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State-of-the-Art Report on Use of Limestone in Cements at Levels of up to 15%

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ABSTRACT

This document is to serve as background technical information for engineers, specifiers, and other concrete technologists on use of limestone in hydraulic cements in amounts up to 15% (focusing on amounts between 5% and 15%). The document also provides supporting data for standardization of limestone blended cements in ASTM C595 and AASHTO M240. Environmental benefits are noted as well as a history of use of cements with limestone. The chemical and physical effects of limestone on fresh and hardened properties of concrete are emphasized.

REFERENCE

Tennis, P. D.; Thomas, M. D. A.; and. Weiss, W. J., *State-of-the-Art Report on Use of Limestone in Cements at Levels of up to 15%*, SN3148, Portland Cement Association, Skokie, Illinois, USA, 2011, 78 pages.

Errata Corrections, September 2014:

1. Table 1.7, page 9: entries for CO_2 calculations.
2. Spelling of Irassar throughout.

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by P.D. Tennis[*], M.D.A. Thomas[†], and W.J. Weiss[‡]

CHAPTER 1 INTRODUCTION

The cement industry continues to introduce more sustainable practices and products for constructing and maintaining our concrete infrastructure and buildings. That sustainable development focus, proposed implementation of more restrictive environmental regulations on cement manufacturing, and potential global climate change legislation have prompted the US cement industry to propose provisions for portland-limestone cements within specifications ASTM C595 and AASHTO M 240. Such provisions are anticipated to be similar to those adopted by CSA A3000, with limestone contents greater than 5% and up to 15%. For many applications, portland-limestone cements (PLC) can provide equivalent performance with reduced environmental impact. The purpose of this report is to document the development, use, and performance of these cements.

Portland-limestone cements are in common use around the world. Similar cements have been produced in the US under ASTM C1157 for several years and have a history of satisfactory performance in field applications. However, C1157 is not widely specified. Therefore, provisions for portland-limestone blended cements in ASTM C595 and AASHTO M 240 are needed if a significant impact on sustainability is to be achieved.

1.1 SCOPE OF REVIEW

This research and development report provides a state-of-the-art overview of hydraulic cements containing limestone as an ingredient, focusing on quantities between 5% and 15% by mass. Technical data on effects of the use of limestone at these levels on the behavior of cement and concrete, as well as on environmental impact of cement production are summarized. Hooton et al. (2007) developed a similar review for Canadian Standards Association Committee A3000.

Topics in this chapter include the use of these cements internationally, as well as the improvement in the sustainability, as quantified by greenhouse gas emissions reductions potential for portland-limestone cements.

Other chapters in this bulletin address the physical and chemical effects of limestone at these levels on cements (Chapter 2), and the practical effects on fresh (Chapter 3) and hardened (Chapter 4) concrete performance. Requirements for maintaining quality of cements are

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discussed in Chapter 5. Several case studies and lessons learned from them are summarized in Chapter 6. Sources of information include experience and published literature spanning the more than 25 years that these materials have been used in Europe and recent data developed to determine appropriate CSA requirements. The report concludes with a summary of the key points from throughout the publication.

Achieving comparable performance in concrete using PLC to that obtained using conventional portland cement is possible because finely ground limestone can contribute to development of microstructure, particularly when fineness and chemistry of the finished cement are optimized by the manufacturer. Mechanisms affecting performance include improved particle packing, establishment of nucleation sites for cement hydration, and reaction with calcium aluminate phases in the portland cement clinker or supplementary cementitious materials to form calcium carboaluminates. These are discussed in more detail in Chapter 2. Chapter 3 covers fresh concrete properties, including workability, bleeding, heat of hydration and setting time. Chapter 4 reviews effects on hardened properties: strength development and volume stability. Durability topics are included in Chapter 4 as well: permeability, chloride resistance, carbonation, freeze-thaw, sulfate attack (including thaumasite formation), ASR, and abrasion resistance. Chapter 5 discusses quality characteristics for limestones used in cements at these levels. Field trials conducted in Canada confirm the performance characteristics of PLC in concrete (Thomas et al., 2010); several case studies are summarized in Chapter 6.

1.2 INTERNATIONAL USE OF LIMESTONE IN CEMENT

1.2.1 Europe

Although specification EN 197-1 was formally adopted in 2000 by members of the European Committee for Standardization (CEN), limestone cements have a long history of use in Europe. Spanish standards permitted up to 10% limestone in 1960 (raised to 35% in 1975), French standards adopted provisions for use of up to 35% limestone in 1979 (Moir 2003), and German standards for PLC were adopted in 1994 (Mans et al. 2000), although cements with up to 20% limestone were manufactured for specialty applications in Germany as far back as 1965.

The European standard EN 197-1 permits use of limestone as an ingredient in cements in three ranges. All of the 27 cement types defined in EN 197-1 may contain up to 5% of a minor additional constituent (MAC), which is commonly limestone. Limestone is used at higher levels in CEM II cements with 6 different designations: CEM II/A-L and CEM II/A-LL cements contain between 6% and 20% limestone (by mass) while CEM II/B-L and CEM II/B-LL cements contain between 21% and 35% limestone. (The -L or -LL suffixes identify the total organic carbon (TOC) content of the limestone used: LL cements use limestone with a maximum TOC of 0.2% by mass, while L cements are made with limestones with a TOC of up to 0.5% TOC.) Limestone is also commonly used in “portland composite cements” CEM II/A-M and CEM II/B-M cements (the -M suffix stands for *m*ultiple ingredients) in which the total amount of non-clinker constituents is less than 20% by mass or less that 35% by mass, respectively. Table 1.1 summarizes the European nomenclature.

Table 1.1 Nomenclature of European Portland-Limestone Cements

Type	Name	Range of limestone content, mass %	Notes
CEM II/A-L	Portland-limestone cement	6 to 20	TOC*≤0.5%
CEM II/A-LL	Portland-limestone cement	6 to 20	TOC≤0.2%
CEM II/A-M	Portland composite cement	Less than 20**	
CEM II/B-L	Portland-limestone cement	21 to 35	TOC≤0.5%
CEM II/B-LL	Portland-limestone cement	21 to 35	TOC≤0.2%
CEM II/B-M	Portland composite cement	Less than 35**	

*TOC=total organic carbon content of the limestone used. The provision for TOC content of the limestone appears to be related to freeze-thaw performance of concretes (see Chapter 5 for additional detail).

**Portland composite cements contain more than one main constituent (besides clinker) totaling less than 20% or less than 35% by mass respectively for CEM II/A-M and CEM II/B-M.

Physical properties of all EN 197-1 cements (whether containing limestone or not) fall into three basic classes, 32.5, 42.5, and 52.5, which refer to the lower end of a 28-d strength range requirement. Basic requirements are shown in Table 1.2. Limestone cements meet the same physical requirements as other cement types.

Table 1.2 Basic Physical Requirements of European Cements*

Strength Class	Compressive Strength, MPa				Initial setting time, min	Soundness (expansion) mm
	Early strength		Later Strength			
	2 days	7 days	28 days			
32.5N	–	≥ 16.0	≥ 32.5	≤ 52.5	≥ 75	≤ 10
32.5R	≥ 10.0	–				
42.5N	≥ 10.0	–	≥ 42.5	≤ 62.5	≥ 60	
42.5R	≥ 20.0	–				
52.5N	≥ 20.0	–	≥ 52.5	–	≥ 45	
52.5R	≥ 30.0	–				

*Due to significant differences between test methods, these values cannot be directly compared with ASTM or CSA requirements.

Figure 1.1 provides a summary of the quantity of various cement types used in Europe between 1999 and 2004. Note that use of portland-limestone cements over this timeframe more than doubled, from about 15% market share to more than 30%.

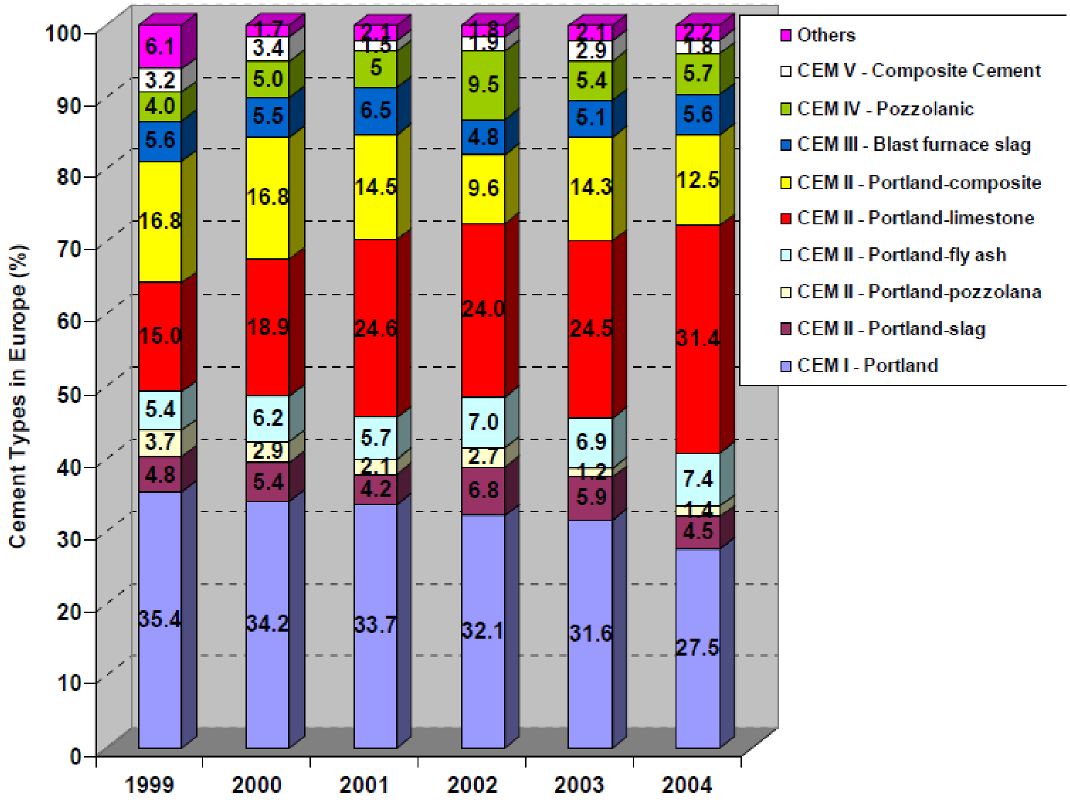

Figure 1.1 Percentage of various EN197-1 cement types used in Europe between 1999 and 2004 (Hooton et al., 2007, quoting Cembureau data.).

1.2.2 Canada

In 2008, Canada's cementitious materials compendium, CSA A3000, adopted provisions for portland-limestone cements, and some of those provisions were amended in 2010. Portland-limestone cements are defined by CSA as containing more than 5% and up to 15% limestone. The following provides a brief synopsis of Canadian portland-limestone cement specifications.

Although it is a prescriptive specification, CSA A3000uses a naming convention for portland cement, blended cement, and portland-limestone cement similar to that used by ASTM C1157, *Standard Performance Specification for Hydraulic Cement*. As an example, a "GU" designation indicates that the cement is intended for general use in concrete construction. CSA lists four types of portland-limestone cement as shown in Table 1.3. In addition, six types of portland-limestone blended cements are also defined.

While the European standard EN 197-1 includes provisions for portland-limestone cements containing limestone in amounts up to 35%, the CSA A3001 limit is set at a maximum of 15% to help ensure comparable performance to conventional portland and blended cements. CSA portland-limestone cements must meet the same physical requirements as portland cements or blended cements of parallel type designation as shown in Table 1.4.

