringent specifications on these matters. Examples of such specifications, taken from the City of Montreal (2005) specifications for **concretes with compressive strengths greater than 50 MPa**, are included. In addition, some specification guidelines will be provided for slip-forming low w/c ratio concrete.

14.2 Controlling the initial temperature

It is important to control the initial temperature of low w/c ratio concrete because its rheology is very sensitive to temperature. Usually, low w/c ratio concretes contain a large amount of binder, often between 400 to 500 kg/m³

and 5 to 10 litres of superplasticizer. In Chapter 11, we have seen that the hydration reaction is accelerated by temperature according to an Arrhenius type of law, which is exponential. Therefore, it is very important to control the initial temperature of concrete to limit excessive slump variations at the delivery point.

To facilitate the placing of low w/c ratio concrete, it is important to deliver concrete that has a constant and adequate slump when it reaches the jobsite. The placing of too stiff a concrete can be very painful, slow, and costly in terms of manpower, particularly when the concrete elements are highly reinforced. The placing of too stiff a mix often results in unfilled parts of the structural element and honeycombing. On the other hand, placing a too fluid concrete can result in segregation and leakage through the form joints.

It is very important not only to specify the average temperature of the concrete at the delivery point, but also the acceptable range of variation of this temperature (e.g. between 20°C and 25°C) that ensures that placing conditions will not vary very much. Consequently, the concrete producer must determine precisely at which temperature the fresh concrete has to leave the batching plant in order to meet the temperature specification at the jobsite. This temperature depends on the initial temperature of the materials used to make the concrete, the external temperature, and the duration of the transportation.

In several cases, during the first experimental projects carried out at Sherbrooke University in the 1990s (Aïtcin, 1998), a test batch was produced a few days before the delivery of the low w/c ratio concrete in order to determine the amount of ice (in summer) or hot water (in winter) that had to be used:

- first, to deliver the concrete at a temperature within the specifications;
- second, to determine the effect of transportation time on the temperature of the concrete at the delivery point; and
- third, to determine the influence of a unit volume of ice or hot water on the final temperature of the concrete at the jobsite.

The amount of ice or hot water that had to be introduced at the batching plant was adjusted according to the phone calls received at the batching plant from the quality control team at the jobsite.

It is very important to specify an average temperature that is feasible with the particular ambient temperature at the jobsite. It is relatively safe to specify an average temperature between 20°C and 25°C in Montreal all year round (Morin *et al.*, 2002); in a hot country, it will be more feasible to specify an average temperature between 25°C and 30°C, or even between 30°C and 35°C in some exceptional cases. What is most important is to deliver a concrete having a constant temperature and consistency, whatever the selected average temperature range, to facilitate its placing.

The relevant City of Montreal (2005) specification (Section 5.7) reads:

Temperatures of material constituents shall be controlled in order to maintain the temperature of concrete at the point of delivery in the range of 5°C to 22°C if the smallest dimension of the cast element is less than 750 mm, or in the range of 5°C to 20°C if the smallest dimension of the cast element is more than 750 mm and in order to ensure that concrete temperature in the center of the element will not exceed 70°C at any time.

Note: It may be difficult to meet the restrictions relative to the concrete temperature whenever the ambient temperature is above 28°C.

14.2.1 Increasing concrete initial temperature

The necessity to increase the initial temperature of the concrete occurs in Canada late in the fall, in winter, or in early spring when the ambient temperature is below 15°C. At such temperatures hydration reactions are so slowed down (Arrhenius law) that they affect significantly the concrete early strength. Moreover, it must be remembered that polynaphthalene sulfonate superplasticizers have dispersing properties that decrease considerably below 10°C. It is therefore imperative to increase the temperature of the fresh concrete in such conditions.

Usually, the temperature of the fresh concrete is increased by using hot water. The formula

$$T = \frac{0.22(T_a M_a + T_c M_c) + T_w M_w + T_{wa} M_{wa}}{0.22(M_a + M_c) + M_w + M_{wa}} \quad (14.1)$$

where

T is the temperature in degrees Celsius of the fresh concrete.

T_a , T_c , T_w , and T_{wa} are the temperatures, in degrees Celsius, of the aggregates, cement, added mixing water, and free moisture on aggregates, respectively; generally $T_a = T_{wa}$.

M_a , M_c , M_w , and M_{wa} are the masses, in kilograms, of the aggregates, cement, free moisture on aggregates, and mixing water, respectively.

can be used to calculate the amount of hot water that has to be added to concrete in order to increase its initial temperature to the desired value (Kosmatka *et al.*, 2004). Of course, when increasing concrete temperature at the batching plant, the temperature decrease during transportation has to be taken into account. It is also important to specify the use of insulating blankets to protect the concrete surface from freezing after concrete placement in the case of sub-freezing temperatures.

14.2.2 Decreasing concrete initial temperature

Two techniques are available to decrease the initial temperature of concrete when it is too hot: ice or liquid nitrogen. In general, crushed ice is easier to work with than liquid nitrogen. The use of crushed ice is very simple and efficient, and it is already commonly used for normal strength concrete. In Canada, in summer it is now possible to rent ice-crushing machines for a specific project and to buy ice blocks or pre-weighed ice cube sacks.

$$T = \frac{0.22(T_a M_a + T_c M_c) + T_w M_w + T_{wa} M_{wa} - 80 M_i}{0.22(M_a + M_c) + M_w + M_{wa} + M_i} \quad (14.2)$$

where

T is the temperature in degrees Celsius of the fresh concrete.

T_a , T_c , T_w , and T_{wa} are the temperatures, in degrees Celsius, of the aggregates, cement, added mixing water, and free moisture on aggregates, respectively; generally $T_a = T_{wa}$.

M_a , M_c , M_w , and M_{wa} are the masses, in kilograms, of the aggregates, cement, free moisture on aggregates, and mixing water, respectively.

M_i is the mass of ice.

Some of the problems with liquid nitrogen are that it necessitates a costly installation, and it weakens the steel components of the mixers and of the trucks that are in direct contact with liquid nitrogen (steel become fragile). It produces a cloud of nitrogen vapour that can cause safety problems at the concrete plant. Nevertheless, many engineers have had good experience with nitrogen cooling and recommend it rather than crushed ice.

14.2.3 Night delivery

In order to avoid excessive variations of concrete temperature at the delivery point during the day, it is often far better to deliver low w/c ratio concrete at night (Aïtcin, 1998). During the day transportation time variations can result in significant variations of concrete temperature and consistency at the delivery point, and thus in variable placing conditions at the jobsite. These variable placing conditions can be costly for the contractor. To avoid this, the specifications of the City of Montreal require that low w/c ratio concrete placing start 30 minutes after sunset and stop 30 minutes before sunrise (Morin *et al.*, 2002).

Night delivery is also very desirable for the concrete producers because they can concentrate all of their effort on the production of a well controlled low w/c ratio concrete, since there are no other customers to deal with at the same time. The control of the water content of the aggregate, of the initial temperature, and of the slump can be monitored regularly.

Moreover, due to a shorter delivery time the concrete producer can save the use of one of two trucks and still provide a smooth delivery schedule to the contractor. Finally, as the control of the quality of the materials at the concrete plant is carried out regularly, very few or even no loads will be refused at the jobsite because they are outside of the specifications. Overall, it is more economical for a concrete producer to deliver low w/c ratio concrete at night in spite of the extra costs associated with night work. It is similarly more economical for the contractor as well. Night delivery also makes it easy to control the development of plastic shrinkage. In general, delivery of low w/c ratio concrete at night should be recommended when possible.

In order to benefit from the delivery of a concrete having a constant consistency and workability at the delivery point, it is important to use a cement–superplasticizer combination that is robust enough. Such a combination must not be much influenced by the predictable variations of delivery conditions that could affect the consistency and workability of the delivered concrete.

The City of Montreal (2005) specification for delivery, placing, and delays for concrete in general (Section 8) reads, in part, as follows:

8.1 Delivery

Concrete shall be delivered to the job site by truck mixers only. Delivery using non-agitating equipment is prohibited ...

The volume of the load of concrete shall not exceed 90% of the rated maximum mixing capacity ...

8.2 Pumping

The pipeline shall be maintained constantly full during pumping. The end of the line shall be provided with a reducer ... The vertical free drop of the concrete at the end of the line shall not exceed 1.5 m.

8.3 Hot Weather Concreteing of Exterior Elements

8.3.1 Unformed Flatwork

If it is expected that the daily ambient temperature may exceed 20°C, placement of concrete shall be performed only during the evening and night. Concrete placing may begin one hour before sunset, and finishing must be completed not later than one hour after sunrise.

8.3.2 Formed Elements

If it is expected that the daily ambient temperature may exceed 20°C, placing of concrete shall be performed only during the period between one hour before sunset and 11 a.m. the next day.

8.4 Evaporation Protection of Exposed Surfaces

Immediately following initial finishing (screeding, bullfloating, and darbying), avoid surface drying by spraying a fine water mist or by spraying an evaporation retarder on all flatwork and apparent unformed surfaces to coat them completely and uniformly ...

The water and evaporation retarder should be applied continuously in order to maintain the surface continuously humid until the end of the final finishing (screeding and bullfloating). The quantity of water or evaporation retarder that is vaporized must not exceed the quantity of water evaporated from the surface. Assign sufficient labor exclusively to this task in relation to the size of work.

All equipment and materials necessary for the application of the evaporation retarder ... shall be available on site ... prior to the beginning of concrete placing.

Provide a mobile working walkway spanning the full width of the freshly placed concrete surface to allow workers to perform localized surface repairs if needed, and to apply the evaporation retarder and spread the curing membranes ...

8.5 Delays or Concrete Placement

Discharge of a load of concrete shall be complete within 90 minutes from the time of batching.

Reject all concrete that has remained longer than 15 minutes in the pipeline of the pump.

14.3 Entrained air or not?

This is not a relevant question in Canada. In order to successfully pass the ASTM C 666 Procedure A test method for freezing and thawing resistance, all low water–binder ratio concretes must contain some entrained air with a maximum spacing factor. The only difference is that in the case of low w/b concrete the maximum value of the spacing factor can be relaxed somewhat. CSA Standard A 23.1 requires a spacing factor smaller than 220 micrometres for usual concrete and of 250 micrometres (with no individual value greater than 300 micrometres) for low w/c ratio concrete. When these last two values cannot be met (which usually occurs after pumping) the ASTM C666 test has to be carried out to find the maximum spacing factor that is acceptable to withstand either 300 or 500 freezing and thawing cycles, depending on the severity of the freezing and thawing conditions in the particular location in which the low w/c ratio concrete will be used.

However, in countries less exposed, or not exposed at all, to freezing and thawing, is it relevant to specify entrained air in low w/c ratio concrete? Our answer is emphatically “yes”!

It is true that the addition of about 3.5% to 4.5% of entrained air will decrease somewhat the compressive strength. However, it so much decreases the stresses necessary to shear the fresh concrete that it greatly facilitates its placement, because air entrained high-performance concrete is much less viscous. The decrease in compressive strength can easily be taken care of by decreasing somewhat the w/c ratio to reach the same compressive strength as the non-air entrained concrete. We recommend that, whatever the field conditions are in regard to freezing and thawing all low w/c ratio concretes contain some entrained air. Of course, the spacing factor of this entrained air is of concern only when freezing and thawing conditions are severe, as in Canada. We are not alone in recommending this practice; in Japan, to improve placing conditions, all low w/c ratio concrete contains some entrained air.

14.4 External curing

All free concrete surfaces must receive external curing in order to reinforce the concrete “skin”, because the durability of a concrete structure is strongly dependent on the quality of the skin. However, as stated in Chapter 13, the type of external curing selected depends on the w/b of the concrete. Consequently, it is absolutely necessary:

- to specify very precisely the type of external curing that the contractor will have to implement: fogging, watering with a hose, wet burlap, geotextiles, and so on;
- to ask the contractor to price each item so that curing becomes a profitable operation for the contractor’s company; and
- to specify the type of control that will be used to check the adequacy of this external curing and its frequency.

14.4.1 Fogging

Fogging must be applied when plastic shrinkage is a concern with any type of concrete. As stated earlier, the use of sprayers such as the ones used in flower nurseries is convenient, efficient, and inexpensive. Fogging should stop when the concrete surface is hard enough to support direct water curing with a hose. Usually, 24 hours of fogging is sufficient. Fogging must start 15 minutes after the finishing of the surface. Specifications must be detailed enough to indicate:

- the number of sprayers to be used;
- the moving system to be installed;

232 *Specifying durable and sustainable concrete*

- the number of workers involved (though usually one is enough); and
- the source of the water to be used.

The contractor must provide a unit cost per hour for fogging.

14.4.2 *Direct water curing*

Direct water curing is mandatory on concrete surfaces when the w/b is less than 0.42, to avoid the development of early autogenous shrinkage within the concrete skin. Specifications must clearly indicate:

- when the direct water curing is to begin;
- how many workers will be involved;
- the source of the water;
- the duration of the direct water curing; and
- the type of water curing; hose, or wet geotextiles (mass/m²).

We do not believe in wet burlap coverings; our experience is that they are almost dry most of the time, and that their capacity of water retention is too low compared to geotextiles.

14.4.3 *Evaporation retarders*

The use of evaporation retarders is mandatory if fogging is not applied to concrete with a w/b less than 0.42 until direct water curing is applied. If fogging is employed, the use of a curing membrane must be prohibited, because it will prevent water from penetrating into the concrete skin when the water curing starts.

14.4.4 *City of Montreal curing specifications*

The City of Montreal (2005) curing specification reads in part (Sections 9.2 and 9.3):

9.2 Curing of Unformed Flatwork

Immediately following final finishing (floating and trowelling) of exposed flatwork surfaces, continue the application of a fine water mist or an evaporation retarder ... until the surface is sufficiently firm, so that it can be covered without danger of marring it, with two layers of absorptive synthetic fiber mats ... The membranes should cover completely the concrete and should be adequately held in place. Maintain the fabric or mats continuously wet by continuous sprinkling of water until the time when the concrete has hardened sufficiently to permit installation of a continuous wetting system without damaging the concrete surface. Maintain water curing 24 hours per day at a temperature above 10°C for an uninterrupted period of 7 days.

9.3 Curing of Formed Elements

As soon as the forms are filled, cover them completely with two layers of prewetted absorptive fiber mats ... Hold the wetted mats in place and maintain them continuously wet by continuous sprinkling water onto the membranes until the concrete has hardened sufficiently to permit installation of a continuous wetting system without danger of damaging the surface by scouring.

If a form liner is used, avoid all presence of free water at the exposed concrete surface at the top of the formwork until the removal of side forms. At the time of form removal, ensure that the concrete is sufficiently hard to avoid the risk of pulling the concrete surface layer with the form liner in case the liner adheres to the concrete surface.

Remove the side forms as soon as possible after concreting ... In the case of elements with a length-to-height ratio greater than 2, as in the case of grade separation walls, retaining walls, or median barriers, remove the side barriers within 12 to 20 hours after concreting. Take necessary precautions to avoid damaging the concrete during form removal.

If form removal requires interruption of curing, take the necessary measures in order to avoid surface drying and to shorten as much as possible the duration of the interruption.

Maintain the mats in place and wet by continuous sprinkling of water 24 hours a day at a temperature above 10°C for an uninterrupted period of 7 days.

In the case of massive, non-reinforced elements, extend the curing time by 3 additional consecutive days.

14.5 Internal curing

As discussed in the previous chapter, internal curing will drastically reduce the risk of early cracking in low w/b concrete ($w/b < 0.35$) due to the rapid development of autogenous shrinkage when the concrete is still weak in tension. It will also permit the long-term hydration of supplementary cementitious materials, which tend to hydrate slowly (Kovler and Jensen, 2007; Villarreal and Crocker, 2007). However, it is very important to specify clearly the type of internal curing that is to be implemented: lightweight sand, lightweight coarse aggregate, or both. Further, the specifications must indicate the proportions of sand and coarse aggregate to be substituted. It is necessary to take into account the porosity of the materials to be used, or to specify the number of litres of water that must be stored in these lightweight materials.

Some companies provide a lightweight sand in a pre-wetted form. Usually, coarse lightweight aggregates are delivered dry, so they must be stored under sprinklers in the field in order to become saturated.

14.6 Expansive admixtures

When expansive admixtures are used (instead of internal curing) to mitigate the early development of autogenous shrinkage, it is important to specify clearly the type (or brand name) and the maximum dosage (in kg/m^3).

14.7 Shrinkage reducing admixtures

When using shrinkage reducing admixtures, the type (or brand name), as well as the recommended dosage rate, must be specified.

14.8 Slip-forming

Slip-forming is a special technique of construction used when the presence of cold joints could decrease the tightness of the structure. It is used mostly to build water-tight or gas-tight reservoirs: silos, offshore platforms, or liquefied gas tanks; it is also sometimes used for very tall structures such as the 553.33 metre high CN Tower in Toronto. These structures are built in a non-stop mode. The forms are moved up by a series of hydraulic jacks that are supported on the reinforcing steel as soon as the concrete starts to harden. Usually, slip-forming is characterized by the upward rate of form movement expressed in metres per day or per shift. This rate of slipping is a function of the placing rate that it is possible to achieve. It depends on the rate of production of the concrete plant, the complexity of the structure, the time necessary to place the reinforcing steel, the temperature, and so on.

When a feasible slip-forming rate has been chosen, it is necessary to produce concrete that leaves the slip-form at a consistency close to that of initial set. If the concrete leaves the slip-form before it has reached this consistency it will be unable to support the stresses induced by its own weight and the hydraulic jacks supporting the weight of the forms, and the fresh unformed concrete will collapse. On the other hand, if the concrete hardens too fast within the slip-form, some of it sticks to the form and tears the surface of the concrete leaving the forms. This may be more or less severe depending on how hard it is, that is, on how long after initial set it leaves the forms. In this case, the first layer of reinforcing steel will no longer have the specified cover.