Table 1.3 CSA A3001-08 (Amendment 2010) Naming Convention for Portland, Blended, and Portland-Limestone Cements

Application	Portland cement type	Blended cement type	Portland-limestone cement type	Portland-limestone blended cement type
General use	GU	GUb	GUL	GULb
Moderate sulfate resistance	MS	MSb	-*	MSLb
Moderate heat of hydration	MH	MHb	MHL	MHLb
High early strength	HE	HEb	HEL	HELb
Low heat of hydration	LH	LHb	LHL	LHLb
High sulfate resistance	HS	HSb	-*	HSLb

* Performance tests are required of blended cements using portland-limestone cements as a base material, MSLb or HSLb, which are permitted in sulfate exposures. Use of portland-limestone cements without supplementary cementitious materials (in a blended cement) is not permitted in sulfate exposures.

Table 1.4 CSA A3001-08 Physical Requirements for Portland Cements and Portland-Limestone Cements

Type	GU	HE	MH	LH	HS	MS
Property	GUL	HEL	MHL	LHL		
Fineness: 45-μm sieve, maximum % retained	28	--	28	--	28	28
Autoclave, maximum % expansion	1.0	1.0	1.0	1.0	1.0	1.0
Initial time of set, minutes						
minimum	45	45	45	45	45	45
maximum	375	250	375	375	375	375
Heat of hydration, 7-day maximum, kJ/kg	--	--	300	275	--	--
Sulfate resistance, 14-day maximum % expansion	--	--	--	--	0.035	0.050
Compressive strength, minimum, MPa						
1-day	--	13.5	--	--	--	--
3-day	14.5	24.0	14.5	8.5	14.5	14.5
7-day	20.0	--	20.0	--	20.0	20.0
28-day	26.5	--	26.5	25.0	26.5	26.5

Table 1.4b CSA A3001 (2010 Amendment) Physical Requirements for Blended Cements and Portland-Limestone Blended Cements.

Type Property	GUb GULb	HEb HELb	MHb MHLb	LHb LHLb	HSb HSLb	MSb MSLb
Fineness: 45-μm sieve, maximum % retained	24	24	24	24	24	24
Autoclave, maximum % expansion	0.8	0.8	0.8	0.8	0.8	0.8
Initial time of set, minutes						
minimum	45	45	60	90	60	60
maximum	480	250	480	480	480	480
Heat of hydration, 7-day maximum, kJ/kg	--	--	300	275	--	--
Compressive strength, minimum MPa						
1-day	--	13.5	--	--	--	--
3-day	14.5	24.0	14.5	--	14.5	14.5
7-day	20.0	--	20.0	8.5	20.0	20.0
28-day	26.5	--	26.5	25.0	26.5	26.5
Sulfate resistance maximum % expansion at 6 months at 23°C	--	--	--	--	0.05*	0. 10
Sulfate resistance** maximum % expansion at 18 months at 5°C.	--	--	--	--	0.10***	0.10***

**If the expansion is greater than 0.05% at 6 months but less than 0.10% at 1 year, the cement shall be considered to have passed.*

***Sulfate Resistance testing shall be run on MSLb and HSLb cement at both 23°C and 5°C as specified in this table. This requirement does not apply to MSb and HSb cement. In addition, MSLb and HSLb cements require special minimum proportions. -*

**** If the increase in expansion between 12 and 18 months exceeds 0.03%, the sulfate expansion at 24 months shall not exceed 0.10% in order for the cement to be deemed to have passed the sulfate resistance requirement.*

CSA A3001 has modified chemical requirements for portland-limestone cements, as shown in Table 1.5. A higher loss-on-ignition limit, a maximum of 10% rather than 3% for portland cements, is included as uncalcined limestone in cement looses approximately half of its weight upon heating to ignition temperatures. For portland-limestone blended cements, the LOI limit depends on the type of SCM used, but ranges from 10% to 17%.

Table 1.5 Other Requirements for Portland-Limestone Cements in CSA A3001-08

Type Property	GUL	MHL	HEL	LHL
Loss-on-ignition, maximum %	10.0	10.0	10.0	10.0
Sulfate content, maximum %*	3.0	3.0	3.0	3.0

*Default sulfate content may be exceeded if CSA A3004-C5 expansion results are less than 0.020% at 14 days.

1.2.3 Other Countries

Several countries outside of Europe also use limestone as an ingredient in cement. Pandey and Sharma (2002), based on a review of the 1991 edition of *Cement Standards of the World* (Cembureau 1993) listed 39 countries that allowed "mineral additions" to cements in amounts up to 20% at that time. Of these, several specifically mention use of limestone: notably, China and the former USSR both permitted up to 10% limestone.

In Mexico, NMX C-414 defines cement Type CPC, termed a blended portland cement, that may contain between 6% and 35% limestone, and may include other ingredients such as granulated blast-furnace slag, pozzolan, or silica fume in amounts such that the clinker and gypsum fraction is not less than 50% by mass.

Brazil and other South American countries also commonly include limestone in several cement types (Tanesi and Silva, in press). Table 1.6 shows quantities permitted.

Table 1.6 Limestone contents permitted in Central and South America

Country	Type	Limestone content (% by mass)
Bolivia	Normal portland cement	≤ 6%
Brazil	Normal portland cement	≤ 5%
Brazil	High early strength cement	≤ 5%
Costa Rica	High early strength cement	≤12%
Argentina	Calcium carbonate modified portland cement	≤20%
Brazil	Calcium carbonate modified portland cement	6% to 10%
Costa Rica	Calcium carbonate modified portland cement	≤10%
Peru	Calcium carbonate modified portland cement	≤15%
Brazil	Slag modified portland cement	≤ 10%
Brazil	Pozzolan modified portland cement	≤10%
Brazil	Portland blast-furnace slag cement	≤10%
Brazil	Portland-pozzolan cement	<5%

Source: Adapted from Tanesi and Silva (in press).

New Zealand (NZS 3125) also has had specifications for “portland-limestone filler cements,” with up to 15% limestone since about 1991. Like EN 197-1, this standard requires a minimum calcium carbonate content of 75% and limits on clay content of the limestone and organic matter content.

Besides EU countries, many countries around the world refer also refer to EN 197-1 for cement specifications, and thus also have experience with portland-limestone cements. Among these is South Africa.

1.3 IMPACT ON SUSTAINABILITY

The primary sustainability effect of using limestone as an ingredient in blended cements at levels of 5% to 15% by mass is that less clinker has to be produced for an equivalent amount of cement, and therefore less energy is consumed and CO_2 emissions (and other greenhouse gases) are reduced. Carbon dioxide emissions for cement plants come predominantly from two sources: calcination of the limestone, a primary raw ingredient for clinker manufacture, and fossil fuel consumption to heat the raw materials to the temperature required to form clinker. Very roughly, limestone is about 50% by mass CO_2 and release of this CO_2 during calcination accounts for about 60% of the CO_2 emissions produced at a cement plant. Both of these quantities are reduced in blended cement production as less clinker is used in the cement. These reductions are roughly proportional to the decrease in the amount of clinker in the blended cement.

Although for other blended cements these effects can be realized with the use of pozzolan and blast-furnace slag (slag cement); the use of limestone would provide an additional option to improve sustainability characteristics with a material that is readily available to all cement plants. For some plants energy use and CO_2 emissions related to transportation of fly ash or blast-furnace slag used in blended cements will likely be higher than for blended cements using limestone since cement plants are situated on limestone quarries. It should also be noted that fly ash and blast-furnace slag may be used in quantities greater than 15%, which is the proposed maximum for limestone. Fly ash and slag are also more chemically reactive than limestone. For some plants and applications, limestone can be used with fly ash or blast-furnace slag to produce ternary blends that further improve sustainability characteristics.

In general, portland-limestone blended cements are ground finer than portland cements and thus they may require higher grinding energy. However, this is a relatively smaller energy usage than clinker production and the net change is for lower CO_2 emissions and energy use to produce blended cements. Figure 1.2 provides specific examples for CO_2 emission reductions for three German cement plants (Schmidt 1992). The calculations include the total energy demand of all steps in the production process taking into account the specific demand of fuel energy. The replacement of about 15% by mass of the clinker by limestone reduces CO_2 emissions on average by 12% (Schmidt et al. 2010). Similar results can be calculated for the emissions of nitrous oxides (NO_x) and sulfur dioxide (SO_2).

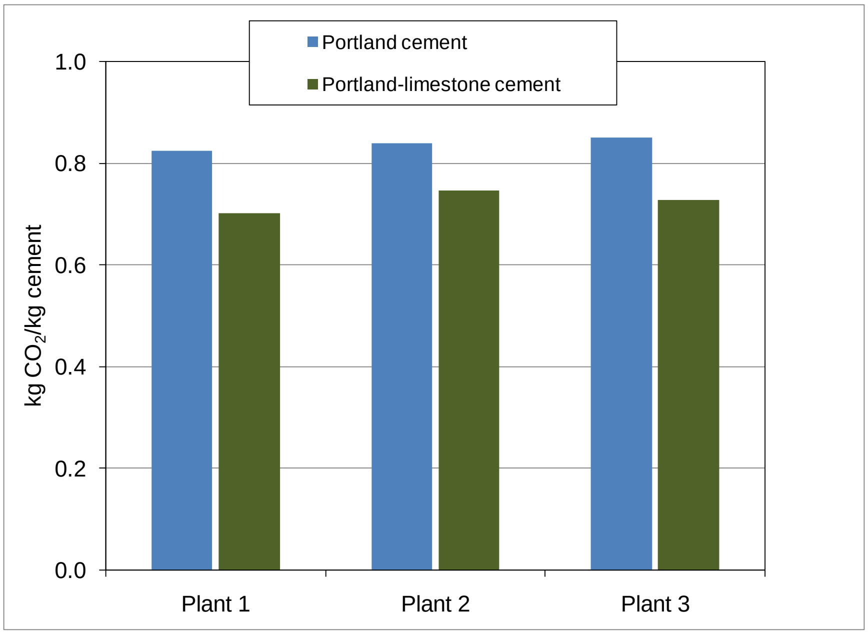

Figure 1.2 Specific CO_2 emissions from the production of portland cement or portland-limestone cement for 3 German cement plants (adapted from Schmidt 1992).

Another benefit of portland-limestone cements is their lower raw material demand which reduces the consumption of natural resources. To produce 1 ton of portland-cement, about 1.3 to

1.4 tons of raw materials are needed. Portland-limestone cements need about 10% less primary raw materials.

An analysis of the environmental impact of up to 5% limestone in the production of *portland* cement is found in Nisbet (1996). Based on the approach used in that analysis, an estimate is given in Table 1.7 assuming 10% or 15% limestone for *blended* cements. These provide conservative estimates of reductions in environmental and energy impacts that can be achieved through use of limestone, as compared to a portland cement without limestone. It should be noted that portland cements in the US are permitted to contain up to 5% limestone (typical level is likely about 3% on average), which will reduce the savings noted in Table 1.7. Even if the maximum amount of limestone (5%) is used in portland cements, use of portland-limestone cements with a total of 10% to 15% limestone will result in significant additional reductions in energy and emissions.

Table 1.7 Estimated Annual Reduction in Energy Usage and Emissions Resulting From Use of 10% or 15% Limestone in Blended Cement*

	10% limestone (per million tons of cement)	15% limestone (per million tons of cement)
Energy Reduction		
Fuel (million BTU)	443,000	664,000
Electricity (kWh)	6,970,000	10,440,000
Emissions Reduction		
SO_2 (lbs)	581,000	870,000
NO_x (lbs)	580,000	870,000
CO (lbs)	104,000	155,000
CO_2 (tons)	94,000	141,000
Total Hydrocarbon, THC (lbs)	14,300	21,400

* Following the approach of Nisbet (1996). Estimates compare portland cement with 5% gypsum, no limestone, and no inorganic processing addition with blended cement containing portland cement clinker, gypsum and the amount of limestone indicated.

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Thomas, M. D. A., Hooton, R. D., Cail, K., Smith, B. A., De Wal, J., and Kazanis, K., "Field Trials of Concretes Produced with Portland Limestone Cement," *Concrete International*, Vol. 32, No. 1, January, 2010, pages 35 to 41.