Therefore, it is usually crucial to adjust very precisely the setting time of concrete to the rate of slip-forming that has been specified. This is usually done by retarding the setting time of the cement using a retarder, taking into account the temperature of the concrete. As already noted, concrete setting and hardening are temperature dependent, according to the Arrhenius law, that is, the rate of hydration is linked to temperature by an exponential law. In the case of a low water–binder ratio concrete, adjustment of the setting time is complicated by the use of superplasticizers that also influence setting time. In Canada, the adjustment of concrete characteristics is even more

complex because the concrete must also be air entrained for frost resistance. However, all of the necessary adjustments can be determined through very tightly controlled laboratory work and quality control programs. As a slip-forming operation can extend over several weeks or even a few months in the case of large offshore platforms, it is very important to readjust the retarder dosage to take into account the seasonal variation of the average temperature.

Moreover, when slip-forming, it is crucial that the concrete hardens everywhere within the forms at the same rate in order to leave of the slip-forms at the same consistency and strength. If the temperature is not uniform all around the slip-formed structure, problems can occur when the concrete leaves the slip-form: in the coldest parts it deforms because it is too soft and in the hottest parts it sticks to the form because it is too hard and tears the surface. To avoid such problems, it is necessary to specify that the slip-forms be covered with an insulating material. This insulating material isolates the concrete inside the slip-form from the influence of external temperature (Aïtcin, 2009). If the slip-forms are insulated, the concrete that is cast at a constant initial temperature leaves the insulated forms at a constant temperature and consistency all around the structure (Lachemi and Elimov, 2007).

14.9 Specifying testing age and testing conditions

As for usual concrete, low w/b concrete is most commonly specified on the basis of its 28-day compressive strength. This is a very simple way to specify low water–binder ratio concrete and, of course, it is easy to check the compliance of the concrete with the specification. We are not at all convinced that low water–binder ratio concretes should always be tested at 56 or 91 days even though they generally contain some supplementary cementitious materials that have not had enough time to react (except when some form of internal curing has been provided). **Testing low w/b concretes at later ages should only be done when curing in the field has been carried out properly and has been strictly supervised.** Otherwise, the supplementary cementitious materials will only act as fillers, which is not the case for the control samples that will be properly cured in a moist curing room in the testing laboratory. The presence of water is essential for the supplementary cementitious materials to react and free water is scarce in high-performance concrete when most of the cement particles have reacted. However, when some internal curing is provided, the water accumulated in the reservoirs introduced in the concrete can react with the supplementary material and increase concrete strength after 28 days

It is better to test low water–binder ratio concrete on 100×200 mm cylinders or $100 \times 100 \times 100$ mm cubes in order to limit the breaking load; it would otherwise require an extremely high capacity (and expensive) testing machine. However, low water–binder ratio concrete cannot be tested like

usual concrete: a capping compound should not be used; instead, the ends of the specimens must be ground. The faces of the specimen in contact with the platens of the testing machine must be absolutely parallel, the applied load must be perfectly centred, the testing machine must be very rigid, and the specimens must be tested within a protective cage because failures can be explosive (Aitcin, 1998).

14.10 Quality control

For low w/b concrete, it is essential that the control of the quality of the concrete is carried out in strict compliance with the specifications; unlike usual concrete, low w/b concrete is not a very “forgiving” material if it is not properly produced at the batch plant and properly handled in the field. The City of Montreal (2005) specification for quality control of low w/b concrete (compressive strength > 50 MPa) in general reads (Section 11) in part:

11.0 Quality Control

11.1 General

The Director may at his discretion take samples of the materials or of the concrete at the batching plant of the concrete supplier or at the site, in order to perform tests to verify their compliance with the data provided by the HPC supplier ...

The Director may verify at the site, at the frequency of his choice, the characteristics of the concrete ... on concrete samples taken at his discretion at the point of delivery or any other location he may consider appropriate.

Note: Slump is usually verified on every second or third load and whenever a sample for compression tests is taken. Air content and temperature are generally verified on every load.

The contractor shall ... provide and ensure the protection of the compression test samples during all the time of their conservation at the site ...

Note: This may require air conditioning of the environment in which the samples are conserved.

11.2 Slump

If the slump of a load of concrete at the point of delivery exceeds 220 mm, that load is rejected. If the measured slump is less than 140 mm, it may be corrected by the addition of superplasticizer. Following the first addition of superplasticizer at the batching plant, only one more addition is permitted at the site.

Addition of water to the concrete at the site is prohibited.

11.3 Air Content

If the air content of a load of concrete exceeds the maximum limits prescribed ... by more than 0.5%, the load of concrete shall be rejected. If the air content is less than 0.5% lower than the lower limits of the ranges of air content (prescribed) ... the load of concrete shall be adjusted using an air-entraining admixture. The adjustment of the air content shall only be carried out by qualified personnel of the concrete supplier.

The above requirements apply also after the addition of superplasticizer at the site.

11.4 Temperature

If the temperature of a load of concrete at the point of delivery exceeds the maximum limit prescribed ... the load of concrete is rejected.

11.5 Delays for Placing

If the delays prescribed ... are exceeded, the not yet placed concrete is rejected.

11.6 Compressive Strength

Compressive strength is verified on cylinders molded from samples of concrete obtained according to the frequency or the opportunity established by the Director.

Note: Generally, the frequency is one sample taken at random for each 50 m³ of concrete placed. In no case shall there be less than one sample taken on any one day of concreting.

Initially, the first samples consist of a group of 6 cylinders, of which 2 are tested at 24 hours, 2 at 7 days, and 2 at 28 days. For regular control, a group of four cylinders are taken, of which 2 are tested at 7 days and 2 at 28 days. Two additional cylinders are taken whenever the compressive strength is specified at 91 days.

If the test results indicate that the concrete does not meet the strength specified in the contract documents ... it is considered as non-complying with this Standard Specification. The Director may at his discretion either reject the concrete, or prescribe additional testing ... and require if necessary appropriate corrections at the expense of the contractor.

11.7 Air-Void System and Durability

If the air-void system or durability does not comply with ... this Standard Specification, the Director may at his discretion either reject the concrete, or require appropriate corrections at the expense of the contractor.

11.8 Chloride-Ion Permeability

If the chloride-ion permeability does not comply with ... this Standard Specification, the Director may at his discretion either reject the concrete, or require appropriate corrections at the expense of the contractor.

11.9 Scaling Resistance

If the scaling resistance does not comply with ... this Standard Specification, the Director may at his discretion either reject the concrete, or require appropriate corrections at the expense of the contractor.

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15 Performance specifications

15.1 Introduction

In recent years, we have learned how to produce a remarkable range of concrete products: ultra-high strength concrete, self-compacting concretes, corrosion inhibiting concretes, “tough” concretes (with the addition of fibres), and now even *sustainable* concretes. In fact, we can now largely “tailor-make” concretes for virtually any project. However, in our approach to mixture proportioning, we still rely largely on *prescriptive* specifications, such as those described in Chapter 14. That is, specifications that generally include requirements such as maximum w/b ratios, minimum cement contents, cement types, limitations on the types and/or amounts of both chemical and mineral admixtures, on the amount of filler material in the cement, and so on. These types of specifications have served us reasonably well in the past, when the cement and concrete industries as a whole were much less sophisticated than they are now. However, such specifications also tend to inhibit the most efficient use of the materials now available to make up a concrete mixture.

An unintended consequence of this approach to the design of concrete mixtures is that it has tended to inhibit the most efficient use of the many materials now available to make up a concrete mixture. Also, these specifications are still primarily strength based. While modern design codes do, of course, include some provisions for durability, it remains the case that the primary criterion now used for judging the adequacy of concrete in a structure is its compressive strength (f'_c). For new construction, the typical acceptance criterion is that the average measured compressive strength must exceed f'_c by a statistical factor that takes into account the variability in the test data. For *in situ* concrete that is suspected of having suffered damage, the North American acceptance criterion is that the average strength of drilled cores should exceed $0.85f'_c$. Unfortunately, this turns out to be far from a guarantee of concrete adequacy. Two batches of concrete, made following exactly the same “recipe”, but with different starting materials, may exhibit very different properties. All too frequently, we encounter concrete durability problems, severely cracked or spalled concrete, and

failures of concrete structures; indeed, at least in North America, concrete construction litigation continues to be a growth industry!

In light of the above, it is now time to embrace a much more extensive use of *performance-based* specifications. If these can be properly devised they would permit concrete producers to be more imaginative, competitive, and innovative in their use of materials, such as supplementary cementing materials, admixtures, blended cements, polymers, fibres, mineral fillers, and so on. They would also provide a means of introducing durability concerns more explicitly into the design of concrete mixtures.

15.2 What is a performance specification?

There are a number of different definitions of performance specifications; the one used by the National Ready Mixed Concrete Association (NRMCA) is perhaps the most useful (Bickley *et al.*, 2006):

A performance specification is a set of instructions that outlines the functional requirements for hardened concrete depending on the application. The instructions should be clear, achievable, measurable and enforceable. For example, the performance criteria for interior columns in a building might be compressive strength and weight since durability is not a concern. Conversely, performance criteria for a bridge deck might include strength, permeability, scaling, cracking and other criteria related to durability since the concrete will be subjected to a harsh environment.

Performance specifications should also clearly specify the test methods and the acceptance criteria that will be used to verify and enforce the requirements. Some testing may be required for pre-qualification and some might be for jobsite acceptance. The specifications should provide flexibility to the contractor and producer to provide a mix that meets the performance criteria in the way they choose. The contractor and producer will also work together to develop a mix design for the plastic concrete that meets additional requirement for placing and finishing such as flow and set time while ensuring that the performance requirements for the hardened concrete are not compromised. Performance specifications should avoid requirements for means and methods and should avoid limitations on the ingredients or proportions of the concrete mixture.

A more succinct definition is given in the Canadian Standard CSA A23.1:

A performance concrete specification is a method of specifying a construction product in which a final outcome is given in mandatory language, in a manner that the performance requirements can be measured by accepted industry standards and methods. The processes,

materials, or activities used by the contractors, subcontractor, manufacturers, and materials suppliers are then left to their discretion. In some cases, performance requirements can be referenced to this Standard [CSA A23.1], or other commonly used standards and specifications, such as those covering cementing materials, admixtures, aggregates, or construction practices.

In both of these definitions, the intent is clear: to prescribe the required properties of the concrete in both the fresh and hardened states, but without saying how they are to be achieved.

15.3 How do we move from prescription to performance?

If we are to move from prescriptive specifications to performance specifications, we must satisfy a number of criteria, the most important of which include:

- the ability to determine in some detail the performance characteristics that are appropriate for the intended use of the concrete;
- the ability to describe these characteristics in a clear and unambiguous manner;
- the ability also to describe these performance characteristics quantitatively, so that they can be measured;
- the availability of widely accepted and reliable test methods, so that the performance characteristics can be measured;
- the ability of the entire group of people involved in the construction (engineer/architect, specifier, contractor, sub-contractor) to make informed choices regarding the materials, mixture design, construction techniques, and so on, so that the project can be planned, bid, and carried to a successful conclusion.

The above would effectively “raise the bar” for concrete construction.

While this would appear to be a straightforward proposition, there are a number of obstacles to be overcome before we can implement performance specifications (Skalny *et al.*, 2006).

- Many concrete producers are not currently prepared to switch from prescriptive to performance specifications, mostly due to a lack of properly trained personnel to provide the necessary technical advice to specifiers and structural engineers, and to deal with complex quality control issues. Indeed, specifications are commonly written “to accommodate the lowest common denominator of technical expertise” (Weir, 2010).
- There is a lack of quick, reliable tests for concrete durability, but such tests are necessary if we are to go beyond our reliance on the

28-day compressive strength as the primary arbiter of concrete quality. This is one of the main factors inhibiting the move to performance specifications.

- There would have to be some way of *assigning responsibility* for the concrete quality. Currently, this responsibility appears to be rather loosely shared amongst the structural engineer, the geotechnical engineer, the cement producer, the concrete supplier, the contractor, and perhaps others as well. This means that all too often oversight of the concrete itself falls between the cracks. This does not inspire much confidence in the entire process.

Of course, the move from prescriptive to performance standards will not be quick or easy, partly because of the lack of durability tests mentioned above, and partly because of the conservatism of the concrete industry. However, it will certainly come eventually. Meanwhile, as we wait for the new durability tests to be developed and accepted, we may have to rely upon the “equivalent performance” concept. That is, a new concrete mix will be deemed to be satisfactory if it behaves as least as well as a mix already known to be durable under the expected service conditions.

15.4 Sustainability and specifications

The link between sustainability and specifications derives from the fact that most specifications remain prescriptive, and these prescriptive specifications tend to be very conservative (some would say old-fashioned) in their approach to concrete as a material. This is in stark contrast to the concrete structural design codes, which tend to incorporate current research findings much more readily.

15.4.1 *Specifications and the use of supplementary cementing materials*

The most obvious and straightforward way of improving concrete sustainability is to replace as much of the cement as possible with supplementary cementing materials (SCMs), without of course reducing the quality of the concrete, or making it too expensive. The technical issues surrounding the use of SCMs have already been discussed in detail (Chapter 5). Here we will deal with the more practical issue of how to increase the use of SCMs by the concrete industry.

Canada’s *National Master Specification* (2004) makes several statements about the desirability of using SCMs and recycled materials:

Choose products and materials with recycled content or resource efficient characteristics whenever possible.

It goes on to say,

... the use of Supplementary Cementing Materials (SCMs) such as fly ash, ground granulated blast-furnace slag (GGBFS), silica fume or natural pozzolans, should be considered as partial replacement of cement in concrete, in order to reduce greenhouse gas emissions (GHG), unless it is not technically or economically feasible. The use of recyclable industrial by-products such as SCMs, results in sustainable “green” concrete and offers additional benefits including an increase in the conservation of raw materials, energy, resource recovery, and a reduction in the quantities of waste requiring disposal.

Consistent with this, the newly constructed Vancouver Olympic Village was built with concrete containing up to a 50% fly ash replacement (Hooton and Weir, 2010), and high fly ash replacement values are becoming increasingly common in Canada. However, the national specifications tend to be modified by the various provinces and municipalities, and there is thus considerable variation from province to province. The permissible amounts of SCMs most commonly range from about 10% to about 30%, depending on the particular jurisdiction. In addition, in some areas, fly ash is not permitted for winter concreting; it may only be used in the summer.

In the United States, there are also no truly binding national specifications; they vary from state to state. Probably the most authoritative specifications in each of the 50 states are those adopted by the individual state Departments of Transportation (DOT). At present, these are all quite prescriptive for structural concrete. Some offer little or no guidance as to the use of SCMs; the Illinois DOT states simply that “substitutes shall not be allowed for Portland cement unless approved by the Engineer”. More commonly, specific limits are imposed on SCMs. For instance, the Michigan DOT limits fly ash to 25% of the total binder, and slag to 40%; the Florida DOT limits fly ash to 18%–22% of the total binder, fly ash to 7%–9%, and slag to between 35% and 70%; the Texas DOT limits fly ash to 35% and silica fume to 10%, with a maximum SCM content (including slag) of 50%. **Note:** The values just given are those used in the current (2010) DOT specification for the various states. These are subject to constant revision, and the interested reader should always refer to the most recent version of these specifications.

A more elaborate limit is imposed by the California DOT (CALTRANS), which *requires* the use of at least one SCM. Their specification states that:

The SCM content in Portland cement concrete shall conform to one of the following:

A. Any combination of Portland cement and at least one SCM, satisfying Equations (1) and (2).

Equation (1):

$$[(25 \times UF) + (12 \times FA) + (10 \times FB) + (6 \times SL)]/MC = X$$

where

UF = Silica fume, metakaolin, or UFFA (ultra fine fly ash), pounds per cubic yard

FA = Fly ash or natural pozzolan ... Class F or N with a CaO content up to 10%, pounds per cubic yard

FB = Fly ash or natural pozzolan ... Class F or N with a CaO content up to 15%, pounds per cubic yard

SL = GGBFS (ground granulated blast furnace slag), pounds per cubic yard

MC = Minimum amount of cementitious material specified, pounds per cubic yard

X = 1.8 for innocuous aggregate, 3.0 for all other aggregates.

Equation (2):

$$MC - MSCM - PC = 0$$

where

MSCM = The minimum sum of SCMs that satisfies Equation (1) above, pounds per cubic yard

PC = The amount of Portland cement, pounds per cubic yard.

This indicates a maximum SCM replacement of 50%, and a minimum fly ash content of about 25% (for a typical mix containing 675 pounds per cubic yard of binder for structural concrete).

B. 15% of Class F fly ash with at least 48 ounces of LiNO_3 solution added per 100 pounds of Portland cement. CaO content of the fly ash shall not exceed 15%.

Note: Lithium nitrate can be used to mitigate alkali-silica reactivity (ASR) in concrete.

These various code limitations stem, in part, from some concerns (both real and perceived) regarding the use of SCMs, and fly ash in particular. These include the possibility of delayed setting time and rate of strength gain, reduced scaling resistance, more stringent curing conditions, finishing difficulties, and a lack of properly trained work crews. While these can all be

overcome by proper mix design and construction practices, they do remain a significant barrier to more extensive use of SCMs.

From the above, it may be seen that the various Canadian and American requirements for structural concrete can be quite different (even though the laws of physics and chemistry are the same everywhere, and the quality of available raw materials is not all that variable)! However, they are all prescriptive to a greater or lesser degree. More particularly, they all place limits on the use of supplementary cementing materials; mostly, these limits are well below the substitution levels that both research and practice have shown to be feasible. This is not necessarily true in other parts of the world, where the use of SCMs is more readily accepted than in North America.

15.5 Establishing performance specifications

With the conventional prescriptive specifications, the owner specifies the mix proportions, the materials to be used (including admixtures), the concrete properties (slump, air content, strength), and any other requirements; *the owner thus assumes full responsibility for the concrete*. The contractor and the materials supplier simply have to follow these specifications to the letter, though they may point out to the owner any potential deficiencies of the mix, and suggest remedies.

The use of performance specifications, however, requires a full measure of cooperation amongst the owner, the contractor, and the materials supplier. In this case, the owner specifies the required concrete properties in both the fresh and hardened states, including strength and durability, architectural requirements, **sustainability**, and any other relevant requirements; the list of potential requirements can be quite long, as shown in Table 15.1 (adapted from Bickley *et al.*, 2006), though it is unlikely that most of these would be required for any particular project. The supplier then assumes full responsibility for delivering the appropriate concrete to the site, and the contractor assumes the responsibility for placing and curing the concrete properly. This requires the contractor and the supplier to work together, taking into account the materials available and the practicalities of placing the concrete for a particular project.

Unfortunately, as mentioned earlier, contractors and suppliers often do not have the expertise to deal properly with performance specifications, and there is no way as yet to “qualify” them in this regard. Even if they are properly qualified, this may be a disadvantage in the common “low bid” situations, since the best solution in terms of compliance with the owner’s requirements may not be the cheapest.

15.6 Examples of performance specifications

At this time (2010), though many jurisdictions are considering the use of performance specifications, and some even have draft provisions for this, the

Table 15.1 Some concrete properties for performance specifications

<i>Fresh concrete</i>	<i>Transition</i>	<i>Hardened concrete</i>
Workability	Rate of slump loss	Compressive strength
Slump	Time to initial set	Tensile strength
Response to vibrator	Time to final set	Flexural strength
Pumpability	Rate of strength gain	Shear strength
Finishability	Rate of stiffness gain	Fatigue strength
Segregation	Time to frost resistance	Fracture toughness
Bleeding	Evaporation rate	Elastic properties
Air content	Plastic shrinkage	Creep
Stability of air bubbles	Drying shrinkage	Porosity
Uniformity of mixing	Temperature changes	Pore size distribution
Consistency of properties		Permeability
Temperature		Air-void system
Yield		Frost resistance
		Abrasion resistance
		Sulfate resistance
		Acid resistance
		Alkali resistance
		Thermal volume change
		Heat capacity
		Thermal conductivity
		Electrical conductivity
		Density
		Radiation absorption
		Colour
		Texture
		Cost
		Carbon footprint (sustainability)

Reproduced from Bickely *et al.* (2006). (Courtesy of the RMC Research and Education Foundation, 900 Spring Street, Silver Spring, MD 20910; www.rmcfoundation.org).

use of pure performance specifications is rare. At best, there are “hybrid” systems, in which there is a combination of (mostly) prescriptive and some performance specifications (Taylor, 2004).

However, there have been some notable examples of the successful use of performance specifications in major projects:

- The Two Union Square building in Seattle is a 230 m high structure. The design specification was based on the elastic modulus of the concrete, which was required to be 49.7 GPa (7.2×10^6 psi), about twice that for usual concrete. This was done to meet the criterion for occupant comfort, by reducing the amount of side sway of the completed structure due to high winds (Godfrey, 1987). Although the design compressive strength was “only” 96.5 MPa, the compressive strength needed to

reach this high elastic modulus ended up being 131 MPa at 56 days, achieved with a w/c of 0.22.

- More recently, a bridge deck in the Boston (USA) area was specified on the basis of its chloride permeability, which was required to be less than 1000 coulombs. This was achieved using a silica fume cement.
- The concrete for the reconstruction project at Ground Zero in New York has also been specified not on the basis of its strength but on the basis of its modulus of elasticity. This will require the importation (by boat) of the coarse aggregate from Nova Scotia, Canada.

These are only three examples of a growing trend to move away from specifying concrete based primarily on its compressive strength. We hope that this trend will continue at an even faster pace in the future.

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16 Statistical evaluation of concrete quality

16.1 Introduction

In spite of all the attention paid to:

- controlling the variability of the materials used to make low w/c ratio concrete,
- weighing or metering these materials in sophisticated automated installations,
- testing the concrete according to precise and stringent standards,

low w/c ratio concrete remains a material made and tested by humans and whose properties are affected by ambient temperature over which we have no control. Therefore, low w/c ratio concrete is variable, like any regular concrete. So, we must still ask:

- How variable is it?
- How is it possible to reduce this variability?
- How can we be sure that this variability does not affect the safety of the structure?

These aspects of concrete require some statistical treatment. It is the objective of this chapter to present some basic and practical notions that are commonly used when establishing statistical control over any concrete production (Valles, 1972; Day, 1995; Schrader, 2007). This matter is often not well covered in concrete courses.

16.2 Normal frequency curve

16.2.1 *Variability of concrete properties*

When measuring any particular characteristic of concrete, the numerical value obtained at the end of the control process depends on a large number of factors that are independent of each other and whose variation is limited.

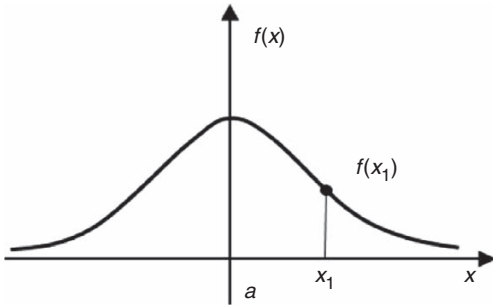


Figure 16.1 Normal frequency distribution curve. In this representation, the y axis has been placed at the average value, a , and $f(x)$ represents the number of samples having the value x_1 .

In such a case, statisticians tell us that the numerical values obtained obey a normal frequency distribution law also called a “normal law”, or “Laplace–Gauss law”, whose graphical representation is the well-known bell-shaped curve (Figure 16.1).

In spite of the fact that the normal frequency curve implies an infinite number of values, it is very useful to know its properties when dealing with the numerical values of a limited number of tests carried out on a selected number of specimens amongst a finite population corresponding to the number of the concrete deliveries that have been tested. Consequently, it is very useful to look at this general law and to apply some of its properties to the statistical control of concrete production.

16.2.2 Mathematical expression of the normal frequency curve

The probability density $f(x)$ for each value X of a characteristic is

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left[\frac{-(x-a)^2}{2\sigma^2}\right] \quad (16.1)$$

where a represents the average value, σ^2 represents the variance, and σ represents the standard deviation. Usually, instead of using X , it is better to use the reduced centre value:

$$x = \frac{X - a}{\sigma}$$

In this case, the origin of the abscissa is the average value, a , and the values are measured with units equal to the standard deviation. Equation (16.1)

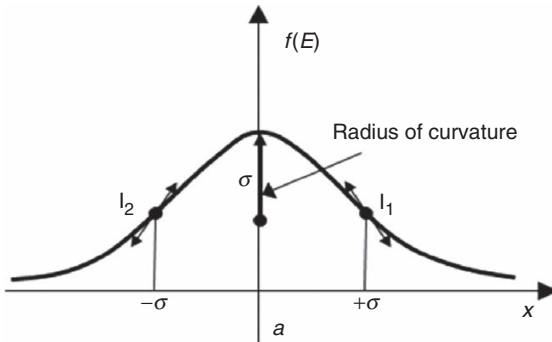


Figure 16.2 Some properties of the bell-shaped curve. I_1 and I_2 are the inflection points of the bell-shaped curve.

then becomes:

$$f(x) = \frac{1}{\sqrt{2\pi}} \cdot \exp\left(\frac{-x^2}{2}\right) \quad (16.2)$$

Equation (16.2) gives the bell-shaped curve that is represented in Figure 16.2.

16.2.3 Some properties of the normal frequency curve

A normal frequency curve corresponding to an infinite number of values is entirely defined when we know the average value, a , and the standard deviation, s . The average value gives the position of the axis of symmetry of the normal frequency curve on the O- x axis and the standard deviation gives the general shape of the curve: the smaller the standard deviation, the sharper the curve. In fact, the standard deviation represents the abscissa of the two inflection points on the bell-shaped curve and at the same time the radius of curvature at the top of bell-shaped curve, as shown in Figure 16.2.

Figure 16.3 shows two normal frequency curves having the same average value but different standard deviations. In the case of the normal frequency curve (I) corresponding to the lowest standard deviation, most of the x values are close to the average value. In the case of the normal frequency curve (II), the values of x are spread over a greater distance from the average value.

16.2.4 Areas under the normal frequency curve

As seen in Figure 16.4, the area under the curve lying between:

- σ and $-\sigma$ is equal to 68.2%

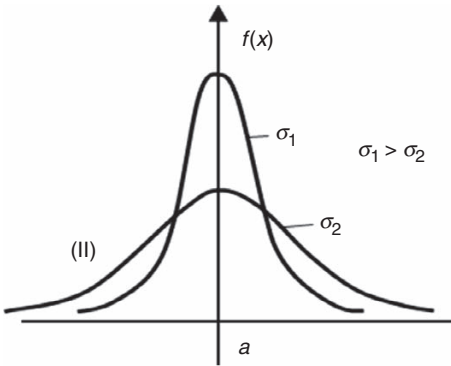


Figure 16.3 Comparison of two bell-shaped curves having the same average value but different standard deviations.

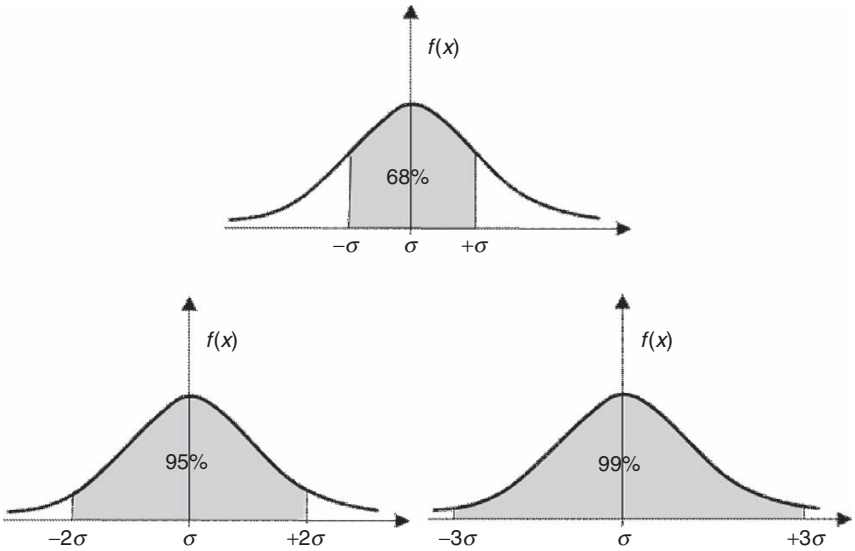


Figure 16.4 Areas under the normal frequency curve for specific values of σ .

- 2σ and -2σ is equal to 95.2%
- 3σ and -3σ is equal to 99%.

In Figure 16.5, the area under the curve to the left of x_1 represents the number of values lower than x_1 . Tables giving the area to the left of x_1 are available; they give the probability of having a value of $f(x)$ lower than x_1 .

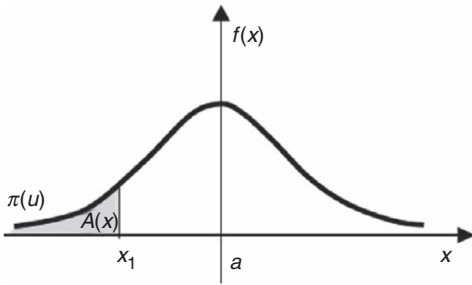


Figure 16.5 When compared to the total area under the bell-shaped curve, the area $A(x)$ at the left of x_1 represents the percentage of the values having a value smaller than x_1 .

16.2.5 Coefficient of variation

The coefficient of variation, V , expressed as a percentage, is frequently used to characterize the shape of a distribution curve. It is calculated as follows:

$$V = (\sigma/a) \times 100\% \quad (16.3)$$

16.3 Controlling the quality of concrete production

Generally, concrete quality is tested by measuring the compressive strength of a set of two or three specimens. When controlling concrete production, it is not practical to measure the compressive strength of each truck load. The control is instead carried out on a limited number of loads, chosen using a random number table. To carry out a useful statistical analysis, it is necessary to have at least 30 individual results. However, before doing any calculations on a set of values obtained when carrying out this control, it is important to check that this set of results has a distribution approaching that of a normal distribution curve.

16.3.1 Histogram

The numerical values are separated in different classes, the number of tests falling within each class are counted, and a histogram is drawn (Figure 16.6). When preparing the histogram, it is important to carefully select the value of the unit cell in which the numerical values are classified. When testing concrete strength, it is often convenient to use a unit cell corresponding to 2 MPa. Usually, when characterizing concrete compressive strength, the histograms obtained have a shape that looks roughly like a normal distribution curve, as seen in Figure 16.6, but there are some cases in which the shape can be quite different, as seen in Figure 16.7.

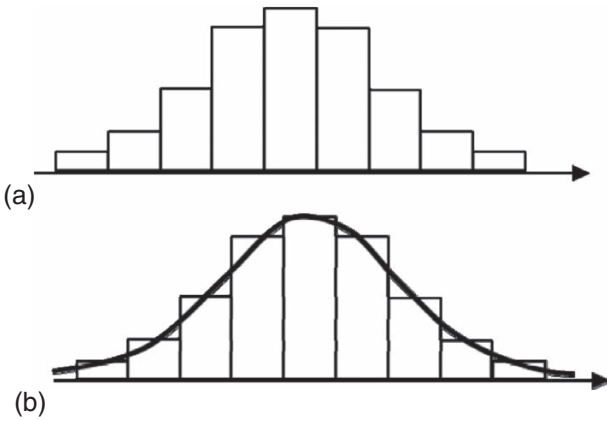


Figure 16.6 (a) Histogram and (b) histogram with a fitted distribution curve.

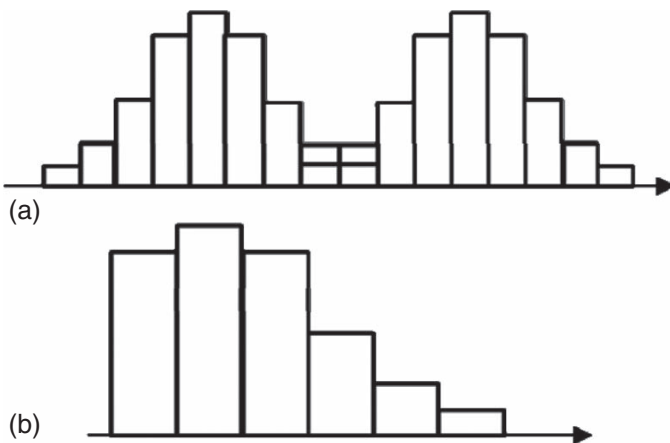


Figure 16.7 Examples of histograms that cannot be fitted by a bell-shaped curve. (a) A mix of two sets of values each obeying a normal distribution curve; and (b) a skewed distribution showing that very low values have been eliminated.

In these two cases, it is not sensible to calculate an average value and a standard deviation because the sets of values obtained cannot be fitted with normal distribution curves. In fact, the curve fitting the histogram (a) corresponds to a mixture of two populations having average values a_1 and a_2 . Each of these populations can be fitted by two separate normal distribution curves as shown in Figure 16.8.

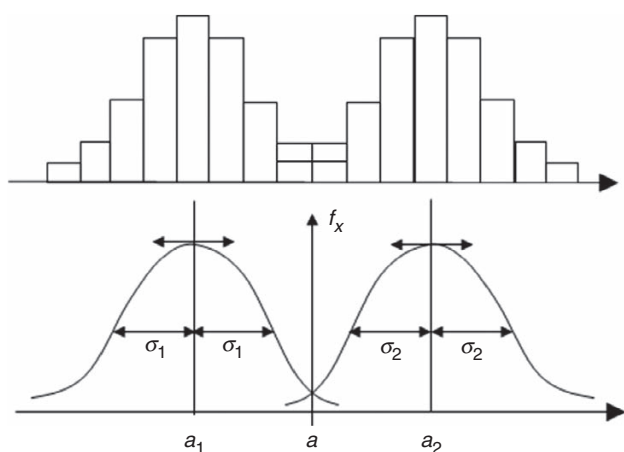


Figure 16.8 Decomposition of Figure 16.7(a) into two mixed populations.

Table 16.1 Factors for computing within-test standard deviation

Number of specimens	d_2	$1/d_2$
2	1.128	0.8865
3	1.693	0.5907
4	2.059	0.4857
5	2.326	0.4299
6	2.534	0.3946
7	2.704	0.3698
8	2.847	0.3512
9	2.970	0.3367
10	3.078	0.3249

Note: This is Table 3.4.1 in ACI Standard 214.

From the ASTM Manual on Quality Control of Materials MNL 7, 1990.

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When it has been verified that the set of values can be fitted with a normal distribution curve, and only then, can average and standard deviation values be calculated.