CHAPTER 2 EFFECTS OF LIMESTONE ON CEMENT

This chapter provides a review of the physical properties of the limestone used for blending or intergrinding with ordinary portland cement to produce a portland-limestone cement. It has been observed that when the limestone is ground to provide a powder with sufficient surface area (> 500 m^2/kg Blaine), it can used in conjunction with portland cement to improve the particle size distribution of the cementitious system to produce a lower water demand and many improved properties (Schmidt et al. 2004). Since limestone is easier to grind than clinker, intergrinding limestone with clinker tends to produce a wider particle size distribution in a finished portland-limestone cement. This chapter reviews many of the properties of the limestone relative to reactions with cement and discusses the influence of limestone on the overall hydration reactions.

2.1 PARTICLE SIZE DISTRIBUTION

It is known that the properties of cementitious materials are influenced by the particle size distribution (PSD) of constituents as this can impact the rheology, volume of voids, and water demand. When limestone is interground with portland cement clinker it is important to recognize that the Blaine fineness of the finished cement will generally be higher than the portland cement since the limestone is softer and more easily ground. Tsivilis et al. (2000) showed an example of the specific surface area increase required (from 260 m^2/g to 366 m^2/g) to have similar strength gain and setting characteristics as the limestone was increased from 0% to 15% of the clinker by mass. Similar surface area increases have been reported by Schmidt et al. (2004) to obtain a similar packing density, voids content, and required water for limestone cements as shown in Table 2.1.

Table 2.1 Characteristics of Portland-Limestone Cements (after Schmidt et al. 2004)

Material	Fineness of grinding	Calculated packing density	Voids content	Water requirement
mass %	cm^2/g	% vol.	% vol.	EN 196
Limestone	5,780	66.6	33.4	
CEM 32.5	2,620	65.5	34.5	25.5
CEM 42.5	3,380	64.8	35.2	27.5
10% LS + 90% CEM 32.5	3,030	65.8	34.2	24.0
15% LS + 85% CEM 32.5	3,310	65.9	34.1	24.0
20% LS + 80% CEM 32.5	3,410	66.0	34.0	24.0
10% LS + 90% CEM 42.5	3,650	65.0	35.0	27.0
15% LS + 85% CEM 42.5	3,820	65.2	34.8	27.0
20% LS + 80% CEM 42.5	3,990	65.3	34.7	26.5

Limestone, when ground for optimum fineness, can lower the water demand, reduce bleeding, improve workability, and increase strength because it improves overall particle gradation of a cement (Schmidt 1992). In general the use of 15% to 20% limestone can result in optimal packing density; however this is less pronounced in cements that are finer (Schmidt et al. 1994). When the clinker and limestone are interground, the limestone is normally easier to grind and tends to become the majority of the smaller particles (Figure 2.1), thus broadening the particle size distribution.

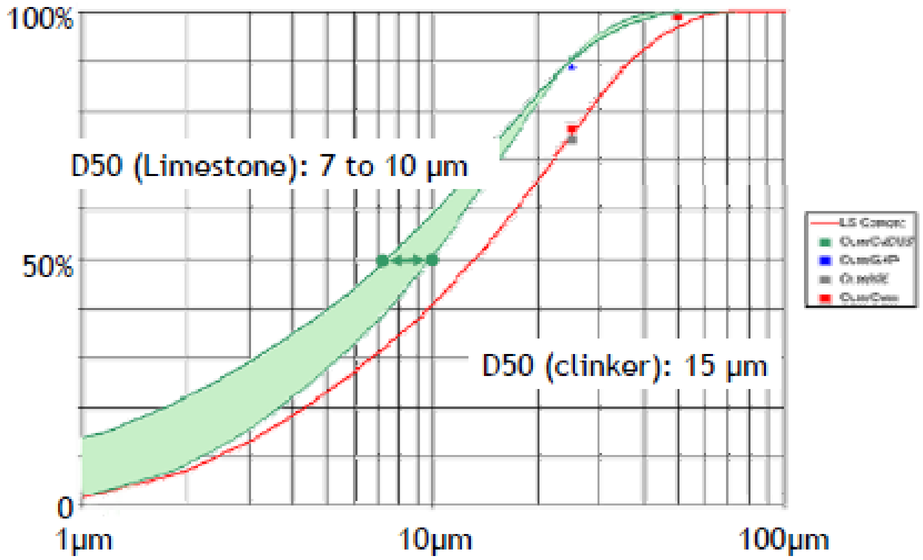

Figure 2.1 Particle size distributions for components of an interground cement. The limestone fraction is finer than ground clinker (Barcelo data as quoted in Hooton 2009).

When ground separately the limestone needs to be sufficiently fine since if it is too coarse, an increase in particle spacing may occur along with an increase in the voids between the particles. This can result in increased water absorption and reduced strength (Cam and Neithalath 2010). Some researchers have suggested a potential benefit of intergrinding on the carboaluminate reaction, for example to reduce porosity slightly (Matschei et al. 2007a) and thereby improve durability.

Computer modeling (Bentz and Conway 2001) and experimental results (Bentz 2005) on pastes and mortars indicate that relatively coarse limestone (relative to its base portland cement) could provide for more efficient use of cement. The microstructure based modeling predicted, for systems with about 15% limestone, that replacing coarse cement particles in low water-to-cement ratio pastes, would result in small reductions in compressive strength, with a maximum of about 7% around 28 days, and decreasing with continued hydration. Experimental work (Bentz 2005) indicated that no strength reduction was observed at 56 days in mortars. In these cements the overall particle size distribution was similar to the portland cement, as limestone replaced predominantly coarse particles (above 30 µm) by about 15% on a volume basis. Bentz notes that intergrinding of limestone in cement provides ecologic and economic benefits, but further hypothesizes that additional benefits may be achieved if limestone is ground separately to a relatively coarser size than if interground, and then blended with an appropriate sized portland cement, as relatively less energy is used to grind the limestone less finely.

Bentz et al. (2009b) provide a comparison of shrinkage for concretes made with cements without limestone and with 10% limestone at three different fineness levels (Figure 2.2). Restrained shrinkage was similar to the control for the finest limestone and somewhat lower for the concrete with the coarsest limestone.

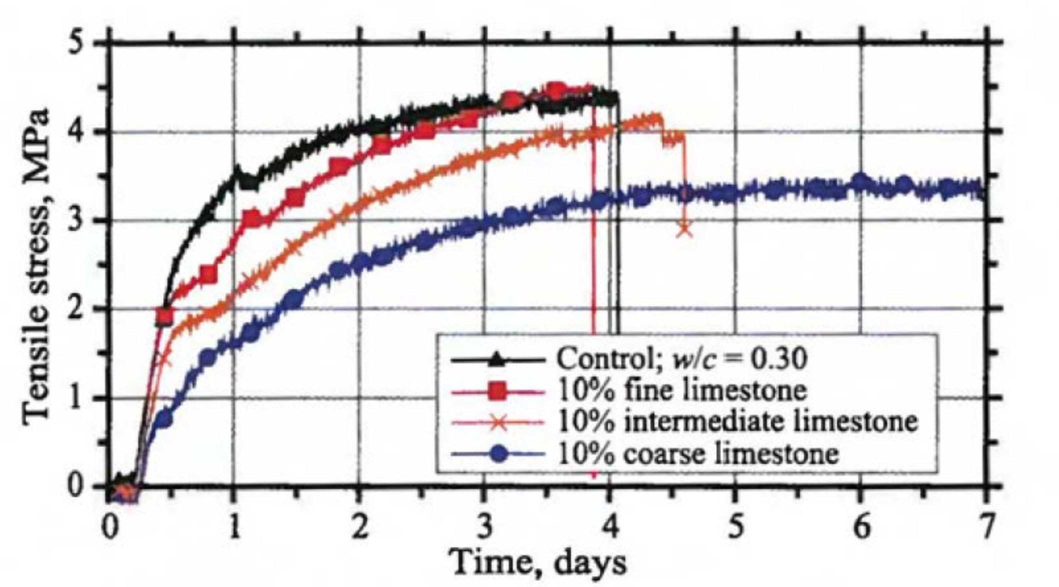

Figure 2.2 Restrained shrinkage results (Bentz et al. 2009b, quoting data from Bucher 2009) showing improved time to cracking results for low water-to-cement ratio concretes made cements with 10% limestone (and control without limestone). The coarse limestone exhibited much longer time to cracking.

Deniz (2004) reported that an increase in ball mill speed was helpful for more efficiently grinding limestone as compared with ordinary portland cement.

2.2 INFLUENCE OF COMPOSITION

Tsivilis et al. (1999) examined the influence of limestone composition on the performance of portland-limestone cements. Three limestones (one with calcite with a higher concentration of calcium carbonate and the others being primarily dolomite) were interground with two different clinkers. They observed that for all the materials and grinding times at up to 15% limestone addition, the limestone provided equal or improved strength and rate of strength development. The concretes containing limestone added as a cement replacement showed a lower water demand (Tsivilis et al. 1998). It was also observed that clinker with a higher C_3A was more reactive with limestone.

Siebel and Sprung (1991) compared effects of characteristics of limestone in cement on concrete performance. Their results are covered in more detail in Chapter 5; however, in summary, although no direct correlation between calcium carbonate content ($CaCO_3$), methylene blue index (MBI), or total organic carbon content (TOC) and the freeze-thaw performance of concretes made with the limestones was observed, limits on these three parameters became the basis for limestone quality for use in cements.

2.3 HYDRATION CHEMISTRY

In most early research it was believed that limestone acted as an inert filler; however more recent research has shown that limestone participates to some extent in hydration reactions. In addition, fine limestone particles may promote silicate hydration by providing nucleation sites for C-S-H precipitation.

Calcium carbonate has been reported to react with the tricalcium aluminate to form high and low forms of carboaluminates (Hooton et al. 2007). Matschei et al. (2007a) observed that small amounts of limestone (calcite) reacted to form various carboaluminate phases. The unreacted calcite increased with an increase in the sulfate content. This work clearly showed the relative amounts of the phases that can be present. Lothenbach et al. (2008) coupled thermodynamic calculations with experimental observations to show that the formation of monocarboaluminate stabilized ettringite, increased the volume of hydrated products, and decreased porosity. These works provide quantitative calculations of the phases that may be present, providing a great step forward in understanding these systems.

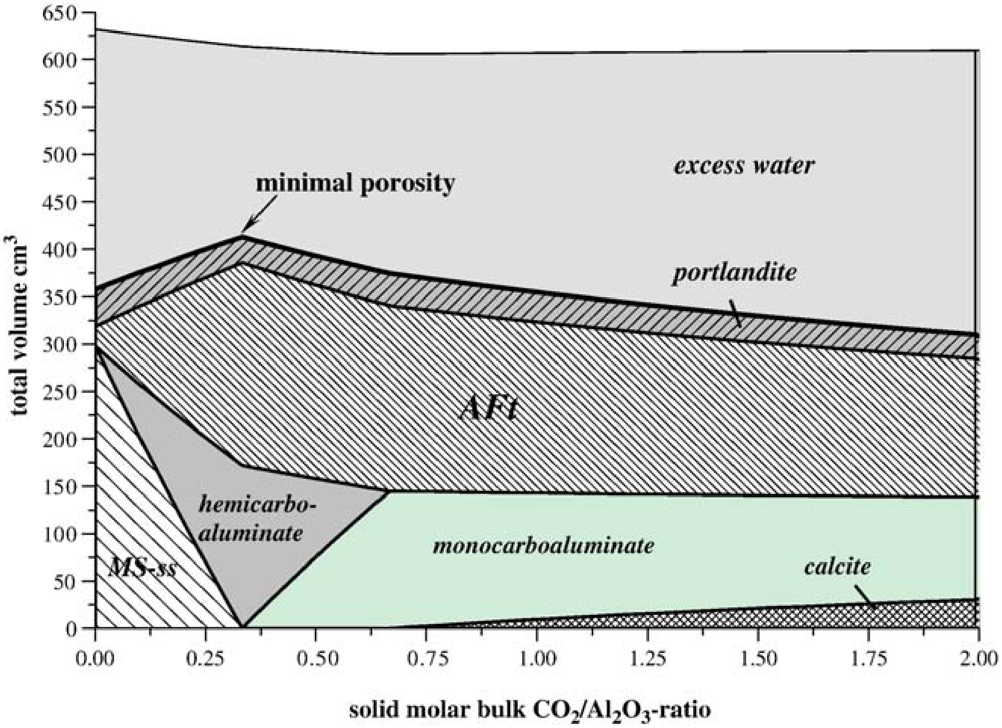

Figure 2.3 Calculated volumes of hydrate phases for a model mixture consisting of C_3A, portlandite and with fixed sulfate ratio (SO_3/Al_2O_3=1) as a function of carbonate ratio (CO_3/Al_2O_3) at 25°C (constant total amount of solids, C_3A+$CaSO_4$+CH+Cc=3.25 mol, reacted with 500 g water) (Matschei et al. 2007a).