16.3.2 Within-test variation

When comparing the values of the individual results obtained from specimen tests representing a particular load of concrete at the same age, it is possible to extend the statistical analysis. In a perfect world, these values should be

identical because they are obtained from a unique concrete. However, the non-homogeneity of the concrete load, the variation in the individual sampling process, transportation and curing of the specimens usually make the individual values different. Then, it is possible to treat the *difference* between a pair of specimens as a set of statistical data, and calculate in each case the range over which these different individual values fall. From this new set of data, it is possible to calculate the within-test standard deviation and coefficient of variation.

$$\sigma_1 = \frac{1}{d_2} \times \bar{R} \quad (16.3)$$

where σ_1 is the within-test standard deviation, d_2 is a constant depending on the number of specimens averaged to calculate a test value (given by ACI 214 Table 3.4.1, reproduced in Table 16.1), and $\bar{R}$ is the average range within groups of companion cylinders.

$$V_1 = \frac{\sigma_1}{\bar{x}} \times 100 \quad (16.4)$$

where V_1 is the within-test coefficient of variation and $\bar{x}$ is the average value. The σ_1 and V_1 values can be used as an indication of the quality of testing. If σ_2 is the batch-to-batch coefficient of variation, the overall standard deviation σ and the within-test standard deviation σ_1 are linked by the relationship:

$$\sigma^2 = \sigma_1^2 + \sigma_2^2 \quad (16.5)$$

16.3.3 *Average of the last five consecutive tests*

The graph showing the individual strength values in the order in which the tests are carried out can be quite variable, with many “ups and downs”. Such a graph is relatively insensitive to changes in concrete quality. It is possible to smooth the shape of this curve by calculating the average of the last five consecutive tests according to the formula:

$$\bar{\chi}_{5i} = \frac{\chi_i + \chi_{i+1} + \cdots + \chi_{i+5}}{5} \quad (16.6)$$

Such a curve is very useful because it indicates the variability of the production, as will be seen in the sample calculations which follow.

16.3.4 *Average of the range of the last 10 consecutive tests*

Similarly, the average of the last 10 consecutive *ranges* indicates the variation of the range, as will also be seen in the sample calculations. A graph of this

type provides a check on the adequacy of the test procedures.

$$\bar{R}_{10i} = \frac{R_i + R_{i+1} + \cdots + R_{i=10}}{10} \quad (16.7)$$

16.3.5 Sample calculation

The 28-day compressive strengths of concrete for a particular construction project have been determined 35 times on sets of two specimens. The results obtained are shown in Table 16.2. The calculations will be carried out with two digits after the decimal point.

- Draw the frequency distribution of the average values using a 2 MPa unit cell.
- Does the population of the average values correspond to a normal distribution curve?
- How do the average compressive strength, standard deviation, and coefficient of variation vary as the test program goes on?
- Using Table 16.2, how can you assess the quality of the control of this production of concrete?

Table 16.2 Results obtained during quality control testing

	1	2	3	4	5	6	7	8	9	10
#1	58.5	64.9	65.0	60.1	64.7	65.0	63.8	64.7	64.7	61.1
#2	58.2	64.8	65.3	60.5	65.9	65.4	66.6	65.5	64.2	61.9
	11	12	13	14	15	16	17	18	19	20
#1	62.7	68.2	64.6	66.7	63.9	67.2	67.6	68.7	59.3	59.5
#2	59.8	69.8	65.2	67.9	64.1	67.2	67.4	67.8	59.7	59.8
	21	22	23	24	25	26	27	28	29	30
#1	55.9	61.3	60.6	63.6	63.3	62.7	63.5	63.0	62.2	63.7
#2	56.4	66.0	60.5	63.6	63.5	62.5	63.5	63.4	62.7	63.9
	31	32	33	34	35					
#1	66.4	56.9	63.2	65.4	62.9					
#2	66.9	57.1	63.4	65.1	63.5					

- What are the average range and the within-test standard deviation and coefficient of variation?
- How can you assess the control of the testing?

16.3.6 Discussion of the results

Tables 16.3, 16.4, and 16.5 can be obtained easily, for instance by using an Excel program.

Figure 16.9 shows the variation of the strength measured as the average of the two individual specimens in each set. It shows that in spite of all the care taken when producing a low w/b concrete, the results obtained in the field display a certain variability. This variability depends not only on the variability of the concrete but also on the variability of the testing.

Figure 16.10 shows that the frequency distribution of the strengths has (approximately) the characteristic bell-shape of the normal distribution law. *Therefore, it is legitimate to calculate the standard deviation and the coefficient of variation of the test results.*

Figures 16.11, 16.12, and 16.13 show the variation of the average strength, the standard deviation, and the coefficient of variation, respectively. It may be seen that after sample #21, these values are quite stable. (ACI 214 recommends at least 30 samples to obtain an average value of statistical validity.)

Table 16.3 Average strength and range

	1	2	3	4	5	6	7	8	9	10
$\bar{X}$	58.35	64.85	65.15	60.30	65.30	65.20	62.90	65.10	64.45	61.5
R	0.3	0.1	0.3	0.4	1.2	0.4	0.6	0.8	0.5	0.8
	11	12	13	14	15	16	17	18	19	20
$\bar{X}$	61.25	69.00	64.90	67.30	64.00	67.20	67.50	68.00	59.50	59.65
R	2.9	1.6	0.6	1.2	0.2	0.0	0.2	0.4	0.4	0.3
	21	22	23	24	25	26	27	28	29	30
$\bar{X}$	56.15	63.65	60.70	63.60	63.40	62.60	63.50	63.20	62.45	63.80
R	0.5	4.7	0.2	0.0	0.2	0.2	0.0	0.4	0.5	0.2
	31	32	33	34	35					
$\bar{X}$	66.85	57.00	63.30	65.25	63.20					
R	0.5	0.2	0.2	0.3	0.6					

Table 16.4 Average strength, standard deviation, coefficient of variation, and average of the last five strengths

#	Average (MPa)	Average of all preceding tests (MPa)	Standard deviation, σ (MPa)	Coefficient of variation, V (%)	Average of the last five strengths
1	58.35	—	—	—	—
2	64.85	61.60	3.25	5.3	—
3	65.15	62.78	2.84	4.5	—
4	60.30	62.16	2.56	4.1	—
5	65.30	62.79	2.55	4.1	62.79
6	65.20	63.19	2.45	3.9	64.16
7	62.90	63.15	2.24	3.5	63.77
8	65.10	63.39	2.17	3.4	63.76
9	64.45	63.51	2.06	3.2	64.59
10	61.50	63.31	2.03	3.2	63.83
11	61.25	63.12	2.02	3.2	63.04
12	69.00	63.61	2.52	4.0	64.26
13	64.90	63.71	2.43	3.8	64.22
14	67.30	63.97	2.51	3.9	64.79
15	64.00	63.97	2.42	3.8	65.29
16	67.20	64.17	2.47	3.8	66.48
17	67.50	64.37	2.51	3.9	66.18
18	68.00	64.57	2.58	4.0	66.80
19	59.50	64.30	2.75	4.3	65.24
20	59.65	64.07	2.86	4.5	64.37
21	56.15	63.69	3.26	5.1	62.16
22	63.65	63.69	3.18	5.0	61.39
23	60.70	63.56	3.17	5.0	59.93
24	63.60	63.56	3.10	3.9	60.75
25	63.40	63.56	3.03	4.8	61.50
26	62.60	63.52	2.98	4.7	62.79
27	63.50	63.52	2.92	4.6	62.76
28	63.20	63.51	2.86	4.5	63.26
29	62.45	63.47	2.82	4.4	63.03
30	63.80	63.48	2.77	4.4	63.11
31	66.65	63.58	2.78	4.4	63.92
32	57.00	63.38	2.97	4.7	62.62
33	63.30	63.38	2.92	4.6	62.64
34	65.25	63.43	2.89	4.6	63.20
35	63.20	63.42	2.85	4.5	63.08

With a standard deviation and a coefficient of variation of 3.8 MPa and 4.5%, respectively, according to Table 16.6 the production and the control may be classified as “good”.

Figure 16.14 represents the variation of the range and Figure 16.15 the within-test standard deviation.

Figures 16.16 and 16.17 represent the within-test standard variation and the within-test coefficient of variation. Here too, it is seen that with 35 samples, stable values are obtained.

Table 16.5 Within-test variation

#	<i>Within-test variation</i>				
	<i>Range (MPa)</i>	<i>Avg. range (MPa)</i>	<i>Standard deviation, σ (MPa)</i>	<i>Coefficient of variation, V (%)</i>	<i>Avg. of last 10 strength ranges (MPa)</i>
1	0.30	—	—	—	—
2	0.10	0.20	0.18	0.27	—
3	0.30	0.23	0.21	0.32	—
4	0.40	0.28	0.24	0.40	—
5	1.20	0.46	0.41	0.62	—
6	0.40	0.45	0.40	0.61	—
7	0.60	0.47	0.42	0.66	—
8	0.80	0.51	0.45	0.70	—
9	0.50	0.51	0.45	0.70	—
10	0.80	0.54	0.48	0.78	0.54
11	2.90	0.75	0.67	1.09	0.80
12	1.60	0.83	0.73	1.06	0.95
13	0.60	0.81	0.72	1.10	0.98
14	1.20	0.84	0.74	1.10	1.06
15	0.20	0.79	0.70	1.10	0.96
16	0.00	0.74	0.66	0.98	0.92
17	0.20	0.71	0.63	0.93	0.88
18	0.40	0.69	0.62	0.91	0.84
19	0.40	0.68	0.60	1.01	0.83
20	0.30	0.66	0.59	0.98	0.78
21	0.50	0.65	0.58	1.03	0.54
22	4.70	0.84	0.74	1.16	0.85
23	0.20	0.81	0.72	1.18	0.81
24	0.00	0.78	0.69	1.08	0.69
25	0.20	0.75	0.67	1.05	0.69
26	0.20	0.73	0.65	1.03	0.71
27	0.00	0.70	0.62	0.98	0.69
28	0.40	0.69	0.61	0.97	0.69
29	0.50	0.69	0.61	0.97	0.70
30	0.20	0.67	0.59	0.93	0.69
31	0.50	0.66	0.59	0.88	0.69
32	0.20	0.65	0.58	1.01	0.24
33	0.20	0.64	0.56	0.89	0.24
34	0.30	0.63	0.56	0.85	0.37
35	0.60	0.63	0.55	0.88	0.31

Figure 16.18 represents the average of the last five tests. It may be seen that between the 18th and the 24th sample this average strength decreased significantly, but after the 24th sample appropriate corrective measures were taken at the concrete plant so that the average of the last five tests started to increase and remain stable.

Figure 16.19 shows that the control deteriorated until the 15th sampling but then improved constantly to the end.

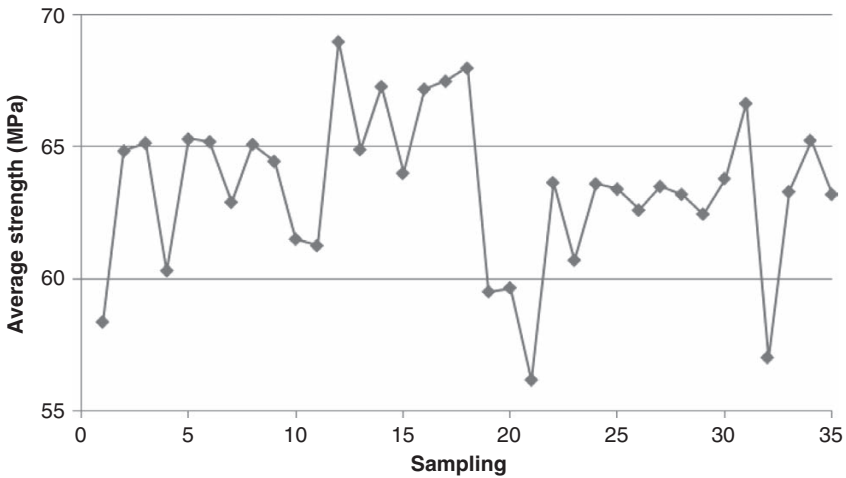


Figure 16.9 Average strength of the samples.

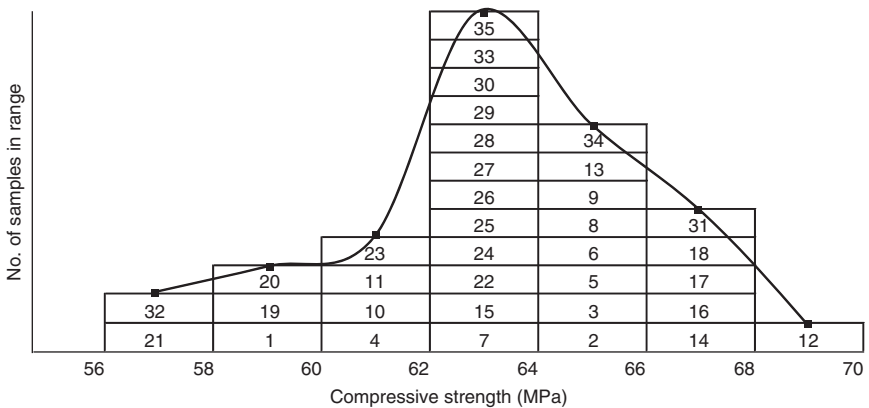


Figure 16.10 Histogram of compressive strengths.

16.4 Specifying concrete compressive strength

Concrete must be specified on a statistical basis. It is not realistic or sensible to write a specification such as: “the concrete must always have a compressive strength greater than X MPa” because it is statistically impossible to produce such a concrete. A specification must always identify clearly how many times it is allowable that the value obtained can be lower than X. It might be 10% of the time, 5% of the time, or 1% of the time, depending on the degree of severity selected by the specifier. In any case, the

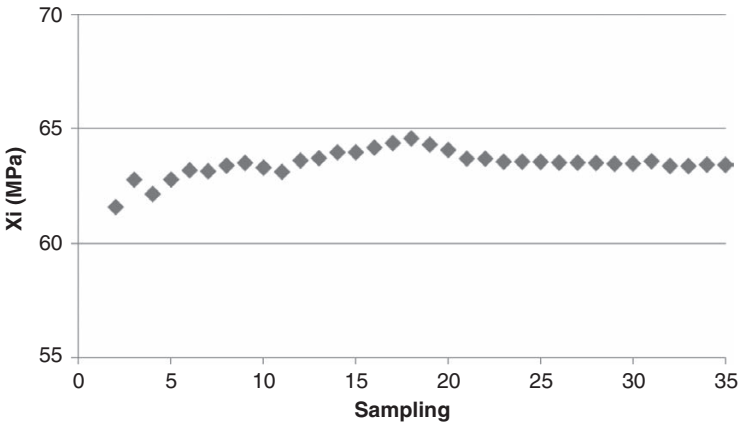


Figure 16.11 Variation of the average strength.

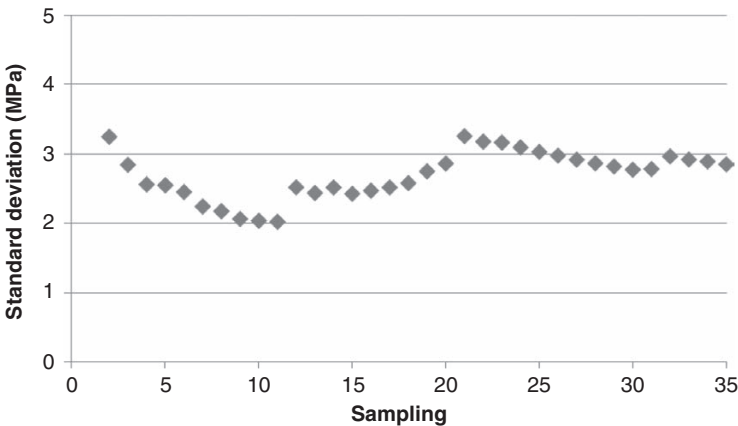


Figure 16.12 Variation of the standard deviation.

specifier must accept that a limited number of test specimens might be lower than the value of X selected for the design.

The second very important point that must be specified is the number of samples that will be tested. Again, it is not practical to test all of the batches to calculate the true average strength and standard deviation. Only a limited number of batches will be tested, but how many?

ACI 214 suggests that to make a “satisfactory” statistical analysis, it is necessary to have at least 30 samples, so that the average value and standard deviation calculated from this limited number of samples is representative of the actual average and standard deviation of the whole production. Statisticians tell us that the population of the average values calculated from

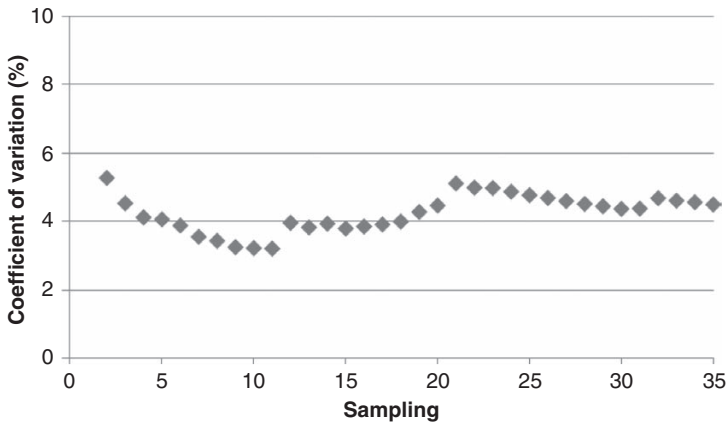


Figure 16.13 Variation of the coefficient of variation.

Table 16.6 Standard deviation and coefficient of variation according to ACI 214 (Table 3.5)

Overall variation

Class of operation	Standard variation for different control standards (MPa)				
	Excellent	Very good	Good	Fair	Poor
General construction	Below 2.8	2.8 to 3.4	3.4 to 4.1	4.1 to 4.8	Above 4.8
Laboratory and batching	Below 1.4	1.4 to 1.7	1.7 to 2.1	2.1 to 2.4	Above 2.4

Class of operation *Within-test variation*

	Coefficient of variation for different control standards (%)				
Field control testing	Below 3.0	3.0 to 4.0	4.0 to 5.0	5.0 to 6.0	Above 6.0
Laboratory trial batches	Below 2.0	2.0 to 3.0	3.0 to 4.0	4.0 to 5.0	Above 5.0

ACI 214 Table 3.5 – Standards of concrete control.

a limited number of samples obeying a normal distribution generates another normal distribution curves. Therefore, the smaller the actual standard deviation of the actual population, the greater the chance that the average value and standard deviation estimated from a limited number of samples will be closer to the actual value of average and standard deviation of the entire population.

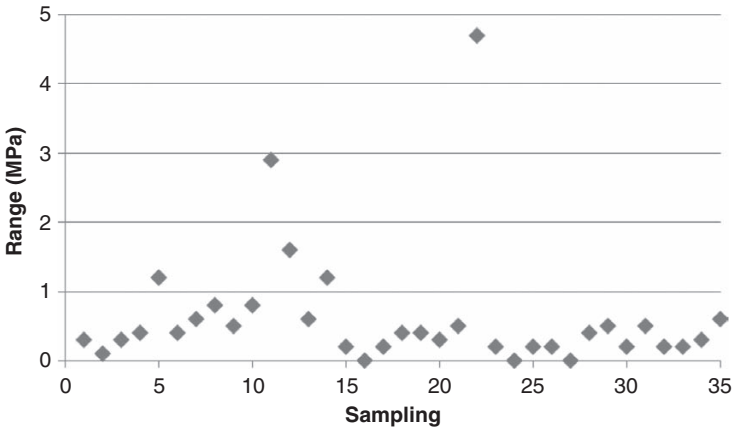


Figure 16.14 Variation of the range.

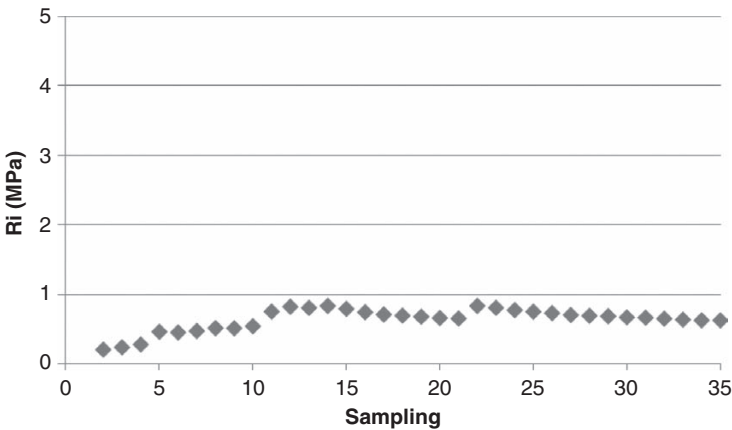


Figure 16.15 Variation of the average range.

16.5 Limitations of a statistical analysis

It is important to realize that a statistical analysis of concrete production can result in an incorrect evaluation of its conformity to the specification because a statistical analysis is carried out on a limited number of samples and not on all batches. The use of a random number table to select the loads that are checked does not limit that risk. Without entering into the field of combinatorial analysis, it is possible that the selected sampling advantages either the producer or the consumer. Let us examine two very simple hypothetical (but likely) cases.

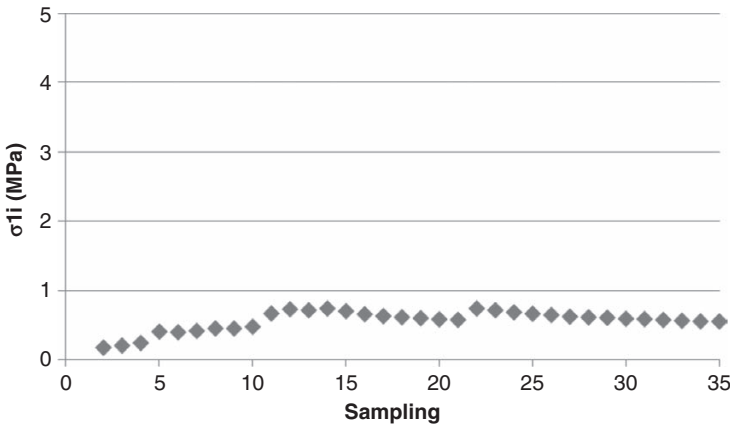


Figure 16.16 Within-test standard deviation.

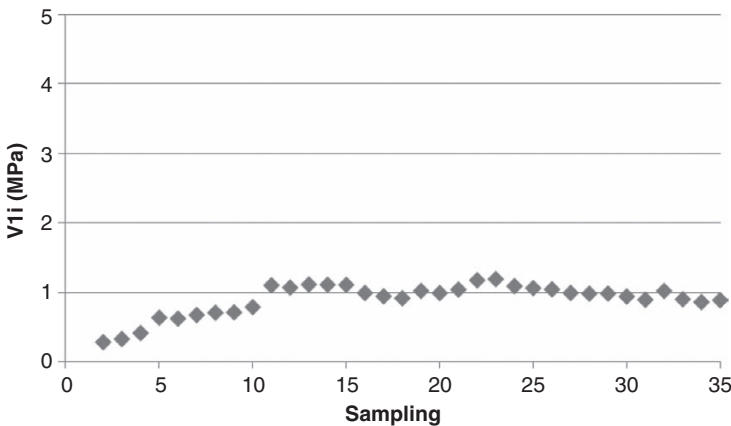


Figure 16.17 Within-test coefficient of variation.

The construction of a particular structure requires the use of 100 loads of concrete. The specification permits the delivery of a maximum of five loads of concrete having a compressive strength lower than the design strength. The statistical analysis of this production is based on the results obtained on 30 samples selected using a random number table.

16.5.1 The case of a good but unlucky concrete producer

The concrete producer is a good one that has adjusted the average strength, taking into account its usual standard deviation, to produce a concrete that statistically meets the specification. But, when the selection of the 30 tested

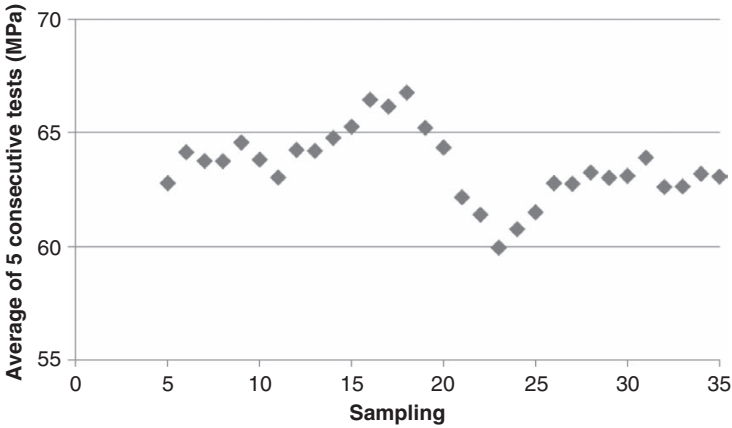


Figure 16.18 Average of five consecutive tests.

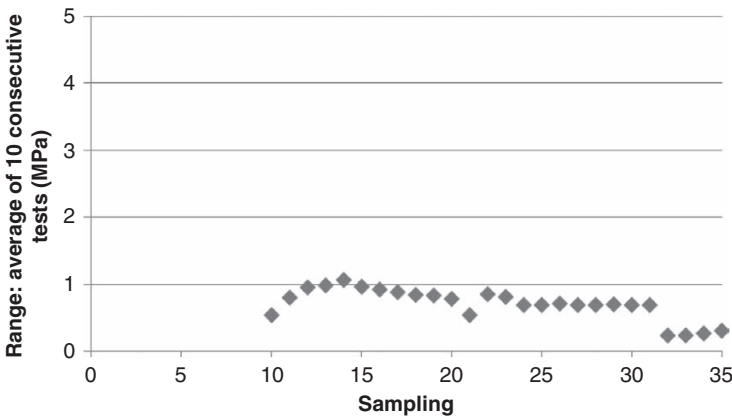


Figure 16.19 Average of the last 10 ranges.

loads is made he is particularly unlucky because the five defective loads have all been selected. As a result, he is judged on 25 satisfactory loads and the five defective ones. His production will be evaluated as not meeting the specification, in spite of the fact that in reality this is not true.

16.5.2 *The case of a bad but lucky concrete producer*

The concrete producer is a bad one. He has produced a concrete that does not meet the specification but he is very lucky: none of the bad loads have been selected for sampling. This production will be evaluated as meeting the specification in spite of the fact that in reality this is not the case.

16.5.3 *The risk to the producer and the risk to the consumer*

The acceptance or the rejection of the concrete for a particular project based on a statistical analysis inevitably includes the risk of rejecting concrete matching the specification or accepting concrete that does not match the specification. In a perfect world, it would be fair that the risks of accepting bad production or refusing good production be equal. However, according to Chung (1978), the present standards favour the producer rather than the consumer, and he proposed a new acceptance criterion to better share both risks. To date (2010), nothing has been done to change this situation!

16.6 Conclusion

In spite of all the attention given to controlling the variability of the materials used to make a low w/c ratio concrete, any low w/c ratio concrete displays a certain degree of variability, because it is made from variable raw materials processed by human beings in more or less sophisticated plants and is delivered under variable temperature conditions. As with any man-made material, concrete must be specified on a statistical basis. It must be admitted that, in spite of all the care taken to produce, to process, to deliver, and to test low w/c ratio concrete, a limited number of samples can fail the design criteria selected by the designer.

Using statistical analysis, it is possible to produce a concrete that matches the design characteristics selected by the designer. Of course, the average value that will have to be obtained by the producer will increase with the severity of the design criteria and the standard deviation of the concrete plant.

When making a statistical analysis of the ranges between the numerical values obtained on the different samples taken from the same concrete sample, it is possible to evaluate the quality of the control by calculating the within-test variation. Consequently, the variability of concrete can be split between the variation due to its production and the variation due to its sampling and testing. It is, however, important to emphasize that when evaluating concrete production on a statistical basis, there is always a risk that good production is rejected or that bad production is accepted.

Low w/c ratio concretes are sophisticated materials, but they remain variable. We must make all necessary efforts to reduce this variability in order to build more durable and sustainable structures. Statistical analysis can help us to achieve this.

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17 Producing sustainable concrete with minimal environmental impact

17.1 Introduction

In order to build sustainable concrete structures with a minimal impact on the environment, it is necessary to start from the beginning: at the ready-mix plant where the concrete is produced. Therefore, it is necessary to examine closely:

- the environmental impact of the transportation of materials;
- the treatment of the unused (“waste”) fresh concrete;
- the treatment of the wash water and any surface water collected at the plant.

To see how, from a practical point of view, these issues might be addressed using “best practice”, it was decided to visit four modern ready-mix plants: two in France and two in Quebec, Canada. In each country, a large plant producing more than 100 000 m³ of concrete annually, and a medium size plant producing between 20 000 and 30 000 m³ of concrete were selected, to see whether the production volume would have an impact on how these issues were addressed. In all four plants, it was found that the solutions implemented to reduce the environmental impact resulted in the production of sustainable concrete with minimal environmental impact at a very reasonable extra cost (about \$1.00 per cubic metre).

Before describing the set-up in each of these plants, the logistics of handling the raw materials will be briefly examined, from a historical perspective.

17.2 Transportation of materials

During the second half of the twentieth century, as Portland cement and concrete production showed a tremendous growth in industrialized countries, the location of cement and concrete plants was dictated primarily by considerations of ground transportation. The plants were located as close

as possible to their potential markets to minimize the transportation costs. Often, concrete plants were built in the downtown areas of cities, or in nearby suburban areas. In some cases, they were built right within a quarry or gravel pit. Where possible in urban centres, the concrete plants were located at harbours or on the banks of navigable rivers. This was done to take advantage of the lower transportation costs of the materials used to make concrete, and to avoid congested road transportation. Portland cement and concrete are heavy materials with a low added value, and so it was not very profitable to transport them over large distances, except in the case of largely unpopulated areas. Generally, it was uneconomic to transport cement more than 200–300 km from a cement plant, and concrete more than 20–30 km from a concrete plant. For cement, railway transportation was considered for larger distances (300–500 km) or for medium-sized markets. Portland cement and clinker were transported by ships in some specific cases of distant medium-sized markets easily accessible by sea. These were markets where it was not practical, for either economic or political reasons, to build a small capacity Portland cement plant; at most, a grinding plant might have been provided.

However, towards the end of the twentieth century, a significant change occurred in the Portland cement industry: from being local or at most national in scope, it became international in its operations. Recent years have seen the creation of very large international cement groups, and this consolidation has not yet ended. Now, for strictly logistical reasons, new Portland cement plants have begun to be built in, or close to, harbours or navigable rivers or canals, in order to supply distant markets at minimum transportation costs. As a result, presently (2010) about 200 million tonnes of cement are transported annually by ship, sometimes over distances of several thousand kilometres. An association of cement importers has even been created. This trend will continue because, in addition to the economic considerations, environmental considerations make water transportation very attractive, because of the low CO₂ emissions associated with it.

Cement plants have also been built very near to colossal construction sites, such as the Three Gorges Dam in China. In addition, a large calcination plant for local clays was built for the construction of the Itaipu Dam (second only to the Three Gorges Dam in its generating capacity), located on the border between Brazil and Paraguay, and very close to the border with Argentina. The artificial pozzolan produced decreased the amount of Portland cement needed to build the dam, and reduced the heat of hydration in the massive dam elements. It should be noted that in the near future, clay calcination will become more common in many developing countries in order to decrease their dependency on Portland cement and oil, and to decrease significantly their CO₂ emissions as well.

Similarly, transportation of aggregates is also most economical and environmentally friendly if it can be done with ships or barges. This has

made possible the economic shipment of aggregates over large distances. The authors are aware of a quarry located in Scotland that provides aggregates to some European and even Middle-Eastern harbours. Another quarry in Nova Scotia, Canada, ships aggregates down the eastern seaboard of the United States as far south as Florida. A quarry operated within an Indian reservation on Vancouver Island, Canada, provides aggregates for the concrete markets of San Francisco and Los Angeles. The transport of aggregates by seas becomes even more attractive when these aggregates are used as ballast in ships, or when they are secondary shipments on the return journeys of bulk transportation ships. For example, the French National Railway Company (SNCF) was recently offered some ballast from a Scottish quarry at a very competitive price, because the boat had to first transport 400 000 tonnes of pine logs from Bayonne (France) to the north part of England and Scotland; these logs had been harvested in the Landes forest after a huge storm had uprooted a large number of pines.

The construction of the Confederation Bridge between New Brunswick and Prince Edward Island (requiring 150 000 m³ of concrete) provides an interesting example of the distances over which materials may now be shipped economically. The cement and admixtures were shipped from Montreal (1500 km), the sand from Sept-Iles, Quebec (750 km), and the coarse aggregate from Nova Scotia (750 km). The only local materials used to build this bridge were the water and the air (6%)! The coarse aggregate could not be quarried from Prince Edward Island or New Brunswick due to a potential alkali-aggregate reaction, and if the closest natural sand deposits on Prince Edward Island had been used, very little sand would have been left in the area for the local concrete industry after the completion of the bridge.

In the near future, transportation by ship or barge of lightweight aggregates will become more common, because lightweight aggregates can be used for internal curing that greatly increases the mechanical properties and durability of low w/b concretes. As discussed in detail previously (see Chapter 13 on curing), in hot and dry climates it is not sufficient merely to replace some of the Portland cement with a pozzolan; it is absolutely essential to provide some long-term means of hydrating the binder materials. If no means of long-term curing is available, the pozzolan ends up acting only as a filler, and this significantly reduces the durability, and hence the sustainability of the concrete. For example, half of the coarse aggregate used in the construction of the Hibernia Offshore Platform in Newfoundland was a lightweight aggregate produced in Texas, and then shipped to Newfoundland by sea. This lightweight aggregate was specified primarily to increase the buoyancy of the platform. However, it was used in a saturated state, and it was found that through its effectiveness in internal curing it greatly improved the mechanical and durability properties of the concrete.

17.3 Examples of modern ready-mix plants

Two modern ready-mix plants in France were visited:

- A CEMEX plant located at Ivry (Paris suburb) located on the bank of the River Seine. It is a large plant, with an annual production of about 150 000 m³ per year.
- An Italcementi plant located in Biarritz in the southern part of France. It produces about 35 000 m³ of concrete per year.

These two plants share some common characteristics:

- Their various pieces of equipment are concentrated in a reduced space.
- Their concrete delivery is carried out by independent companies or independent truck drivers.
- The elimination of the sludge resulting from the treatment of their washing operations is subcontracted out.
- They estimate a surcharge of about 0.7 euros/m³ (\$1/m³) that is invested in the maintenance and modernization of their recycling operations.

In Canada, the two plants visited were:

- The DEMIX BETON ready-mix plant (owned by the HOLCIM group) is located in Ville LaSalle, a near suburb of Montreal. It produces about 100 000 m³ of concrete per year. This concrete is delivered by 28 trucks, but if necessary extra trucks can be provided by sister companies operating in the Montreal area. The plant occupies 2.16 hectares, and includes a garage, a parking lot for the trucks, and a large space used to store concrete from demolition works.
- The BÉTON MEMPHRÉ ready-mix plant is located in Magog, near to Sherbrooke, Quebec. The company belongs to Carrière St-Dominique. It occupies an area of 1.24 hectares. Usually, it operates a fleet of 10 trucks, each with a capacity of 6 to 12 m³; if necessary, it can call upon a few extra trucks from a sister company located near Sherbrooke.

17.3.1 *The CEMEX plant at Ivry*

As stated earlier, this plant is located (like some of its competitors) on the bank of the River Seine at a crossroad of the Boulevard Périphérique that surrounds Paris. This particular site is very advantageous because almost all of the materials necessary to produce the 150 000 m³ of concrete are delivered by barges (Figures 17.1 and 17.2), with the exception of some special cements (<5%) (Figure 17.3), and the admixtures which are delivered by truck.



Figure 17.1 Aggregates delivered by barges; Cemex plant at Ivry.

The washing sludges, after being concentrated by means of a filter-press system are taken away by barge by a subcontractor, and transported to a certified site. The plant also provides the service of elimination of demolition wastes, which are also barged to a specialized certified site. Clearly, the transportation of the cement and the aggregates by barge minimizes both the operating costs and the CO₂ emissions associated with the transportation of the raw materials used to make concrete. Waiting barges also are used to smooth out the logistics of the aggregate transportation. As well, in order to further limit CO₂ emissions, an electric crane is used to unload the aggregate barges.