Additionally, there may be a chemical effect that accelerates the hydration of tricalcium silicate in the presence of calcium carbonate. Pera et al. (1999) reported an acceleration of the C_3S reaction in the presence of limestone.

Tsivilis et al. (2002) found that the addition of limestone as an interground material increased the reactivity of the clinker. Campiteli and Florindo (1990) found that the addition of limestone decreased the optimum SO_3 content. Production of CH appears to increase at early ages, which was attributed in part to the dissolution of limestone and in part to the role of the limestone in acting as a nucleation site (Turker and Erdoğdu 2000).

Ye et al. (2007) reported that the limestone did not participate in chemical reactions; however it is important to note that in their study, the limestone was relatively coarse compared than the base cement.

2.4 MICROSTRUCTURE

Zelić et al. (2009) reported that the use of limestone increased the porosity of the paste fraction of mortars at 15%; however it should be noted that in this study the limestone had a similar size distribution relative to the base portland cement, and the limestone was added to the cement and not interground. Schmidt et al. (2004) reported that materials (limestone and ground clinker) of similar size would result in increased porosity when used together, while finer ground limestone could be combined with a relatively coarse clinker to reduce the overall porosity. Matschei et al. (2007b) suggested that carboaluminates would reduce porosity (increasing density), which in turn can increase properties such as strength (Figure 2.4).

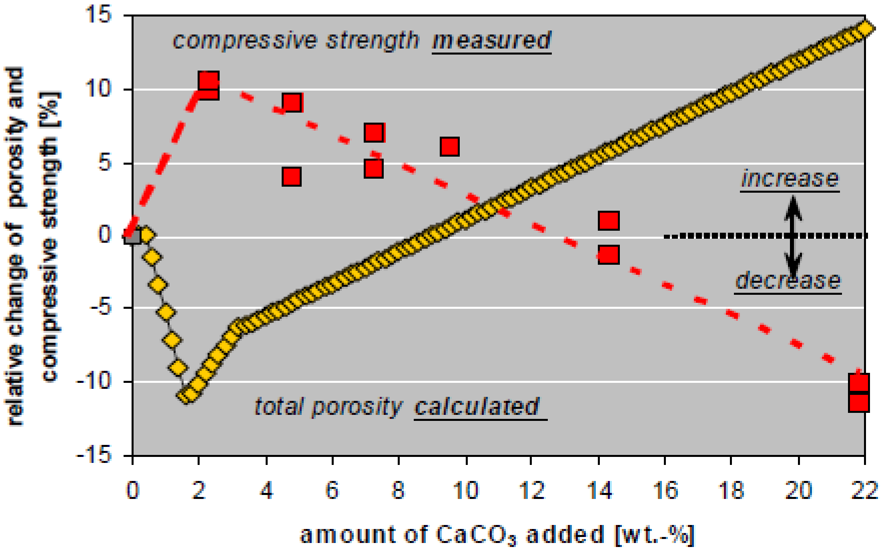

Figure 2.4 A correlation between porosity and strength development with limestone (Matschei et al. 2007b).

Liu et al. (2010) reported that limestone did not have pozzolanic properties; however, they did report that it led to the densification of the microstructure and interfacial transition zone in systems where limestone was used.

De Weerdt et al. (in press) observed that limestone led to the formation of mono- or hemi-carboaluminate hydrates instead of monosulfoaluminate hydrate. This effect helped to stabilize ettringite, leading to an increase in the volume of the hydrates and a reduction in porosity. This is similar to the findings of Lothenbach et al. (2008). They observed that fly ash could beneficially be blended with this system to obtain even greater porosity reductions. This was however noticed for relatively low limestone additions (<5%). Matschei et al. (2007b) reported that if aluminates are available from supplementary materials, the improved properties shown in Figs. 2.3 or 2.4 could occur at a higher limestone contents.

Bentz (2006) added limestone to the CEMHYD3D cement hydration modeling system to model its influence. While this was focused on lower limestone concentrations, additions of up to 20% were permitted. The model incorporated both physical and chemical effects. The revised model predicts a significant acceleration of cement hydration only in lower water-to-cement (e.g., 0.35) ratio cement pastes. Thus, limestone substitutions are projected to be particularly advantageous (from an energy and emissions standpoint) in mortars and concretes with low water-to-cement ratios.

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CHAPTER 3 EFFECTS ON FRESH CONCRETE PROPERTIES

This chapter provides a review of literature on the influence of portland-limestone cements on fresh concrete properties. The focus will be on limestone contents of up to 15%, but in some cases, studies involving higher amounts, up to 30%, are reviewed to illustrate specific points. The results indicate that limestone can be used effectively as an ingredient in cement with relatively minor impact on the fresh properties of the paste, mortar, or concrete.

Some important points should be considered when evaluating the literature. First, in some laboratory studies ground limestone is added to conventionally manufactured cement; however, other studies use commercially-produced portland-limestone cements in which limestone is interground. A subtle difference between the resulting materials is that intergrinding likely results in clinker and limestone particles with a different size distribution. Further, the intergrinding of cement and limestone may alter the properties of the component grains (Tsivilis 1998). In addition, in commercially manufactured portland-limestone blended cements, the sulfate content and particle size distribution can be optimized.

Another point is that many studies use limestone as a concrete filler (i.e., an ingredient separate from hydraulic cement) that is used in addition to the cementitious component of the system. This is common in self consolidating concretes (SCC) where limestone powders are added to alter the rheological properties. In general when limestone is used in this manner as a concrete ingredient, it demonstrates properties somewhere between a system with only hydraulic cement and a diluted system, as the limestone is practically inert. These effects depend strongly on the particle size distribution of the limestone added and the thoroughness of its mixing (homogeneity).

3.1 WORKABILITY

Based on the information provided in the literature, it appears that there are conflicting results on the role of portland-limestone cements on workability. In general the fineness of the limestone is the main factor that influences workability. No studies were found that reported an inability to use systems with limestone based on workability. The results of this review suggest that the use of limestone may alter the water demand, resulting in a slight increase or decrease when portland-limestone cements are compared to conventional cements. Therefore it appears that portland-limestone cements can be used following the same approach as for conventional portland cement.

Matthews (1994) reported that the water-to-cement ratio needed to be increased slightly to maintain workability (by about 0.01 for limestone additions less than 5% and 0.02 for limestone additions less than 25%). This differed from Schmidt et al. (1993) who observed an increase in workability for concrete with portland-limestone cements (13% to 17% limestone content), resulting in a reduction in water to cement ratio from 0.60 to 0.57 for the same consistency (compared to similar strength class cements without limestone).

Moir and Kelham (1997) reported that coarse limestone resulted in less workable concrete than finer limestone for cements blended with 20% limestone. Nehdi et al. (1998) used portland cement and limestone to make concretes in which the rheological properties could be measured and likewise found that decreasing the average particle size of the limestone (from 3 µm to 0.7 µm) provided improved flow properties (defined as flow resistance) of concrete; however for all mixtures except those with 10% limestone content, the superplasticizer dosage was increased to maintain a similar slump, presumably as a result of adsorption by the finer limestone particles. Further, they observed that the addition of the limestone did not result in as significant a demand for chemical admixtures as other fine additives like silica fume.

A lower water demand for mortar and concrete containing various portland-limestone cements was observed by Tsivilis et al. (1999, 2000) as compared with conventional mixtures with portland cements. They observed that limestone with higher fineness increased the water demand. This is consistent with the results reported by Schmidt et al. (1993).

Ghezal et al. (2002) studied the use of limestone in self consolidating concrete (SCC) and reported slump loss in some SCC mixtures depending on the limestone addition rate and the amount of high range water reducer. They developed a surface response model to describe the complex interactions between cement content, limestone replacement volume, and chemical admixture addition.

El Barrak et al. (2009) also examined the role of limestone used as filler in SCC. They used a coaxial rheometer with six-blade vane to determine both the static yield stress and the apparent viscosity of the mixtures. The experimental results were analyzed using multi-variable regression. They noticed that the limestone filler had less influence in workability, stating that it acted more as a ‘lubricating agent’ than a reactive material after the first few minutes of mixing. The influence of limestone addition on rheology (yield stress) was less than that of the water-to-cement ratio or the use of chemical admixtures. The influence of limestone addition on viscosity was more influenced by the interparticle friction than the yield stress was.

For mortar mixtures with limestone used as a replacement for cement (15% and 30% by mass), an increase in slump was reported by Sahmaran et al. (2006). This was observed even in the case where the limestone was finer that the cement it was replacing (although the Blaine fineness could not be determined, it was reported that the cement had an average particle diameter of approximately 20 µm while the limestone had an average particle diameter of approximately 8 µm).

In contrast, Bucher et al. (2008) observed no major difference in slump for two commercially-produced cements from the same source (a conventional portland cement and a cement with 10% interground limestone).

Hooton and Thomas (2009) investigated cements with 12% limestone content and companion cements made using the same clinker in field applications. These mixtures also contained supplementary cementitious materials. It was reported that the crews placing all eight mixtures did not have any problems casting and finishing all eight mixtures, nor was any difference in the fresh properties including workability, bleeding, and finishing observed.

3.2 BLEEDING

In general the bleeding rate is dependent on the surface area of the cement or the limestone. As such increasing the fineness of the cement or limestone generally decreases the bleeding rate. A comprehensive study conducted at the BRE (1993) showed that both control cements as well as cements containing limestone show similar behavior based on the specific surface area of the cement (Fig. 3.1). In general, there appears to be no concern with bleeding for mixtures containing cements with limestone.

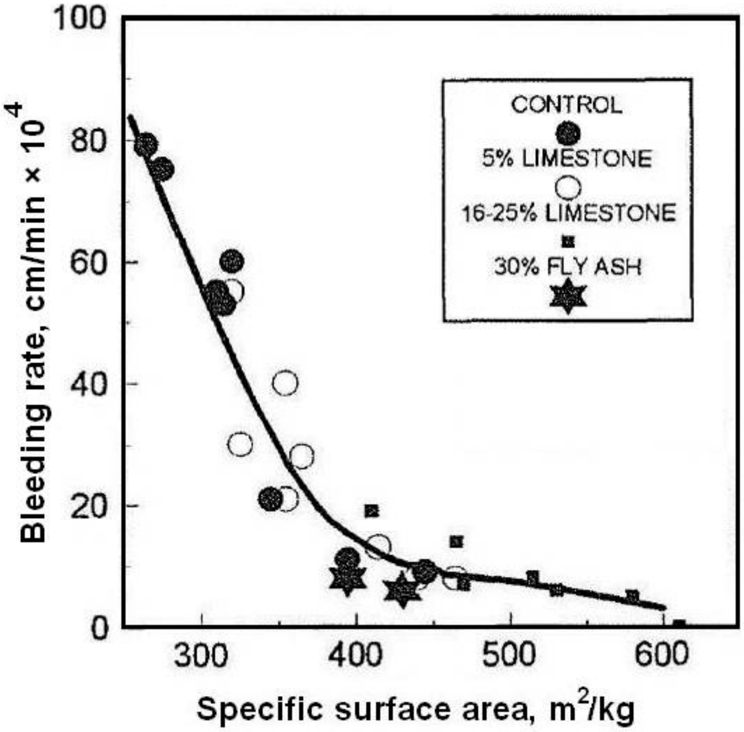

Figure 3.1 The influence of specific surface area on the bleeding rate (Moir and Kelham 1997, quoting BRE 1993).