The water from the Seine is used as mixing water (after treatment) in two mixers, each having a capacity of 2 m³. Since the transportation of the fresh concrete is subcontracted to contractors or independent truckers, there is no need of a garage or parking lot on the production site.

The surface waters, which may contain some oil or fuel, are treated in a special installation that recovers all of the organic material. These are then transported to a certified site by a subcontractor. The wash waters used for cleaning both the outside and the inside of the concrete mixers (Figure 17.4) are treated separately by centrifugation. The unused (or returned) fresh concrete is treated in a third installation that removes most



Figure 17.2 Cement barge; Cemex plant at Ivry.

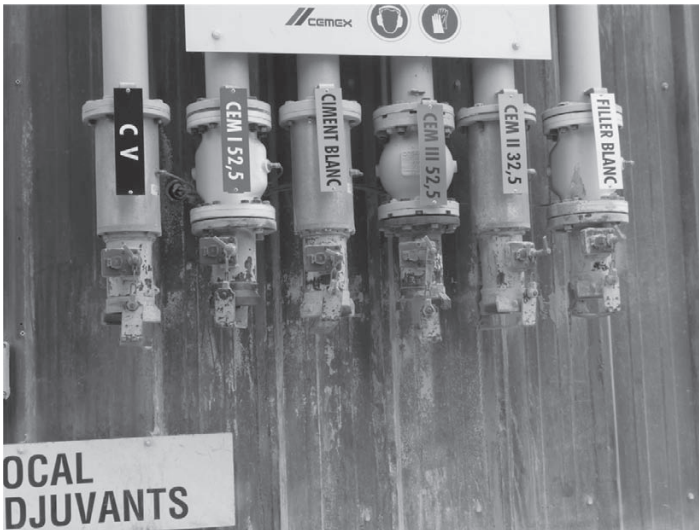


Figure 17.3 Delivery of special cements by truck; Cemex plant at Ivry.



Figure 17.4 Cleaning a ready-mix truck; Cemex plant at Ivry.

of the fine particles. The recovered aggregates are sold to contractors as fill material (Figure 17.5). The solids remaining in the water (Figure 17.6) are concentrated by centrifugation and then concentrated in a filter-press before being barged out.

One person is devoted exclusively to the operation and maintenance of the system. All of the equipment is concentrated in a relatively small space, and it operates very efficiently; the site is definitely kept clean, as shown in Figures 17.7 and 17.8.

17.3.2 *The Italcementi plant at Biarritz*

The Italcementi plant is a medium-sized plant, built near the airport and very close to the crossroads of three major urban highways. When there is more than 1 m^3 of concrete left in a delivery truck, it is used to make blocks. When there is less than 1 m^3 , this concrete is poured into a decantation pit through a grate. The wash and surface waters are also directed to this pit (Figure 17.9). The treatment of these waters and of the unused fresh concrete is carried out in a very compact installation, represented schematically in Figures 17.10 and 17.11, and shown in Figure 17.12. The sand and gravel that are separated are sold to contractors as fill materials (Figure 17.13). After settling, the sludge containing all of the fine particles is transported by a subcontractor to a certified site.



Figure 17.5 Recovered aggregates; Cemex plant at Ivry.



Figure 17.6 Decantation of the charged water; Cemex plant at Ivry.

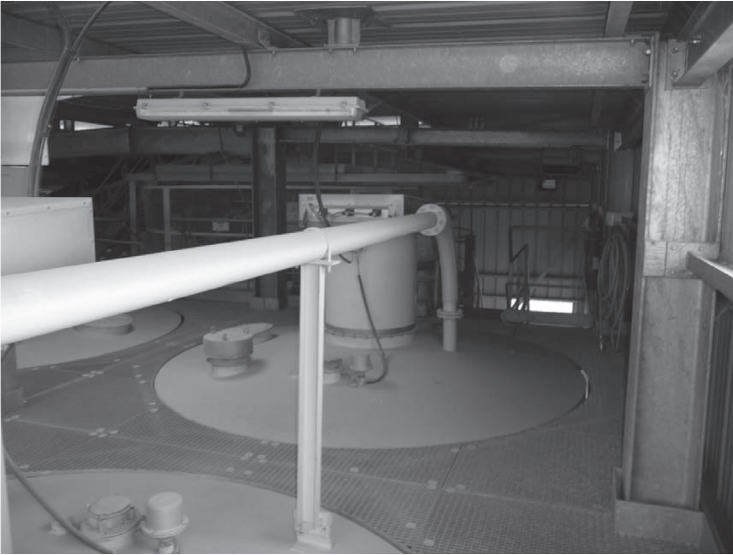


Figure 17.7 Cleanliness inside the batching plant; Cemex plant at Ivry.



Figure 17.8 Coarse aggregate storage; Cemex plant at Ivry.



Figure 17.9 Cleaning a truck in the decantation pit; Italcimenti plant at Biarritz.

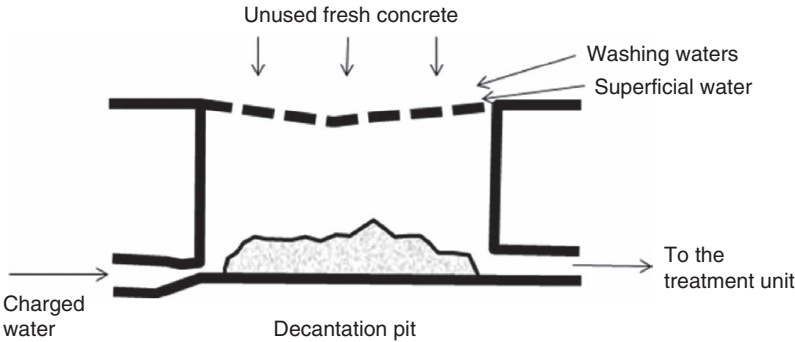


Figure 17.10 Schematic of the decantation pit; Italcimenti plant at Biarritz.

The water charged with contaminants of various kinds is permanently agitated (Figure 17.14). It is pumped from the decantation basin to clean the insides of the concrete mixers and the decantation pit itself. Before it enters the bottom of this pit, the water passes through a Venturi where it gains enough pressure and velocity to carry away the sand and gravel to the helical screw where they are separated. The charged water is then sent back to the decantation basin to be again used to clean the pit. The overflow from this basin is directed to two sedimentation basins (Figure 17.15) that

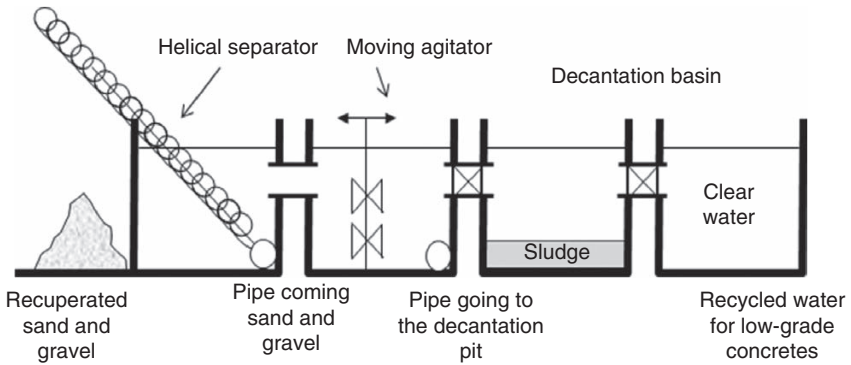


Figure 17.11 Schematic of the treatment unit; Italcimenti plant at Biarritz.



Figure 17.12 The treatment unit; Italcimenti plant at Biarritz.

are emptied alternately. The relatively clean water recovered from these two basins is used as mixing water for producing low-grade concretes.

17.3.3 The DEMIX BETON plant near Montreal

Although this plant is located on the Lachine canal, all of its raw materials are brought in by truck. It was built near a cement terminal operated by its mother company, HOLCIM Canada. The sand used is a natural sand, while the coarse aggregate is crushed stone. Usually, the plant operates

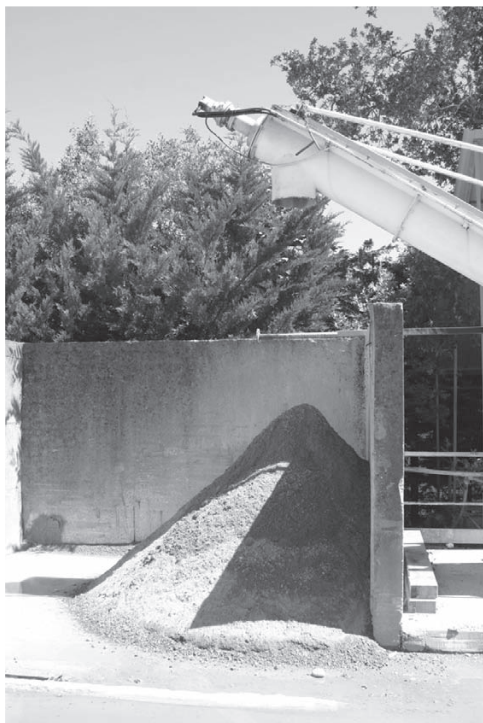


Figure 17.13 Recovered sand and gravel; Italcementi plant at Biarritz.

with 18 concrete mixers having capacities varying from 5 m³ to 12 m³ (Figure 17.16). These mixers are maintained in a garage built near the parking lot. On site, contractors are provided with a large storage space (70 000 m³) for their demolition concrete (Figure 17.17). From time to time, a portable crushing plant is brought in to crush this concrete to produce sub-base and base course material for road construction. However, no recycled aggregate is used to make new concrete.

The fresh (returned) concrete remaining in the mixer drums is used either to make concrete blocks (Figure 17.18), or is treated immediately in an installation that separates the sand and the gravel by screening (Figure 17.19). These recovered materials are then sold to contractors as fill materials. When the concrete blocks cannot all be sold, they are moved to the waste concrete area. The surface waters are treated in a special installation that removes all of the hydrocarbons; the pH of the treated water is monitored and adjusted automatically (Figure 17.20). The resulting clean water is then discharged into the municipal sewage system. The wash waters are treated by centrifugation, and again the pH of the clean water is



Figure 17.14 Charged water basin; Italcementi plant at Biarritz.

monitored and adjusted before being discharged into the municipal sewage system. The hardened sludge is directed to a specialized site (Figure 17.21).

17.3.4 The BÉTON MEMPHRÉ plant at Magog

This ready-mix plant is located in the industrialized zone of the small city of Magog, Quebec. Usually, it operates with 10 concrete trucks for an annual production of about 30 000 m³. The cement and aggregates are delivered to the plant by truck. The sand is a natural sand, while the coarse aggregate is crushed stone provided by its mother company, Carrières St Dominique.

The unused fresh concrete is used to make blocks. The “imperfect or slightly damaged” blocks are given free of charge to the city of Magog, which uses them for its own needs. Any unsold concrete blocks are returned to the quarry where they are crushed with the virgin rock and diluted into the regular production of coarse aggregate. The washing sludge (Figure 17.22), after decantation, is removed by a specialized company to a certified disposal site (Figure 17.23).



Figure 17.15 Sedimentation basins; Italcimenti plant at Biarritz.



Figure 17.16 Ready-mix trucks; Demix Béton plant.



Figure 17.17 Crushed demolition concrete; Demix Béton plant.



Figure 17.18 Forms for making concrete blocks; Demix Béton plant.



Figure 17.19 Recovery of the aggregates from the unused fresh concrete; Demix Béton plant.



Figure 17.20 pH control of the treated water; Demix Béton plant.



Figure 17.21 Hardened sludge before its elimination; Demix Béton plant.



Figure 17.22 Washing a truck; Béton Memphré plant.



Figure 17.23 Hardened sludge before its elimination; Béton Memphré plant.

17.4 Concluding remarks

From these four brief case studies, it may be seen that it is now quite possible to operate a ready-mix concrete plant in an environmentally responsible manner, without incurring unreasonable production costs. As well, the amount of waste material directed to specialized certified disposal sites can be minimized. However, to do this effectively, someone in the organization must take responsibility for the environmental aspects of the concrete production and delivery.

Index

- Al₂O₃ content 55
- ASTM first standard on Portland cement 91
- Abram's law 16, 17, 32
- Abrasion resistance 41
- Absolute volume 178
- Absorption of recycled aggregates 160
- Acceleration 124, 130
- Acceptance standard 91: weakest point 88
- Ackermanite 65
- Addition of cementitious material: at the cement plant 92; at the concrete plant 92
- Addition of water 214: effect on durability 105, 113; effect on strength 105, 113; effect on sustainability 105, 113
- Adiabatic conditions 180, 198
- Admixture science of admixture 138
- Adsorption of an aggregate 142: definition 14; expression 143; influence on slump 141; influence on strength 141;
- Aggregate: adsorption 142; cleanliness 139; derived from industrial wastes 160; effect on shrinkage 209; grain size distribution 139; origin 162; reactivity 139, 195; "sink" effect 105;
- Aggressive ions 43, 200: penetration 214
- Air bubbles 61
- Air entrained cement 40
- Air entrainment 94: influence of mixing 173; influence of mixing time 173; influence of placing 173; influence of sand 173; influence of temperature 173
- Air entraining agent 130, 169
- Alite 13, 39
- Alkali 195: content 57, 58; low alkali cement 58; soluble 195, 271
- Alkali/aggregate reaction 118, 119, 195, 163: fly ash 196; slag 196
- Alkaline impurities 58
- Alkali-silica reaction 245
- Alkali sulphates 50, 85, 196: Influence on compatibility 117; role during hydration 105
- Alternative fuels 34, 162: use 5; to reduce production costs 86; variability 86
- Aluminous hydrates 193
- Amorphous-like microstructure 41
- Angle of contact 203
- Anhydrite (natural) 128, 194
- Anorthite 33
- Apparent volume: expansion 179; variations 209
- Architectural concrete 163
- Artificial pozzolans: influence on the w/b 20; in blended cement 86; in-situ plant 270;
- Autogenous shrinkage 42, 62, 106, 180, 181, 201, 202, 215, 223: as a function of w/c 202; catastrophic consequence 181; compared to drying shrinkage 202 ; consequence of cement hydration 202; effect on internal curing 154; eradication 198; influence of curing 181; influence of the w/b 21, 107, 108, 181; influence of w/c 43, 107; influence on durability 107; influence on sustainability 107; origin 188, 116, 117; reduction 205; uncontrolled development 107; unavoidability 203
- Automation in cement plant 30

- Average distance between cement particles 18; influence of grain size distribution 19; influence of specific surface area 19
- Average: of the last 10 ranges 266; of the last 5 tests 256, 259, 266; range 256, 257; strength 257, 259, 261, 262; temperature 226; value 250, 251;
- Barge transportation 270, 272, 274
- Batch-to-batch: coefficient of variation 256; standard deviation 256
- Belite 39: definition 13; influence of slow cooling 51; nest 51, 85; secondary 51
- Bell-shaped curve 249–251: unit cell 253
- Beneficiated fly ash 72
- Best bidder 32
- Béton Memphré plant 282, 286
- Binary cement definition 12
- Binder: à la carte 92; CO₂ content 12; definition 12; importance 44; optimization 111; testing 86
- Binder paste, effect on air entrainment 169: selection 93
- Bisulphite process 125
- Blaine fineness maximum 58
- Blast furnace slag *see* slag
- Bleeding 104, 203: effect of entrained air 169; external 170; influence of the w/c 203; internal 170
- Blended cement 36, 38, 206, 212: action of superplasticizer 110; definition 12; for economics 48; heat of hydration 197; in Belgium 36; in Netherlands 36; present maximum substitution rate 37; sustainability 17, 48; to limit thermal shock 208; variability 86
- Blocks 275, 280, 281, 283
- Bogue composition 58
- Bottom ash coal combustion 164
- Branding of an admixture 130
- Business opportunities 29
- C₃A 50, 55, 56, 5.45, 5.60, 128, 190, 197: content 58; cubic form 196; electrical charges 113, 114, 116; for RPC 62; heat of hydration 197; hydration 60, 105; influence on DEF 61; influence on dispersion 60; influence on rheology 60, 99; in white cement 63; maximum 58; orthorhombic form 196
- C₄AF 50, 55, 56, 60, 85, 190: electrical charges 113, 114; heat of hydration 197; hydration 105
- CaO content 55
- CH 189, 191, 192
- CKD production and use 5, 7, 27
- CO₂: carbonation 9; content of a binder 12; emission 13; sequestration 5, 8; emission 3, 98; as a percentage of world production 44; decrease 44; reduction 28, 98; reduction per MPa 29; taxation 29; 1 t of Portland cement 44
- C/S ratio 189
- C₂S 85, 50, 60: electrical charges 113, 114; heat of hydration 197; hydration 105
- C₃S 85, 100, 50, 60: electrical charges 113, 114; heat of hydration 197; hydration 105; influence on dispersion 60; influence on rheology 99, 100
- C-S-H 58, 189, 200
- Calcination plant of clay 270
- Calcined clay 76, 77: influence on the w/b 20; temperature of calcination 76; use 7
- Calcined shale 76, 77
- Calcium carbonate 194
- Calcium silicate hydrates 189
- Calcium sulphate 59, 85, 128, 193: absence 59; addition 39; alternative 86; influence on compatibility 117; influence on rheology 90; in fly ash 72
- Capillary forces 142
- Capillary network 187
- Capillary pores 204: size distribution 201
- Capillary porosity 214
- Capillary water 103, 184, 187
- Capping compound 235
- Carbonation 9
- Carbonation shrinkage 106, 201
- Carbon content of fly ash 174
- Carboxylate 39, 60: effect on setting 60; early strength 60
- Cement: definition 12; grindability 93; hydration 204; specific gravity 144
- Cement consumption: per capita gross national income 46; world wide in 1900 44; world wide in 2000 44
- “Ciment du jour” 92