3.3 SETTING TIME

Based on the information provided in the literature, it appears that cements with limestone may have a slight effect on setting time; however this does not appear to be a concern for the addition rates of interest (i.e., up to 15%). In general it has been reported that the influence of limestone on setting time was strongly related to the fineness of the limestone. As the limestone was ground finer, the setting time decreased (Hooton et al. 2007).

Ingram and Daugherty (1991) reviewed the influence of limestone additions on the setting of portland cement mixtures. While the report was focused on low levels of limestone (less than 5%), they quoted interesting work from Bobrowski et al. (1981) indicating that limestone-cement systems may reduce the potential for false setting.

El-Didamony et al. (1995) reported that low levels of limestone addition (up to 5%) showed an increase in the set time of cement pastes; however, as the limestone content increased, the set time began to decrease, resulting in a similar final set between 10% and 15% addition rates (as compared to the same cement without limestone. The times of set continued to decrease at higher rates of addition (20%). Moir and Kelham (1997) also reported that higher replacement levels (about 20%) led to a shorter setting time, relative to a control without limestone.

Hooton (1990) reported results from a study in which commercial cements were produced from the same clinker to manufacture ordinary portland cements and cements with up to 5% limestone. No consistent effect of the limestone on the heat of hydration or in setting times was observed.

Heikal et al. (2000) reported on results where limestone was used as a filler (from 0% to 20% by mass in which the limestone replaced a pozzolanic powder in the mixtures). Heikal reported that all of these materials had a surface area of approximately 310 m^2/g. They reported a decrease in setting time due to a particle packing effect as well as the carboaluminate reactions that occur in these materials; however, the results showed that the final set time was increased with limestone replacement.

Sahmaran et al. (2006) reported little difference (see Fig. 3.2) in the time of set for mortars when fine limestone particles were used as a replacement for cement (15% and 30% by mass) with 3 superplasticizers. The initial setting time decreased slightly on average with an increase in limestone content while the final setting time was slightly higher at 15% limestone content (than mortars without limestone), but slightly lower at 30%. Tsivilis et al. (2009) reported an increase in set time with an increase in limestone content. Bucher et al. (2008) demonstrated that when a conventional commercial portland cement was compared with a commercial portland-limestone cement with up to 10% limestone interground from the same plant, the time of set decreased as the limestone content increased. It should be noted however that the cement was optimized, as the fineness of the finished cements and their gypsum contents varied.

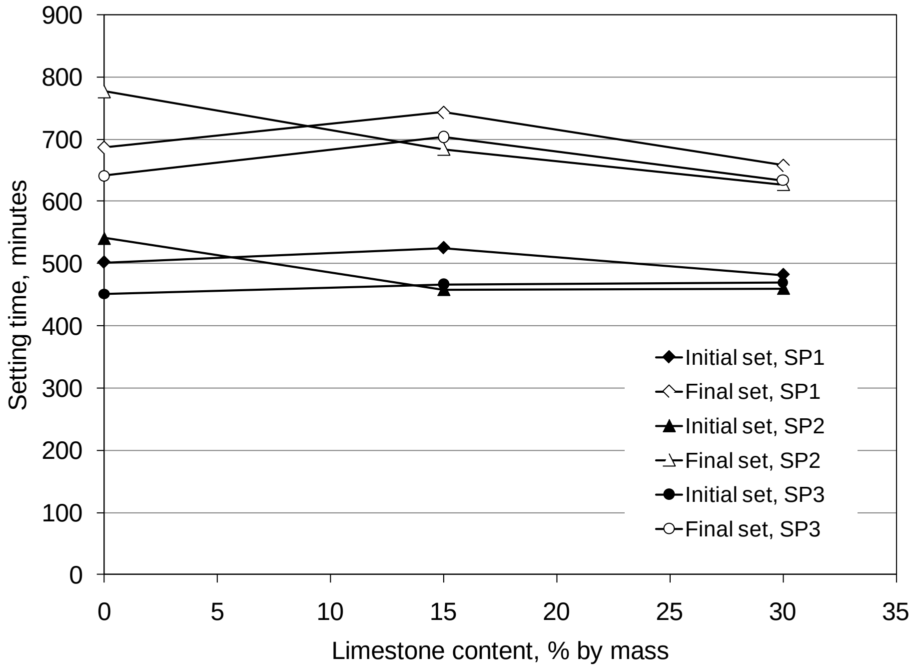

Figure 3.2 Effects of a limestone (added as a cement replacement) on setting time of mortars with three different superplasticizers (SP) (after Sahmaran et al. 2006).

Mounanga et al. (2010) reported that limestone filler could be used to reduce the setting time for concrete systems containing fly ash and blast-furnace slag. They suggested synergistic benefits of using other supplementary cementitious materials in systems where a portion of the cement has been replaced with limestone.

In field trials of concretes made with commercially-produced cements without limestone or with 12% limestone (manufactured at the same plants), by Hooton and Thomas (2009) did not observe any notable differences in the time of set (±15%).

Ezziane et al. (2010) reported that the replacement of cement with limestone increases the time of set in mortar. The limestone was added to the cement and not interground and was similar in size to the portland cement (340 m^2/g and 310 m^2/g respectively). This was related to the dilution effect considering the cement as the primary reactive particles. It should be noted however that this is similar to the delay in set reported for slag additions, as shown in Figure 3.3. The data also indicates that there is less of an influence of limestone addition on setting time as the temperature increases. They reported an 'optimal' concentration of 15% as the activation energy remained constant for initial set for levels above this concentration.

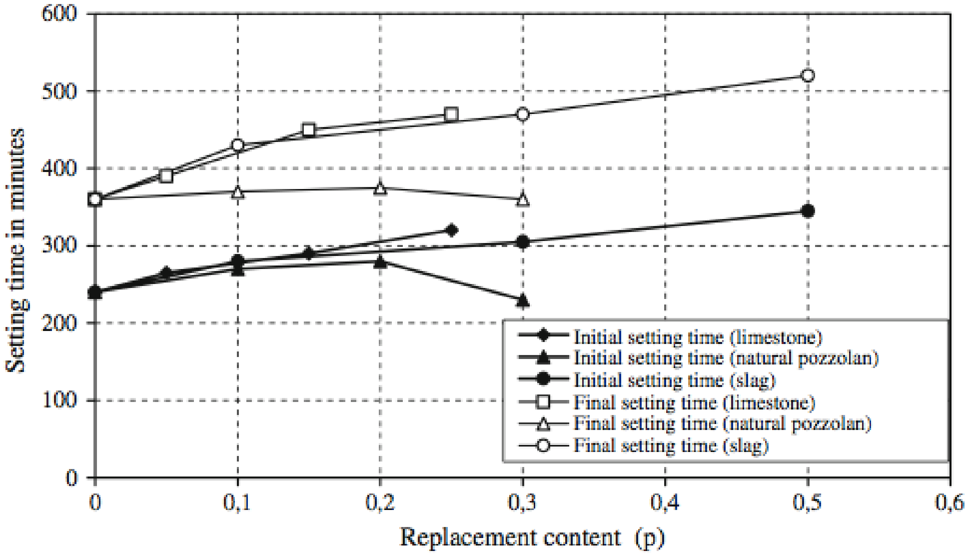

Figure 3.3 Influence of limestone addition on initial and final setting (Ezziane 2010).

3.4 INFLUENCES ON HYDRATION AND HEAT OF HYDRATION

It has been reported that limestone influences heat of hydration. Heats are generally increased when limestone is used as an addition to concrete, but decreased slightly when the limestone is used as a replacement for cement; however, it does not decrease to a point where the limestone can be considered to be completely inert (i.e., simple dilution effect). It appears that limestone can act as a site for nucleation of cement hydrates which would thereby increase heat of hydration at early ages. In general the influence of limestone on heat of hydration can be observed at early ages (up to 48 hours), which is generally attributed to dilution or nucleation effects. The influence of limestone on heat of hydration is much less significant at later ages. Further limestone is thought to contribute to a hydration reaction, forming carboaluminates, which may decrease setting time and reduce the induction period.

Hooton (1990) performed a study using commercial cements where same clinker was used to manufacture ordinary portland cement and cement with 5% limestone. He found that there was no consistent effect of the limestone on the heat of hydration.

Bonavetti et al. (2000) reported results from a study on concrete in which an increase in the rate of hydration occurred when limestone (10% and 20%) was added to cement. This can presumably be attributed to increased nucleation sites at early ages. Xiong and Van Breugel

(2003) noticed that limestone additions (and the limestone was relatively coarse as compared to the cement) in cement paste resulted in a slight acceleration of hydration by isothermal calorimetry and SEM; however, this effect decreased in higher water-to-cement ratio mixtures. This would be consistent with nucleation and dilution. Ezziane et al. (2010) also reported that limestone additions to portland cement in mortars provided nucleation sites which accelerated hydration according to Vicat testing results.

Poppe and DeSchutter (2005) noted that hydration of cement was influenced in pastes by the addition of limestone powder as a filler. The induction period was reduced and a greater heat was generated for each mixture with limestone filler in the concrete. Similarly, Heikal et al. (2000) reported that using limestone as a filler provided a carboaluminate reaction.

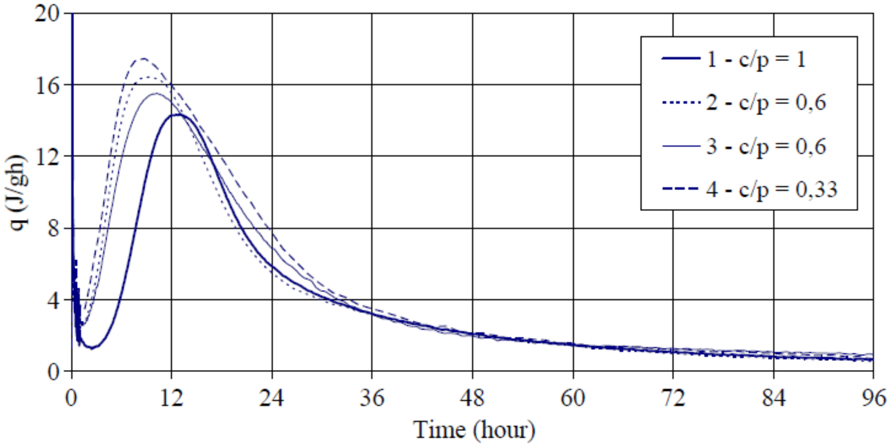

Figure 3.4 Heat production rate for mixtures with a CEM I 52.5 cement and high limestone contents at 20°C. "c/p" refers to the cement/powder (cement+limestone) ratio (Poppe and De Schutter 2005).

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CHAPTER 4 EFFECTS ON HARDENED CONCRETE PROPERTIES

4.1 MECHANICAL PROPERTIES

4.1.1 Strength and Strength Development

4.1.1.1 Compressive strength. Like other properties, the strength of concrete produced with portland-limestone cement (PLC) is influenced by the quality and quantity of the limestone, the clinker and other cement ingredients, and the particle size distribution of the finished cement. Limestone contents up to 15% may actually increase early-age strength as a combined result of improving particle packing (Sprung and Siebel 1991), increasing the rate of cement hydration (Vuk et al. 2001; Bonavetti et al. 2003), and production of calcium carboaluminate (Voglis et al. 2005). Schmidt (1992a) reported similar strengths for limestone levels up to 10%. However, Hawkins et al. (2005) showed that finer grinding is required in some cases even at lower levels of limestone (up to 8%). Figure 4.1 shows the data from Hawkins et al. (2005) indicating that equivalent strengths can be achieved with PLC with up to 8% limestone provided that the PLC is ground to a higher surface area or equal 45 µm (No. 325) sieve value. Fineness values for the cements used in this study are presented in Table 4.1; in these cements, clinker, limestone and gypsum were interground in a laboratory ball mill.

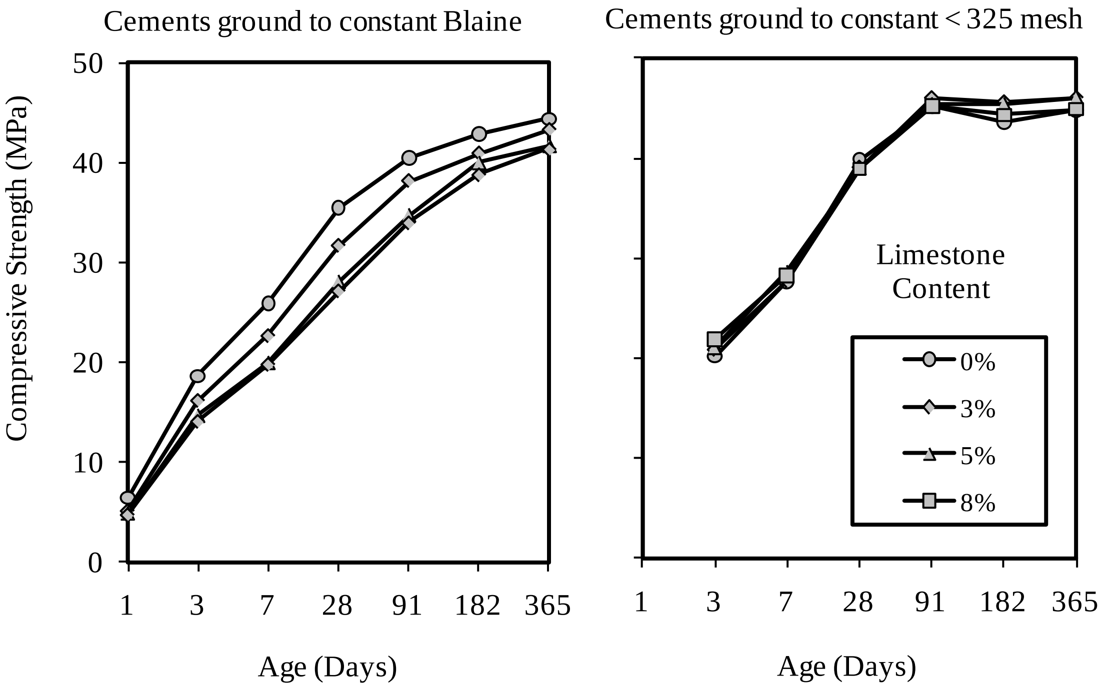


Figure 4.1 Strength development of mortars produced with PC and PLC ground to constant Blaine fineness (left) or constant Sub-325 Mesh (right) (Hawkins et al. 2005).

Table 4.1 Details of Cements used in Study by Hawkins et al. (2005)

	Limestone Content, %			
	0.0	3.0	5.5	8.0
Cements at “Constant” Blaine fineness				
< 45-µm sieve (325 mesh), %	90.0	85.5	81.0	82.4
Blaine fineness, m^2/kg	371	351	346	364
Cements at “Constant” < 45-µm sieve (325 mesh)				
< 45-µms sieve (325 mesh), %	94.7	91.9	91.2	91.6
Blaine fineness, m^2/kg	390	387	433	470

Dhir et al. (2007) showed that strength decreased with limestone content with addition levels in the range of 15% to 45%. Figure 4.2a shows the impact of the limestone content on the strength development of concrete with w/cm = 0.60. Strength is reduced at all ages with increasing limestone content. Figure 4.2b shows the impact of the limestone content on the 28-day strength of five series of concrete mixtures at varying w/cm. The strength reduction with 15% limestone is relatively small, but at higher levels of limestone the reduction in strength appears to be linearly related to the reduction in the portland cement content. Figure 4.2c shows that the w/cm needs to be reduced by 0.08 for every 10% increase in limestone content to achieve the same 28-day strength. In this study the limestone was added to the concrete mixer and was neither pre-blended nor interground with the cement. Matthews (1994) reported similar findings and concluded that the performance of concrete produced with cement containing 25% limestone (blended) was equivalent to what would be expected due to a 25% replacement of the portland cement with an inert diluent.

In a number of full-scale plant trials in Canada, it has been demonstrated that equivalent strength can be achieved in concrete produced with PLC containing up to 15% limestone by intergrinding the limestone with clinker (Thomas et al. 2010a; 2010b; 2010c; 2010d). The practice has been to grind the PLC to a higher fineness compared to the portland cement (PC) from the same plant. Figure 4.3 shows compressive strength data for concrete (w/cm = 0.49 to 0.51) produced with PLC (12% limestone) at a range of different Blaine fineness values. Typically, an increase in the Blaine fineness of between 100 m^2/kg to 120 m^2/kg is necessary to achieve the same 28-day strength. Table 4.2 shows strength data for three series of concrete mixtures (w/cm = 0.78 to 0.80, 0.45 and 0.40) produced with PC (4% limestone and 380 m^2/kg Blaine) and PLC (12% limestone and 500 m^2/kg Blaine). The strength varies with w/cm and the presence of SCM, but no significant differences are observed in the 28-day strength between equivalent mixes with PC or PLC. The early-age strength is increased for concretes with PLC compared with PC.

Alunno-Rossetti and Curcio (1997) compared the performance of industrial cements produced from two different plants (designated B and G) in Italy. A PC and a PLC with 20% limestone was collected from each plant. Table 4.3 shows the fineness of the four cements and the 28-strength of concrete mixes produced with these cements. There is little significant difference in the strength of the concrete produced with cements from the same plant.

In summary, with regards to the impact of PLC on the compressive strength of concrete, for cements with up to 15% limestone, the published data support the conclusions of Tsivilis et al. (1999a) “*… that the appropriate choice of clinker quality, limestone quality, % limestone content and cement fineness can lead to the production of a limestone cement with the desired properties.*”

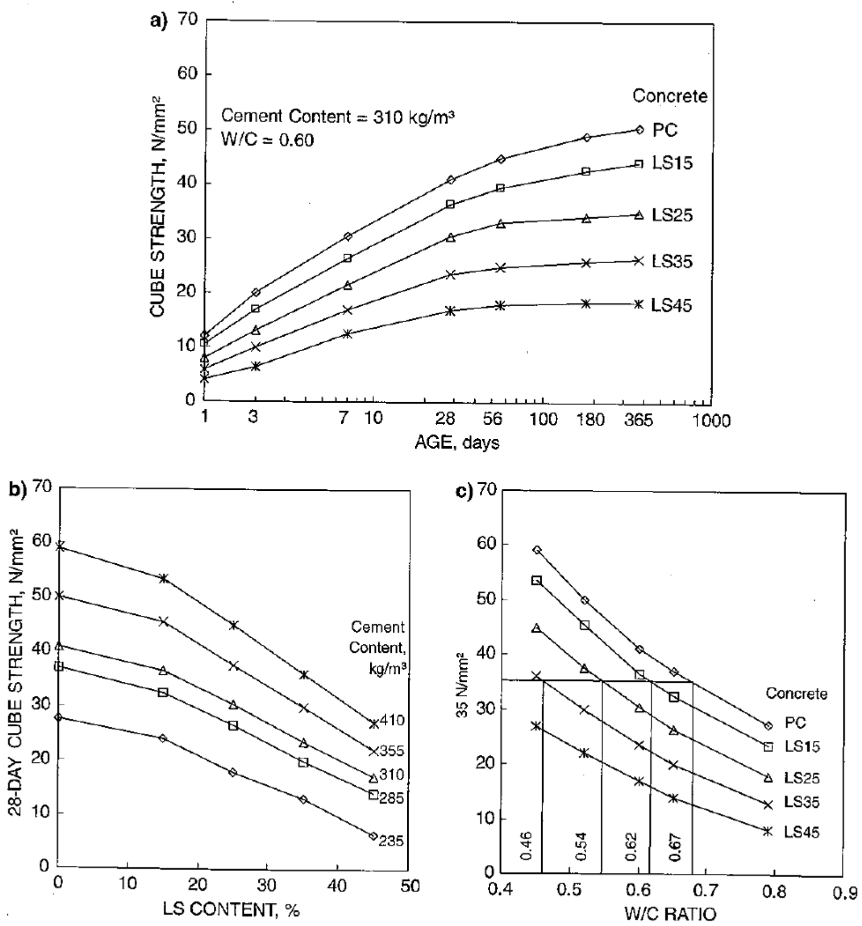


Figure 4.2 Effect of replacing cement with 15% to 45% limestone on the strength of concrete produced at a range of w/cm values (Dhir et al. 2005).

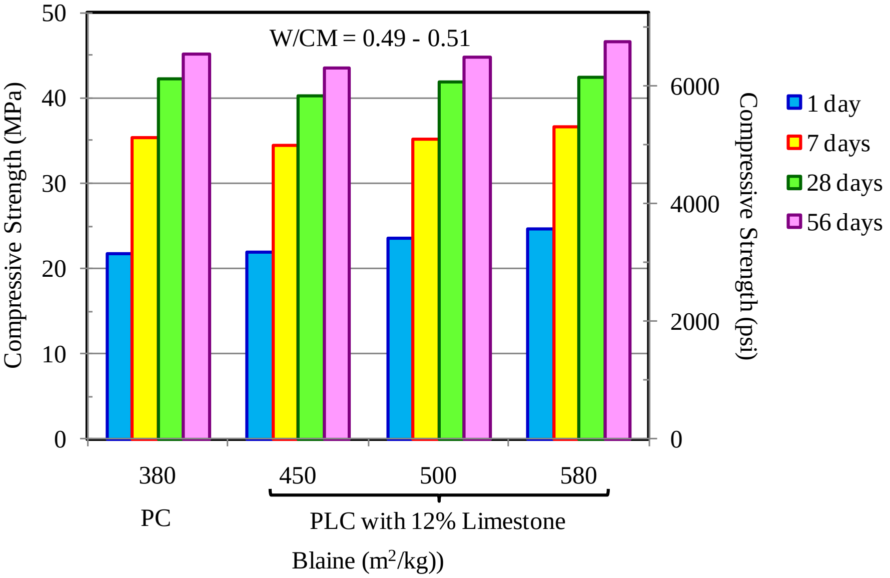


Figure 4.3 Effect of surface area (Blaine) on the strength of concrete (w/cm = 0.49 to 0.51) produced with PLC and PC from the same cement plant (Thomas et al. 2010b).