- Cementitious binder 63
- Cementitious properties 164
- Cement gel 182
- Cement kiln dust *see* CKD
- Cement particles: electrical charges 113; morphological characteristics 40, 117; physicochemical characteristics 40
- Cement paste: Dale Bentz' model 19; model 18; suction 108;
- Cement plant location 269, 270
- Cement/superplasticizer: combination 229; interaction 7.12
- Cemex plant at Ivry 272–277
- Centrifugation 275–280
- Challenge of the cement industry 88
- Charged water 278, 281
- Chemical action of water 104
- Chemical admixtures 31
- Chemical composition: fly ashes 70, 71; natural pozzolan 76; of different cementitious materials 64; Portland cement 55; raw meal 53; silica fume 74
- Chemical contraction 107, 176, 204
- Chloride ion permeability specification 267
- City of Montreal specifications 232, 233
- Class C fly ash 33, 71
- Class F fly ash 71
- Clay 33
- Cleanliness of the aggregate 139
- Clinker 85: definition 12; energy to produce 1 t 5; lower C₃S content 35; manufacture 27; manufacturing 50; morphology 52; no-clinker cement 37; wet process 27; with less fuel 32; with less limestone 32
- Clinkering zone 117
- Clinkerisation temperature 35
- Closed system 183, 184
- Closeness of cement particles influence on strength 188
- Coalescence of air bubbles 169
- Coarse aggregate: as a function of w/c 146; compressive strength 139, 145, 146; effect on entrained air 169; from glass 163; from waste material 157; influence on compressive strength 145; influence on drying shrinkage 222; influence on modulus of elasticity 145; modulus of elasticity 139
- Coefficient of variation 253: batch-to-batch 256; sample calculation 259; variation 263
- Co-grinding 68
- Cohesive forces 104: in the fresh paste 107
- Cold grinding 195
- Cold joints 234
- Cold weather 62
- Commercial superplasticizers 124
- Compatible admixtures 138
- Compatibility 117, 138: cement/superplasticizer 110; evaluation 119, 120; general rules 111; influence of impurities 117; influence of main phases 117; polyacrylates 132; selection of compatible combination 111; slump loss 111
- Competitiveness: of the cement industry 29; of the concrete industry 29
- Compressive strength 195: capping compounds 235; influence of w/c 123; influence of coarse aggregate 144; of concrete 16, 17; of the coarse aggregate 139; of the paste 16, 17; of recycled aggregate 161; specification of the age 235; specimen size 235
- Concrete: economic performance 90; energy to produce 3; perfect 188; skin 188, 206, 231, 232; use 2; blocks 275, 280, 283; durability 240, 242; involvement of cement groups 47; compressive strength 253; statistical evaluation 249; rheology influence of temperature 105; slump increase 39; strength 215
- Concrete structures: durability 91, 200; quality 91; sustainability 200
- Concrete temperature: decrease 228; increase 227
- Confederation bridge 271
- Cold weather 62
- Connectivity 201
- Consolidation: of he cement industry 46; of the concrete industry 46
- Construction waste 157
- Contaminants in recycled concrete 158
- Contraction: chemical 178; Le Chatelier's 178; of the concrete 201; of the paste 201; thermal 201

- Contractor responsibility 246
- Cost of cement: in a new structure 30;
in a repair 30
- Cost of disposing 162
- Cost of transportation 270
- Cracking 202: due to shrinkage 201;
superficial 206
- Cracks presence of ettringite 61
- Creep 200
- Cristobalite 82
- Critical w/c 213
- Crucial role of water: bleeding 103;
dispersion 103; electrical
conductivity 103; initial solubility
103; on rheology 103; segregation
103; thermal conductivity 103
- Cube strength of cement 87, 110, 111:
influence of the w/b 87
- Curing 212: adequate 104; as a function
of w/c 213; cementitious materials
94; external 94; compound 107; good
practice 212, 213; implementation
222; importance 94, 98, 188; in air
178; influence on durability 212;
influence on service life 222; influence
on sustainability 212; influence of the
w/b 181; influence on autogenous
shrinkage 181; in insulated form 221;
internal 94; in water 178; membrane
203, 217, 218, 232; paying
contractors 94, 104; poor practice
212, 215, 216; pozzolanic reaction
94; profitability 222; regulations 97;
specifications 223
- Crushing plant 280
- Crystalline fly ash 71
- Dale Bentz' model 19
- Damaged concrete presence of
ettringite 61
- Dead burned lime 221
- Decantation pit 275, 278
- Decarbonation 27
- Decorative concrete 163
- Decrease of the w/c with a
superplasticizer 111
- DEF 61
- Deflocculation 40
- Defoaming agent 124
- Degree of hydration 182
- Degree of sulphonation polynaphthalene
127, 130
- Degree of polymerization
polynaphthalene sulphonate 127
- Deicing salts 97: fly ash and silica fume
97; slag 97
- Delayed ettringite formation *see* DEF
- Deleterious substance maximum
amount acceptable 159
- Demix plant 279-285
- Demolition 30
- Demolition concrete 280, 283
- Demolition waste 157: elimination 273;
production 157
- Density of concrete influence on the
elasticity modulus 148
- Design criteria severity 267
- Design specification: durability 248;
elastic modulus 247, 248
- Desiccation 205
- Diatomeaceous earth 80: influence on
the w/b ratio 20
- Dicalcium silicate *see* C₂S
- Diffusion process 41
- Direct water curing 232: as a function
of w/b 232; concrete skin 232
- Dispersing agent to decrease the w/c 40
- Dispersion 60, 89: of binder particles
89; of cement particles 113; of
flocks 89
- Dissipation of energy effect of entrained
air 169
- Dissolution/precipitation process 41
- Distance of cement particles as a
function of w/c 41
- Draining forms 219
- Drying shrinkage 41, 62, 106, 107, 181,
201, 214: compared to autogenous
shrinkage 202; mitigation 221, 222
- Durability 62, 181, 186, 187: as a
design criteria 32; cementitious
materials 97; concern 16; concrete
structure 200; drawbacks 16; effect of
aggregates 209; effect of an addition
of water 105; effect of entrained air
169; effect of internal curing 207;
effect of shrinkage 209; important
factors 30, 31; improvement 203,
204; influence of autogenous
shrinkage 41, 107; influence of curing
212, 217; influence of mixing water
30, 31; influence of statistical analysis
267; of concrete 271; of concrete
structure 28; profitability 30, 31;
weakest link 31
- Durable concrete: effect on service life
8; role of superplasticizer 110;
sustainability 4

- Durable structures 25, 29, 31
- Duration of transportation influence on temperature 226
- Early compressive strength 146
- Early cracking 107, 108, 11.6, 12.4
- Early curing 213
- Early strength 198
- Ecological curing condition 221
- Economic performance: of cement 90; of concrete 90
- Economic waste 16
- Education: importance 43; educational effort 29
- Elastic modulus 189, 195, 215: influence of lightweight aggregate 220
- Elastic modulus of concrete 147, 148: as a function of density 148; as a function of the elastic modulus of the aggregate 150; as a function of the type of aggregate 148
- Electrical conductivity 105
- Electrical forces in water molecules 104
- Electrostatic repulsion 39, 111, 112, 128
- Elimination of demolition wastes 273
- Energy to produce: concrete 3; 1t of clinker 5
- Entrained air 41, 105, 123, 130, 169, 230, 231: as a water reducer 170; benefits 169, 9.2; effect on bleeding 169; effect on damaging 171; effect on dissipation of energy 169; effect on durability 169, 230, 231; effect on fluidification 169; effect on permeability 171; effect on pumpability 171; effect on rheology 169, 230, 231; effect on sorptivity 169, 171; effect on strength 169, 230, 231; effect on workability 169, 9.3; factors affecting 169; freeze-thaw cycles 169; percentage 169; sustainability 169, 170; volume 169
- Entrapped air 169: percentage 169; volume 169
- Environment: effect of the cement industry 1; effect of the concrete industry 1
- Environmental conditions 30
- Environmental impact of transportation 269
- Ettringite 41, 59, 171, 172, 179, 189, 193: expansive 61; needles 59; low lime 61; organomineral 60; secondary 61; supersulfated cement 61
- Eutectic point 65
- Evaporation 107, 201, 213, 214, 216: influence on shrinkage 107; prevention 107; rate 202; retarder 107, 201, 203, 232
- Exothermal reactions 201
- Expanded clay 220
- Expanded shale 220
- Expansion: of the apparent volume 180; of the hydrated paste 179
- Expansive admixtures: dead burned lime 221, 234; sulfocalcic 221;
- Expansive gel 171, 172
- Exportation of clinker 33
- External bleeding effect of entrained air 170
- External temperature 198
- External water 89, 107, 178, 184, 186, 188, 205, 206, 214, 222, 231: as a function of w/c 231; control 231; curing 218, 219; influence on slip forming 234; pricing 231
- Fe_2O_3 content 55
- False set 59, 194, 195
- Feret's law 16, 17, 32, 41
- Fibers 41
- Fillers 441, 84, 189, 212: definition 12; use 7
- Fill material 275, 280
- Filter-press 273, 275
- Final grinding 193: influence of flocculation 38
- Final setting 59
- Fine aggregate: from waste concrete 157, 158; recycled 161
- Fineness 62: influence on gypsum content 85, 86; influence on rheology 90; influence on thermal shrinkage 207
- Finite population 250
- Fitted distribution curve 253
- Flash set 59, 193-195
- Flexibility of concrete 162: effect of rubber 162
- Flexural elements, influence of low w/c 23
- Flocculation 38, 60, 113, 244, 245: elimination 116; influence on durability 38; influence on strength 38; trapped water 38; why 113

- Flowability 124
- Flow test 90
- Fluidification effect of entrained air 169
- Fly ash 48, 63, 71: beneficiated 72; chemical composition 71; carbon content 72, 174; grain size distribution 73; in blended cement 86; influence of the w/b 20; mineral composition 72; production 69, 70; spherical shape 69; sooth 72, 174; to limit thermal cracking 196, 208; unburned carbon 72, 174; unburned coal 72; use 6; x-ray diffractogram 71
- Fogging 42, 203, 231: duration 231; starting 231; unit cost 232
- Fog nozzles 216
- Foundry sands used as an aggregate 165
- Fragmentation of the concrete industry 47
- Free lime 85
- Freezing-thawing cycles 61, 230: effect of entrained air 169
- Freeze-thaw durability 172: maximum value of w/b 173; maximum value of w/c 173; number of cycles 172; spacing factor 172
- Freeze-thaw resistance 97, 169
- Fresh concrete properties 226: importance of water 102
- Freyssinnet 32
- Full hydration w/c 89, 182

- Gehlenite 33, 65
- Gel: cement 182; water 182, 183, 184
- Geotextiles 231, 232
- Glass 163: as a coarse aggregate 163; as a fine aggregate 163; clear glass 163; coloured glass 163; effect on workability 163
- Glass aggregate: architectural concrete 163; decorative concrete 163
- Glass filler 84, 85
- Glassy particles 69
- Globalization of the markets 47
- Grain size distribution of cement: influence of the average distance of cement particles 19; of aggregate 139
- Green house gas emission 4, 110
- Grindability: cement 93; slag 93
- Grinding 60: co-grinding 68; influence on electrical charges 60; separate 68, 93
- Ground granulated slag *see* Slag
- Ground transportation 269

- Gypsum 128: addition 40, 191–193; content 85, 99; reactivity 193; solubility rate 193; wastes 194

- Hardened concrete: age of testing 94; compressive strength 94; importance of water 102; influence of fly ash 94; influence of natural pozzolan 94; influence of slag 94
- Harshness of the environment 41
- Heating of structural elements 96
- Heat of hydration 176, 196, 197
- Heat losses 207, 208
- Hemihydrate 13, 194
- Hidden meaning of the w/c 19
- Hidden water 20, 102, 108 140, 206
- High-performance concrete *see* HPC
- High-performance concrete sustainability 5, 8
- Histogram 253, 261
- Hollow columns 23
- Homogeneity of the initial temperature 208
- Homogenization: clinker 54; of gypsum 194; of the raw meal 86; Portland cement 54;
- Honey combing 226
- Hot water 226
- HPC 61: compare to an artificial rock 151; key products 39
- Hybrid systems 247
- Hydrated paste: expansion 178; swelling 179
- Hydrates 184
- Hydration: effect of insulated forms 154; effect of internal curing 154, 155; of a 0,60w/c paste 183; of a 0,42 w/c paste 184; of a 0,36 w/c paste 186; of a 0,30 w/c paste 187; of C₂S 105; of C₃S 105; of C₃A 105; of C₄AF 105; role of the sulphates 105; role of the temperature 105
- Hydration conditions: influence of w/c 87
- Hydration reaction 176: chemical reactions 191; concrete properties 176; porosity 177; practical consequences 187; self activation 198; thermodynamic consequence 176
- Hydraulic binder 63
- Hydrogarnets 59, 193
- Hysteresis 151

- Ice 226
- Ice-crushing machine 228
- Ideal binder 88
- Ideal concrete 214
- Ideal Portland cement 58, 59
- Impermeability 206
- Impervious membrane 213, 214, 216
- Importance of w/b 102
- Importance of water 102
- Importation of clinker 33
- Incinerator bottom ash 164
- Increase of slump with a superplasticizer 111
- Increasing early strength 95
- Increase of initial temperature effect on compressive strength 96
- Influence of temperature on concrete rheology 105
- Infrastructures sustainability 4
- Initial curing 41, 205: effect on durability 207; effect on impermeability 207; effect on strength development 207
- Initial rheology 31, 59
- Initial setting 59, 90, 234
- Initial temperature 61, 62, 207, 227
- In situ concrete acceptable strength 240
- Insulated forms 95, 179: autogenous shrinkage 96; effect on hydration 154; influence of the thickness 96; internal curing 96; sustainability 96, 154; thermal conditions 198, 208
- Insulated slip forms 235
- Internal bleeding effect of entrained air 170
- Internal curing 42, 108, 179, 188, 205, 214, 215, 217, 233, 235, 271: as a function of w/b 233; calcined clay 76; control of autogenous shrinkage 154; diatomaceous earth 78; effect on cementitious material 154; effect on hydration 140, 154; effect on pozzolanic reaction 154; in insulated forms 221; lightweight aggregates 207, 233; lightweight sand 207; rice husk ash 78; supplementary cementitious materials 233; sustainability 155; with lightweight aggregate 108; with superabsorbant polymers 108
- Internal source of water 108, 179, 207
- Interstitial phase 39, 85: content 58; fusibility 58; influence on rheology 59
- Interstitial solution 61, 203
- Introduction of cementitious materials: at the cement plant 92; at the concrete plant 92, 94
- Isothermal conditions 178–180
- Italcementi plant 278, 279
- Jensen and Hansen Model 89, 176, 182, 183, 187
- Kiln: diameter 27; length 27; output 27; solid emission 27; SO₃ and NO_x emissions 27
- Laplace-Gauss curve 250: unit cell 253
- Large capillaries 202
- Leaching 214
- Le Chatelier experiment 176, 180, 187, 201, 204
- Life cycle 31, 108
- Lightweight aggregate 207, 219, 233, 271: for internal curing 108; influence on density 154; influence on elastic modulus 220; influence on strength 154, 220; partial substitution 154; porosity 233; proportion 233
- Lightweight sand 207, 219: advantages 220; influence on elastic modulus 220; influence on strength 220
- Lignosulphonates 39, 60, 111, 124: efficiency 125; presence of sugars 125; presence of surfactants 125; retarding effect 130; water reduction 125
- Lime clusters 51
- Limestone: filler 104; pulverized 12
- Limestone filler: addition 84; in blended cement 86; in masonry cement 6.3; influence on the w/b 20
- Limits of statistical analysis 264
- Liquid nitrogen 228
- Liquified gas tanks 234
- Lithium nitrate 245
- Logistic 270, 273
- Long term compressive strength 147
- Loss of water 201
- Low alkali cement 62, 118, 119, 195: compativity with polysulfonates 127, 128
- Low heat cement 197, 198, 208
- Low w/b concrete sustainability 22

- Lowering the w/c: influence on early strength 95, 96; influence on compressive strength 95, 96
- Lowest bidder 32
- Macrostructure of the cement paste 187
- Manufactured sand improvement of workability 170
- Manufacturing of Portland cement efficiency 5
- Marine environment: silica fume and fly ash 97; slag cement 97
- Markets globalization 47
- Marsh cone test 120: duration 121; reference cement 120
- Masonry cement 49, 104: composition 49
- Mass concrete 62
- Materials to make concrete 4
- Mathematical model on thermal effect 208
- Maximum temperature 146: influence of the forms 207, 208; influence of the w/b 192; insulated forms 198
- Mechanical properties 86: influence of coarse aggregate 144
- Mechanical relationships 145
- Melilite 65
- Menisci 103, 107, 108, 1178, 188, 201, 202, 205, 215, 219
- Metakaolin 76, 5.44, 123: in blended cement 86; influence on the w/b 20; use 7, 245
- Microcracks: network 209; sealing 198
- Microstructure: of concrete influence on mechanical properties 144; of the hydrated cement paste 182, 188; of the paste 40
- Mid-range water reducer 124
- Mineralizers 35: influence on cost 35; influence on CO₂ and NO_x emissions 35
- Mini slump test 120: duration 121; reference cement 120
- Mix design 246: recycled aggregates 161
- Mixing time influence on air content 173
- Mixing water: decrease 39; definition 15; from the Seine river 273; influence on durability 39
- Models: Dale Bentz' 19; of a cement paste 18, 19; quantitative 19
- Modern binders 50
- Modulus of elasticity of coarse aggregate 139: influence on concrete modulus of elasticity 144, 150; measurement 151
- Moisture: absorbed 14; free 14; content 14
- Moisture content 143: calculation 143; definition 2.5, 143
- Monosulphoaluminate 59, 190
- Morphology: of cement particles 117; of clinker 52, 118
- Moving from prescriptions to performance 242, 243
- Na₂O equivalent 58, 196
- Nano-indentation 200
- National associations 91
- National standards societies 91
- Natural pozzolans 48: chemical composition 76; effect on concrete properties 76; hydraulic properties 76; in blended cement 86; influence on the w/b 20; origin 74, 76; use 8, 245
- Natural resources preservation 28
- Night deliveries advantages 228, 229
- Non-clinker binders 37, 49, 85
- Non-porous solid 214
- Normal frequency curve 249, 250: unit cell 253
- Normal law: curve 249, 250; unit cell 253
- Offshore platforms 234
- Organomineral ettringite 60
- Optimization: of the binder 93, 105; of the binder composition 86, 87
- Osmotic pressure 103
- PH monitoring 280, 285
- Partial substitution of aggregate 154
- Past errors 46
- Peak value 151
- Penetration of water 206
- Percolation 103
- Perfect concrete 188
- Performance specifications 9: appropriate characteristic 242; definition 240, 241; establishment 246; examples 246, 247; obstacles 242
- Performance standard 89
- Periclase 85