Table 4.2 Concrete Mixture Proportions and Test Results for Concrete Produced with PC and PLC (Thomas et al. 2010b)

	Series A		Series B						Series C	
W/CM	0.78	0.80	0.45						0.40	
SCM	No SCM		No SCM		35% Slag		20% Fly Ash		No SCM	
Proportions (kg/m^3)										
PC	235	-	354	-	230	-	286	-	409	-
PLC	-	235	-	358	-	231	-	287	-	413
Slag	-	-	-	-	125	125	-	-	-	-
Fly Ash	-	-	-	-	-	-	72	71	-	-
Water	184	188	159	161	160	160	161	161	164	165
Proportions (lb/yd^3)										
PC	396	-	597	-	388	-	482	-	689	-
PLC	-	396	-	603	-	389	-	484	-	696
Slag	-	-	-	-	211	211	-	-	-	-
Fly Ash	-	-	-	-	-	-	121	120	-	-
Water	310	317	268	271	270	270	271	271	276	278
Air	1.5	1.4	6.2	5.3	6.0	5.6	5.2	5.0	6.2	5.4
Slump (mm)	120	115	120	120	110	110	130	110	130	115
Slump (in.)	4.75	4.50	4.75	4.75	4.25	4.25	5.00	4.25	5.00	4.50
Set time (min)	340	310	340	290	380	345	425	345	395	355
Strength (MPa)										
1 day	10.8	12.0	23.2	27.0	11.7	15.9	16.9	19.2	30.6	33.5
7 days	22.0	22.4	34.0	38.0	32.8	38.1	31.8	32.6	45.6	48.8
28 days	27.9	27.0	39.4	44.8	44.9	50.4	43.4	43.6	54.6	57.3
56 days	29.1	27.4	43.4	47.5	48.9	53.0	50.8	49.3	58.5	60.6
Strength (psi)										
1 day	1566	1740	3365	3916	1697	2306	2451	2785	4438	4859
7 days	3191	3249	4931	5511	4757	5526	4612	4728	6614	7078
28 days	4047	3916	5714	6498	6512	7310	6295	6324	7919	8311
56 days	4221	3974	6295	6889	7092	7687	7368	7150	8485	8789
Durability Factor[1] (%)	-	-	101	102	98	101	100	100	101	102
Scaling mass[2] (g/m^2)	-	-	52	113	520	368	189	516	61	48
Scaling mass[2] (oz/yd^2)	-	-	1.52	3.31	15.22	10.77	5.53	15.10	1.79	1.40
RCPT[3] (Coulombs)										
28 days	-	-	2610	2571	1016	925	1184	1433	2017	2048
56 days	-	-	2344	2354	807	708	639	678	1716	1900

[1] Durability factor after 300 freeze-thaw cycles - ASTM C666 Procedure A

[2] Mass loss after 50 freeze-thaw cycles ponded with salt solution - ASTM C672 “Salt Scaling Test”

[3] Charged passed after 6 hours - ASTM C1202 “Rapid Chloride Permeability Test”

Table 4.3 Strength of Concrete Produced with PLC from Italian Cement Plants (Alunno-Rossetti and Curcio 1997)

	Plant B				Plant G			
Cement Content, kg/m^3	270		330		270		330	
Limestone, %	0	20	0	20	0	20	0	20
Fineness, m^2/kg	345.0	482.5	345.0	482.5	362.0	489.5	362.0	489.5
28-day strength (MPa)								
Compression	30.7	30.0	39.7	38.0	31.6	29.1	37.5	36.5
Splitting	2.3	2.7	2.9	2.7	3.2	2.1	4.1	2.6
Flexure	5.0	4.8	6.4	5.3	3.6	4.7	4.7	4.7
28-day Modulus (GPa)	26.0	24.5	28.0	27.5	25.1	25.4	27.2	27.1
*Shrinkage (μm/m)	635	640	680	690	540	560	614	595
*Creep (μm/m)	718	1102	778	914	824	972	756	869
*Carbonation (mm)	20	10	18	13	19	21	15	16

*Shrinkage, creep and carbonation measured at 900 days

4.1.1.2 Tensile strength, flexural strength and modulus of elasticity. Studies of tensile (cylinder splitting) and flexural strength, and modulus of elasticity have been made by a number of authors (Alunno-Rossetti and Curcio 1997; Bonavetti et al. 1999; Irassar et al. 2001; Dhir et al. 2007). Generally the trend in behavior is the same as that observed for compressive strength and predictive equations used to estimate these properties from the compressive strength (e.g. relationships in Eurocode 2) are valid for concrete produced using PLC.

Figure 4.4 shows compressive and flexural strength data for concrete mixtures produced using the three types of cement described in Table 4.4 which were manufactured in a Canadian cement plant and ground to the required fineness to give equivalent performance (Thomas et al. 2010d).

There is no significant difference in the compressive and flexural strengths of these concretes produced with different cements ground to achieve equivalent performance.

Table 4.4 Cement Ingredients in Cements used in Figure 4.4 (Thomas et al. 2010d)

	Limestone	Slag	Target Blaine (m^2/kg)
Portland Cement	4	0	380
Blended Cement	4	15	450
Blended Limestone Cement	12	15	500

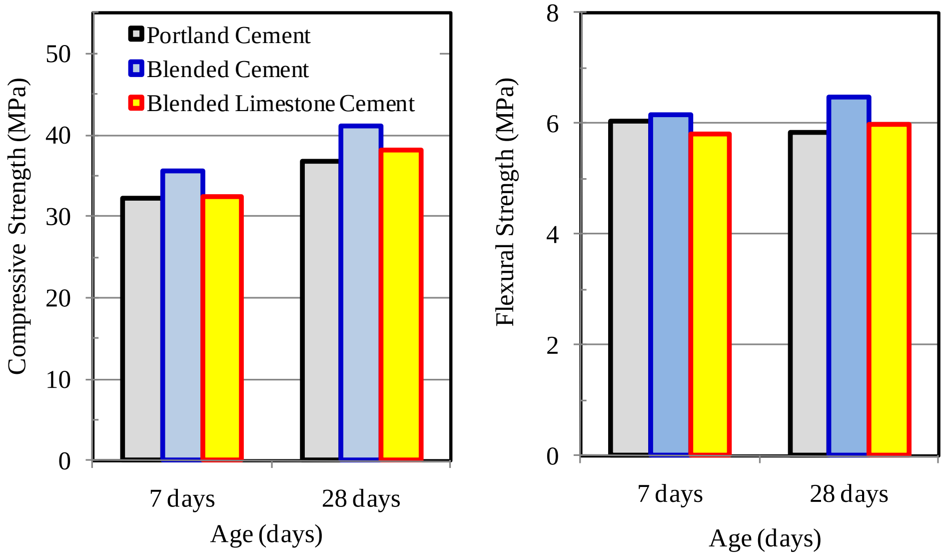


Figure 4.4 Strength data for concretes produced with different cements from the same plant (Thomas et al. 2010d).

4.1.2 Volume Stability

Alunno-Rossetti and Curcio (1997) measured creep and shrinkage on concrete mixtures produced using four cements manufactured at two plants. Details of the cements and the results of the tests are given in Table 4.3. The rate of shrinkage and total amount of drying shrinkage at 1 year was essentially the same for comparable concrete mixes produced with PC and PLC from the same plant. Creep tests were performed by loading concrete specimens at an age of 28 days to a stress equal to one-third of the compressive strength; the specimens were stored at a relative humidity of 50 ± 5%. The total deformation due to creep and shrinkage over 360 days was significantly lower (by 17% on average) for concretes produced with PC compared with those produced with PLC. The authors concluded that this was due to the reduced volume of "cement gel" available to resist the compressive stress in concrete containing PLC.

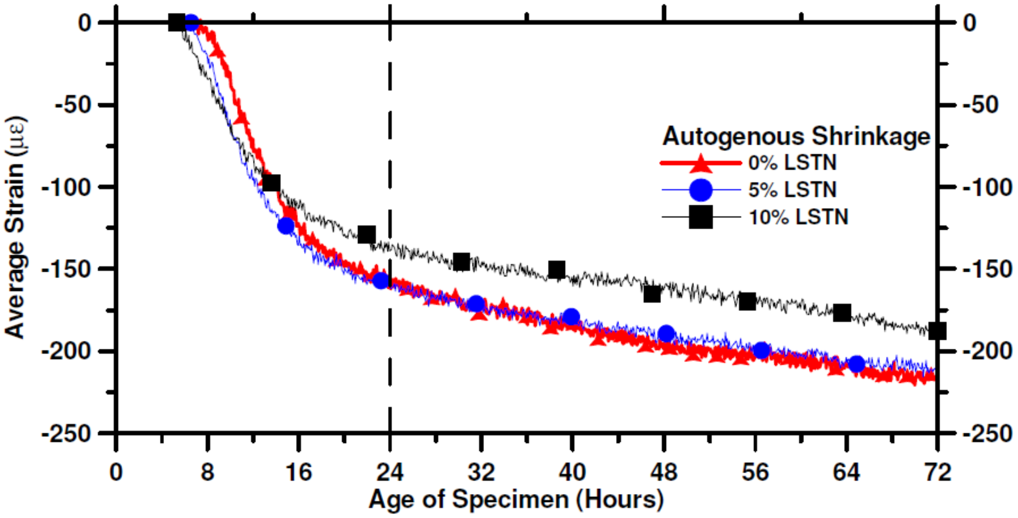
Dhir et al. (2007) reported slightly reduced shrinkage and similar creep for concretes produced with cements containing up to 45% ground limestone (blended not interground). The data are shown in Table 4.5. The concretes were produced with 310 kg/m^3 and w/cm = 0.60. Creep tests were performed by loading specimens to 40% of the cube strength at 28 days and drying shrinkage tests were performed by storing specimens at 55% RH starting 24 hours after casting.

Table 4.5 Creep and Shrinkage Results for Concrete with w/cm = 0.60 after 90 days

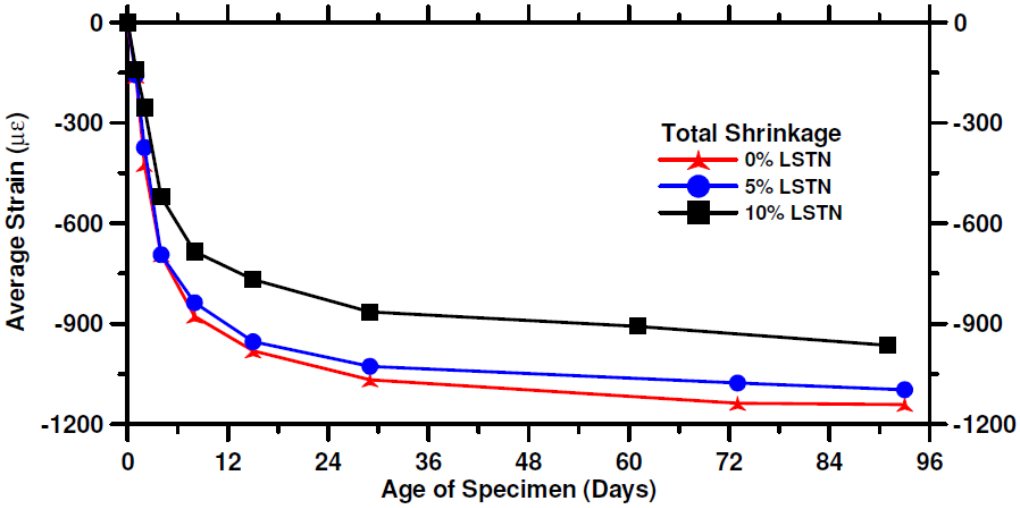
	Limestone Content,%				
	0	15	25	35	45
Cube strength (MPa)	41.0	36.5	30.5	23.5	17.0
Creep (μm/m)	790	780	775	770	760
Drying shrinkage (μm/m)	680	630	605	590	575

It is not clear why there is such a marked difference in the effect of limestone on the creep of concrete as reported by Alunno-Rossetti and Curcio (1997) and Dhir and coworkers (2007). Intuitively one would expect the creep for a given stress-strength ratio to decrease as the volume of cement paste decreases and the amount of aggregate (including filler) increases, which is consistent with the observations of Dhir et al. (2007). However, further work is required to confirm this effect.