- Perlite: absorbtivity 78, 79; origin 78, 79
 Permeability 195: effect on entrained air 172; to aggressive agents 40
 Pessimum particle size waste glass 163
 Petroleum shocks 27
 Phase composition: influence on rheology 90; influence on thermal shrinkage 207
 Physical action of water 104: on shrinkage 106, 109
 Pig iron 64
 Placing influence on air content 173
 Placing and curing: influence on durability 41; specifications 30
 Plastic shrinkage 41, 62, 106, 201, 209, 229: curing to avoid 216; preventing 203
 Plastic wastes use as an aggregate 165
 Poisson's ratio influence on compressive strength 149
 Polarity of water molecule 38, 113
 Polyacrylate *see* polycarboxylate
 Polycarboxylate 60, 62, 111, 126, 196: compatibility 132; configuration 131; control of rheology 60; development 110; efficiency 131; influence on dispersion 60; saturation point 132; solids 132; steric repulsion 116, 117; use in precasting 132
 Polyelectrolite 116
 Polymelamine 62, 111, 114, 128
 Polynaphthalene 11, 124, 126: effect of low temperature 127; efficiency 127; solid content 127
 Polysulphonates 39, 60, 62, 111, 124, 126, 196: amount of residual sulphate 127; B sites 127; characteristics of the cement 7.26; commercial 7.27; compatibility 128; control on rheology 5.17; degree of polymerization 127; degree of sulphonation 127; double introduction 129; inhibition of reactive sites 125; influence on dispersion 60; introduction 129; reactive with C₃A 125; retarding effect 129, 130; robustness 128; superficial action 129; use in Europe 130; use in North America 129, 130; use in precast industry 131; use in ready mix industry 130
 Porosity 178, 184, 186
 Portland cement: chemistry 33; clinker 86; different ASTM types 48; ideal 58; influence of impurities on compatibility 117; influence of main phases on compatibility 117; low alkali 58; production in 1900 44; production in 2000 44; production in Europe 47, 48; production in North America 47, 48; proper use 30; resistant to sulphate 55; technical weakness 4.11; testing 86; white 55
 Portlandite 41, 59, 97, 179, 189, 191, 192
 Post-tensioning 32
 Powers 176, 182, 187, 204
 Powdered glass influence on the w/b 20
 Pozzolans 63, 64: as a filler 271; use 7
 Pozzolanic materials use 6
 Pozzolanic reaction: effect of internal curing 154; importance of curing 94
 Pozzolanicity rapid evaluation 82
 Precasting use of polyacrylate 132
 Prescriptive specification 9, 240: hybrid systems 247
 Pricing water curing 231
 Priorization: of rheology 88; of strength 87
 Probability 252
 Production: of blended cement 48; clinker 55; Portland cement 44; slag 64, 65, 68
 Profitability 30, 31, 43
 Pulp and paper sludge 79, 80
 Pumpability effect of entrained air 171
 Quality control program 235, 253: number of tests 253
 Quality of water 102
 Quartz 33
 Quaternary blend 12, 13, 123
 Quenching 63, 65, 66
 Random number table 264
 Range: average of last 10 257, 260, 266; variation 264
 Rapid cracking 188
 Rate of slipping 234
 Raw materials 196
 Raw meal: alkali content 58; chemical composition 53
 Reactive aggregate 139, 195
 Reactive powder concrete *see* RPC
 Reactivity of slag according to its color 66, 67

- Reconstruction 30
- Recycled aggregates 157: absorption 160; relative density 160
- Recycled concrete 158: processing 158; use 5, 8
- Recycled fine aggregate 161: effect on concrete properties 161
- Recycled tyres 162: effect on concrete properties 162
- Recycled waste material 157
- Recycling: of washing water 109
- Reduced center value 250
- Reference cement 120, 121
- Reference concrete, slump loss 91
- Reference superplasticizer 120, 121
- Rehabilitation 30
- Reinforcing steel 200
- Repairs 30
- Replacement of Portland cement: sustainability 5; use of fillers 5
- Reservoirs 234
- Residual sulphates in polynaphthalene 127
- Responsibility 243: of the contractor 246; of the supplies 246
- Restraintment 201
- Retarder 124, 130, 234: dosage 235; to keep workability 105
- Returned concrete 160, 161, 273, 280
- Rheological: needs 124; problems influence on durability 87, 88; properties influence of w/c or w/b 86, 87
- Rheology: control by water 105; effect of entrained air 169; influence of calcium sulphate 90; influence of cement materials 104; influence of external temperature 105; influence of fineness 90; influence of interactions 99; influence of phase composition 90; monitoring 99; of cement paste 111; prioritization 88; sensitivity to temperature 225
- Rice husk ash: chemical composition 78; in blended cement 86; influence on the w/b 20; morphology 76, 78; texture 76, 78; unburned carbon 76; use 7
- Risk of cracking 215
- Risk of the consumer 267
- Risk of the producer 267
- Road base 157
- Robustness 117, 229: cement/superplasticizer combination 110; definition 112; evaluation 120
- Rock fracture 152
- Rock strength 145
- Roller-compacted concrete 61
- RPC 61, 87, 215
- Rubber tyres 157
- SO₃ content: maximum 58; termination 128SO and NO_x emission 27
- Sacrificial water reducer 129
- Safety of concrete structures 249
- Safety hazard from recycled glass 163
- Sample calculation, statistical evaluation 257
- Sampling process 255
- Sand, influence on air content 173
- Saturated lightweight aggregate 42: partial substitution 139, 140
- Saturated surface dry state *see* SSD state
- Saturation point: definition 121; polyacrylate 132
- SCC 240
- Sea transportation: aggregates 271; cement 271
- Sea water: durability of concrete 61; influence on strength 108; use 108
- Secant modulus 151
- Secondary belite 51
- Secondary C-S-H 97
- Sedimentation basin 278, 282
- Segregation 104: effect of entrained air 170
- Self-activation 99
- Self compacting concrete *see* SCC
- Self-desiccation 205, 219
- Self-healing 215
- Self levelling concrete 124
- Sensitivity of concrete: to aggregate 225; to autogenous shrinkage 225; to compatibility 225; to external temperature 225
- Separate grinding 68
- Service life: effect of curing 222; influence of durability 8
- Setting, initial and final 59, 193, 344
- Severity of the design criteria 267
- Sewage system 280
- Ship transportation 270
- Shrinkage 103, 106, 117, 200, 201: autogenous 62, 176, 202; carbonation 201; different types 41, 106; drying 62, 201; effect of the

- aggregates 209; effect of recycled rubber 162; in air 180; of the paste 178; plastic 62, 201; thermal 201
- Shrinkage compensating cements 221
- Shrinkage reducing admixtures 203, 222, 234
- Silica: pulverized 12; uncombined 86
- Silica filler 84; influence on the w/b 20
- Silica fume 64, 73, 123: chemical analysis 74; diffractogram 75; fineness 74; colour 73; handling 75; in blended cement 86; influence on the w/b 20; production 73; use 32, 244, 245; white 73
- Silica fume cement 48
- Silos 234
- Skewed distribution 254
- Skin of concrete 188, 206, 219, 231 232
- Slag 33, 48, 63, 65, 196: cement 68; chemical composition 65; colour 66; content 68; grindability 93; in blended cement 86; influence on the w/b 20; use 6, 244, 245
- Slip-forming 225, 234: rate of slipping 234
- Slow cooling influence in belite nests 51
- Slow hydration, role of water 103
- Sludge 275, 281, 285, 286
- Slump loss 60, 117
- Social cost 30
- Socio-economic needs 4, 45
- Soft solid 178
- Solid content: of polyacrylates 132; of polynaphthalenes 128
- Solid emissions 27
- Soluble alkalies 60, 195: rapidly soluble 62
- Solubility rate: of calcium sulphate 193
- Soot in fly ash particles 174
- Sorptivity: effect of entrained air 169
- Spacing factor 169, 170, 172, 173, 230: of HPC 173; of usual concrete 172
- Spalling 200
- Special binders for special environment 41
- Specifications 9, 225: for placing and curing 30, 32; on curing 223; of compressive strength 261
- Specific gravity: calculation 144; definition 15, 143; of cement 144; SSD state 142
- Specific surface area 197: definition 13; influence on the distance of cement particles 19
- Specifying for sustainability 243
- Spent pot-liners 81: chemical composition 81; hydraulicity 81; production 81
- Spent solvents 157
- SSC 61
- SSD state: as a reference state 139, 140; definition 14; measuring the characteristics 140, 141, 142; specific gravity definition 15
- Stabilization of air bubbles 169
- Standards 249
- Standard deviation 250, 251: average 259; batch-to-batch 256; variation 262; within-test 255
- Statistical analysis 255: influence on durability 267; influence on sustainability 267; limits 264; risk of the consumer 267; risk of the producer 267
- Statistical evaluation 249: sample calculation 257
- Statistical treatment 249
- Steel forms, influence on maximum temperature 208
- Steric repulsion 111, 116, 117
- Stoichiometric water 182
- Strength: average 257; effect of an addition of water 105; influence of the closeness of cement particles 188; range 257
- Strength based specification 240
- Strength development 207
- Strength of the source influence on concrete strength 159
- Strength requirement maximum and minimum 59
- Stress strain curves 150, 151, 152: equations 152; shape 153
- Stress transfer 144
- Stopping of hydration 103
- Structural design improvement 5, 9
- Structures durable and sustainable 25
- Sub-base material 157
- Substitution of coarse aggregate 219: disadvantages 220
- Suction 201
- Sulphoaluminates 189
- Sulfocalcic expansive compounds 221
- Sulphonate 39

- Sulphates: Portland cement resistant 58; role during hydration 105
- Superabsorbant polymers 207, 219, 221
- Superficial charges 60
- Superplasticizers 39, 60, 68, 99, 234:
 - action on blended cement 110; active solids 133; as a dispersant 113; commercial 124; dosage 132; for HPC 123; influence on durability 138; influence on strength 138; influence on sustainability 138; in precast industry 123; key components 137; melamine 133; practical utilization 123, 132; pure base 124; saving of material 110; solid content 133; specific gravity 133; to restore workability 105; use in slag cement 5.27; use to decrease w/b 111; use to increase slump 111
- Superplasticizer dosage: definition 15
- Supplementary cementitious materials 157, 233, 243: content 13; curing 217; definition 12; effect on air entrainment 173; use 6
- Supplier responsibility 246
- Surface cracking 206
- Surface tension 203
- Surface water 273, 280
- Sustainability 43, 98: acceptability 16; as a design factor 16; as a function of the curing 186; as a function of the w/c 186, 187, 212, 213; effect of aggregates 209; effect of an addition of water 105; effect of entrained air 109; errors made in developed countries 4; improvement 44, 203, 204; influence of autogenous shrinkage 107; influence on curing 212, 213; influence of statistical analysis 267; leitmotif of the development 28; more cement with less clinker 32; more clinker with less fuel 32; more clinker with less limestone 32; more durable structure 32; more kN with less cement 32; of cement 41; of concrete 41; of concrete structures 28, 201; of low w/c concrete 22
- Sustainable concrete 240: economist of recycling 287; establishing performance specification 246; production 269; ready mix plant 272; role of superplasticizer 110
- Sustainable development 1, 90
- Sustainable structures 25
- Swelling 198, 221: of the hydrated paste 179
- Synergistic effect: cementitious material 95; quaternary blends 95; ternary blends
- Synthetic fibres 203
- Tangent modulus 151
- Temperature: acceleration of hydration 226; influence on rheology 225
- Tensile forces 178, 219
- Tensile strength 197
- Tensile stress 201, 205
- Ternary cement definition 12, 13
- Test method 242
- Testing: age of testing 97; binders 85, 89; cement paste 86; concrete with cement materials 97; Portland cement 85
- Tetracalcium ferroaluminate *see* C₃A
- Thermal contraction 201
- Thermal cracking, use of fly ash 208
- Thermal expansion 208
- Thermal gradients 197, 198, 208: cracking 208; limiting the effect 208
- Thermal shock 189, 208
- Thermal shrinkage 207
- Thermodynamic conditions in the clinkering zone 117
- Thermomechanical process 126
- Total water content 143
- Tough concrete 240
- Toughness effect of recycled rubber 162
- Transition zone 40, 144, 145, 195: effect of entrained air 170; presence of ettringite 61
- Transportation 270
- Trapped water 38, 60
- Treatment of waste 269
- Tricalcium aluminate *see* C₃A
- Tricalcium silicate *see* C₃S
- Truck transportation 272, 274, 281, 282
- Truck washing 286
- Type I/II cement 48
- Type I/II clinker 130
- Type V cement 61

- Types of Portland cement: according to ASTM 48; according to European standards 49, 50
- Tyres as alternative fuel 162
- Ultra fine fly ash use 245
- Ultra high strength concrete 240: influence of cement composition 87
- Unburned carbon in fly ash 174
- Underwater concrete 61
- Undulatory extinction 172, 195
- Unhydrated cement particles 186, 189
- Unit cell 253
- Unused concrete 273: recovery of aggregates 284
- Used oil 157
- Use of waste materials as fuels 5
- Vaporizers 107
- Variability: of concrete properties 249; of low w/c concrete 249; of the materials 249
- Variance 250
- Variation: of properties 161; of the average strength 262; of the average of the range 265; of the coefficient of variation 263; of the range 264; of the standard duration 262; of the within-test variation 264
- Variation of the water content of aggregate: influence on durability 102; influence on strength 102; influence on sustainability 102
- Vibration: effect on air entrainment 169
- Virgin aggregates 162
- Viscoelastic behaviour: linear 151; non-linear 151
- Viscosity: of concrete mixture 105
- Viscosity modifying agent 104, 105, 124
- Vitreous glass 63
- Vitreous slag 33, 63
- Volcanic ashes 63
- Volumetric change 200
- Volumetric contraction 107, 176: absolute 180; consequence 107
- Vulnerability of concrete 214
- w/b critical value 145; influence on autogenous shrinkage 181; influence on hydration 86; influence on rheology 86
- w/c critical value 145; influence on compatibility 123; influence on curing 213, 215, 216; influence on compressive strength 62, 123
- w/c ratio law 176
- w/c reducers 40
- Wall effect 219
- Washing sludges 273, 281
- Washing water: influence in concrete properties 109; limitation 109; recycling 109; use 109
- Wash waters 273
- Waste glass 163: as a coarse aggregate 163; as a fine aggregate 163; pessimum particle size 163
- Waste gypsum 193
- Waste water treatment 269
- Water: addition 102; beneficial action 103; capillary 103, 184; chemical function 104, 178; control of the rheology 105; crucial role 103; curing 198, 214, 215; external source 107; facility of use 103; gel 182, 184; hidden water 20, 102; importance 102; in aggregates 102; influence on rheology 103; internal source 107; osmotic pressure 103; percolation 103; physical action 104, 178; slow hydration 103; stoichiometric 182; tightness 212; use 9; w/c for full hydration 182
- Water-binder ratio: definition 13, 14; influence on compressive strength 17; how to transform it into MPa 21; the most important characteristic 16; strength relationship 21
- Water-cement ratio: calculation 21; definition 13, 14; determination 20; influence on compressive strength 17; influence on early strength 21; influence on impermeability 21; the most important characteristic 16
- Water-cementitious materials ratio: definition 13, 14
- Water content: calculation 143; definition 14, 143; moisture content 143; total 143; variation in aggregate 102
- Water curing importance 205, 209, 214, 215
- Watering with a hose 231

- Water molecule 60, 104: as an electrical dipole 113; polarity 60
- Water reducer 60, 5.49, 124: entrained air 170; midrange 124; influence on flow test 89; to restore workability 105; use 30
- Water spraying 42
- Water tightness 212
- Water transportation 270
- Weakest link 144, 145
- Weak inclusion 162
- Wet burlap 42, 231, 232
- Wet-process 27
- White cement 55, 128, 164: C₃A content 63; colour of the superplasticizer 129; compatibility with polysulfonate 128;
- Within-test 255: sample calculation 260; variation 265; within-test coefficient of variation 256; within-test standard deviation 256
- Wood chips used as an aggregate 165
- Wood forms, influence on maximum temperature 208
- World consumption of Portland cement 44
- Workability: effect of entrained air 169; influence of water 104; of rich mixes 171; restoration 103, 105
- X-ray diffractogram: of diatomaceous earth 83; of fly ashes 71; of metakaolin 83; of rice husk ash 83; of silica fume 75; of vitreous slag 67