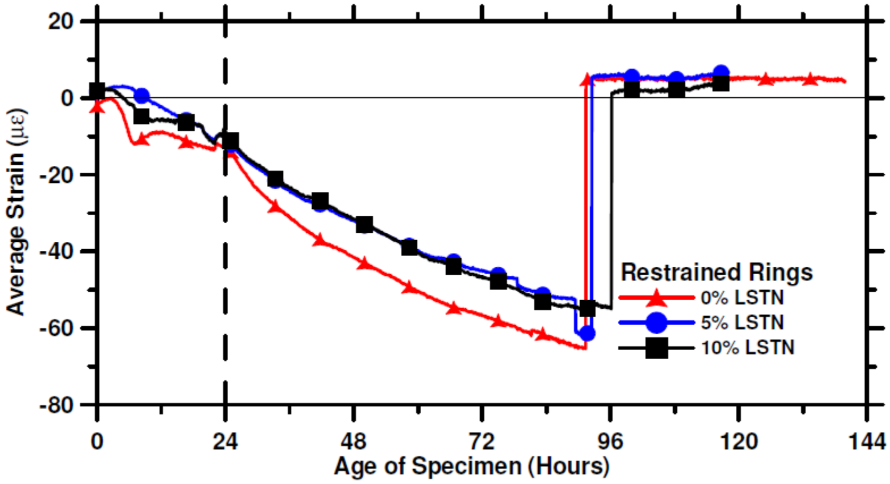
Bucher and coworkers (2008) reported shrinkage data for three cements produced with 0%, 5% and 10% limestone. Their testing included measurements of autogenous shrinkage, and unrestrained and restrained drying shrinkage of mortars. The autogenous shrinkage during the first 3 days was highest for mortars without limestone (215 με) and the lowest for mortars with 10% limestone (185 με). The amount of unrestrained drying shrinkage also decreased with increasing limestone content. Restrained mortar samples produced with cement without limestone exhibited cracking at 87 hours. The presence of limestone increased the time to cracking slightly, but all samples cracked after 96 hours. Overall the data indicate that mortars produced with PLC show slightly reduced shrinkage and a lower tendency to crack compared with equivalent mortars produced with PC. Bentz et al. (2009) attribute these differences to particle size distribution and note that the impacts may be slightly larger with coarser limestones.



a. Autogenous shrinkage



b. Unrestrained shrinkage



c. Restrained shrinkage

Figure 4.5 (a) Autogenous, (b) unrestrained, and (c) restrained shrinkage (ASTM C1581) for cements with no limestone, 5% and 10% limestone (Bucher et al. 2008).

4.2 DURABILITY

4.2.1 Permeability and Chloride Resistance

Tsivilis et al. (2003) measured the gas permeability, K_g, water permeability, K_w, sorptivity, S, and porosity, P, of concretes produced with 7 different cements. The cements were produced by intergrinding clinker (7.3% C_3A), limestone of high purity (95.5% $CaCO_3$) and gypsum (5% by mass of clinker) in a pilot plant ball mill. The cements differed in the quantity of limestone and the fineness of the finished cement. The cements were used to produce concrete samples which were cured for 28 days prior to conducting the tests. Details of the cements, the concrete mixtures and the results of the tests are shown in Table 4.6. In general, the concretes produced with PLC had higher gas permeability coefficients (K_g) than the PC concrete, with the exception of the concrete produced with the PLC with 35% limestone, which recorded the lowest gas permeability value. On the other hand, the PLC concretes showed reduced permeability to water (K_w) and lower water sorptivity values (S). The porosity (P) of the concrete was unaffected by the presence of up to 15% limestone in the cement, but increased with higher limestone contents. The authors concluded that overall the PLC concrete had "competitive properties" with the PC concrete (Tsivilis et al. 1999b). Earlier work at the same institute (Tsivilis et al. 1999a) reported that the quality and composition of both the clinker and the limestone had a significant impact on the permeability of concrete.

In a related study, Tsivilis et al. (2000) produced concretes with five cements with limestone contents ranging from 0% to 35%, and conducted the "Rapid Chloride Permeability Test" (RCPT) (ASTM C1202) after 28 days of moist curing. Table 4.7 shows details of the cements and concrete together with the results of the RCPT. The results show little significant impact due to increasing limestone content up to 15% to 20%. The mix with 35% limestone had a higher RCPT value despite being cast with a lower w/cm, indicating that permeability increased at this level of limestone.

Table 4.6 Permeability Test Results for Concretes Produced with PLC (Tsivilis et al. 2003)

Cement Properties			Concrete Properties					
Limestone (%)	Blaine (m^2/kg)	Strength at 28d (MPa)	W/CM	Strength at 28d (MPa)	K_g (10^{-17} m^2)	K_w (10^{-12} m/s)	S (mm/min$^{0.5}$)	P (%)
0	260	51.1	0.70	31.9	2.26	2.39	0.237	12.5
10	340	47.9	0.70	27.4	2.65	2.30	0.238	12.3
15	366	48.5	0.70	27.3	2.80	2.22	0.226	12.3
20	470	48.1	0.70	28.0	2.95	2.00	0.220	13.1
20	325	39.8	0.62	28.2	3.03	1.81	0.228	12.9
25	380	40.0	0.62	26.5	2.82	2.07	0.229	13.6
35	530	32.9	0.62	26.6	2.10	2.23	0.224	14.6

Dhir et al. (2007) produced five series of concretes with w/cm ranging from 0.45 to 0.80 and, within each series, concretes were produced with 0%, 15%, 25%, 35% or 45% limestone which was added at the concrete mixer. These concretes were subjected to tests to determine, among other properties, water absorption (using the initial surface absorption test or ISAT) and chloride diffusion (using an electrical migration test). At a given w/cm there was little difference in the ISA or chloride diffusion coefficient between concrete produced with PC or the PLC with 15% limestone. At higher levels of limestone there was an increase in both the ISA and chloride diffusion. However, if the concretes are compared on the basis of compressive strength there was no significant difference in the performance of PC or PLC concretes of the same 28-day strength.

Tezuka (1992) measured the steady-state diffusion coefficient using 3-mm thick cement paste samples in standard diffusion cells. Cement pastes with 5% limestone showed the lowest diffusion coefficient, pastes with 0% or 10% limestone were approximately equal to one another, whereas pastes with 15% or more limestone showed increased diffusion.

Irassar et al. (2001) immersed concretes, which were produced with cements with 0%, 10% or 20% limestone, into 3% NaCl solution. Chloride profiles were determined after various exposure periods and chloride diffusion coefficients were calculated from the profiles. The results are summarized in Table 4.8. Generally, significant increases in the chloride diffusion coefficient are observed with either increasing w/cm or limestone content. Concrete produced with the highest w/cm and limestone content showed very low resistance to chloride ion penetration. However, Hooton et al. (2010) performed ASTM C1556 chloride bulk diffusion tests and found that 10% to 15% interground limestone did not change diffusion coefficients appreciably, with or without 30% slag replacement, as shown in Table 4.9.

Table 4.7 Effect of Limestone Additions on the "Chloride Permeability" of Concrete (Tsivilis et al. 2000)

Limestone, %	0	10	15	20	35
Fineness, m^2/kg	260	340	366	470	530
Mortar: strength at 28 days (MPa)	51.1	47.9	48.5	48.1	32.9
Concrete: W/CM	0.70				0.62
Concrete: strength at 28 days (MPa)	31.9	27.4	27.3	28.0	26.6
Concrete: RCPT (Coulombs)	6100	5800	6000	6400	6600

Table 4.8 Diffusion Coefficients ($\times 10^{-12}$ m^2/s) for Concrete Determined after 360 Days Immersion in 3% NaCl Solution (Irassar et al. 2001)

	Water-to-cementitious materials ratio		
Limestone,%	0.40	0.50	0.60
0	5.0	6.9	25.7
10	11.2	20.3	21.6
20	10.5	23.8	41.4

Table 4.9 Diffusion Coefficients ($\times 10^{-12}$ m^2/s) for Concrete after 35 days Immersion in 3% NaCl Solution (Hooton et al. 2010)

	GU 100%	PLC10 100%	PLC15 100%	GU 70% SLAG 30%	PLC10 70% SLAG 30%	PLC15 70% SLAG 30%
C_s (% mass)	0.73	0.84	0.8	1.1	1.07	0.98
D_a (m^2/s * $10^{-12)}$	15.9	15.6	22.5	8.07	6.11	8.25

Alunno-Rossetti and Curcio (1997) reported increased chloride ion penetration in concretes produced using PLC with 20% interground limestone compared with similar concrete produced with PC from the same plant. Bonavetti et al. (2000) reported increased chloride ion penetration in water-cured concrete produced with PLC compared with PC, but the opposite effect for air-stored concrete.

Table 4.2 shows strength and durability data for three series of concrete mixtures (w/cm = 0.78-0.80, 0.45 and 0.40) produced with PC (4% limestone and 380 m^2/kg Blaine) and PLC (12% limestone and 500 m^2/kg Blaine). The results from the "Rapid Chloride Permeability Test" (ASTM C1202) are plotted in Figure 4.6. It is clear from these data that w/cm, age and supplementary cementitious materials (SCM) content have a profound impact on the permeability, but that the impact of the level of limestone in the cement (4% to 12%) is not significant.

The balance of evidence would seem to indicate concrete produced with PLC up to 15% can produce concrete with similar resistance to the penetration of fluids. However, there is evidence that increased chloride ion penetration can occur in PLC concretes produced at the same w/cm as PC concretes. PC and PLC concretes may be expected to give similar performance when they are proportioned to give the same compressive strength at 28 days.

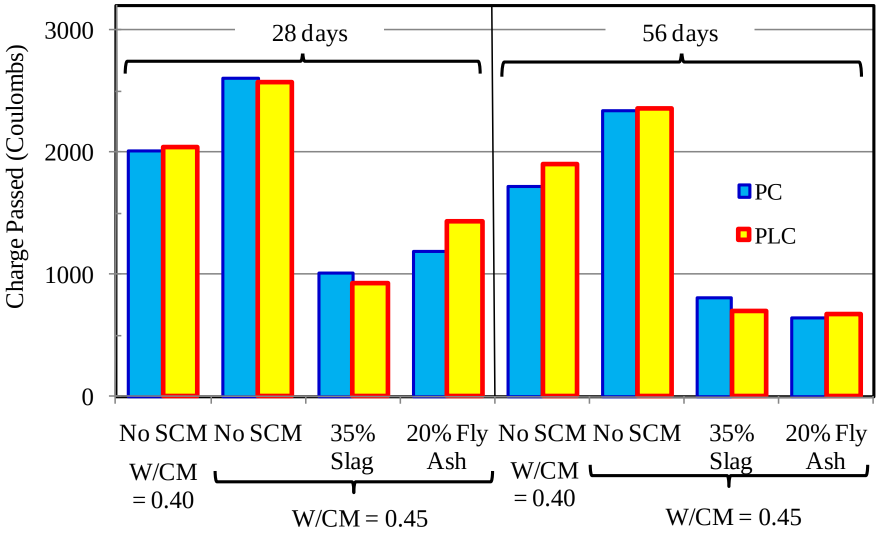


Figure 4.6 "Rapid Chloride Permeability Test" (ASTM C1202) data for PC and PLC concrete with and without SCM (Thomas et al. 2010b).

4.2.2 Carbonation

Matthews (1994) reported carbonation data for concrete mixtures produced with five series of cements. Within each series cements were produced with 0%, 5% or 25% limestone. In one series the limestone was interground with the portland cement clinker and in the other four series ground limestone was blended with the portland cement. The depth of carbonation measured at 5 years increased with w/cm and limestone content, and was reduced by extending the initial moist-curing period. The depth of carbonation correlated with the water-to-portland-cement-content ratio (w/PC) of the concrete mixture indicating that the limestone component of the cement did not contribute to carbonation resistance. The depth of carbonation was also reliably correlated with the 28-day strength of the concrete.

Barker and Matthews (1994) studied the effect of limestone (0%, 9%, 15% and 24% interground with the portland cement) on the carbonation of two series of concretes; Series A was produced to the same w/cm (0.60) and Series B was proportioned to achieve the same 28-day compressive strength (44 MPa; cube strength). Figure 4.7 confirms the findings of Matthews (1994) that concretes of equal strength carbonate at similar rates even when the concretes are produced with PLC with varying limestone contents.

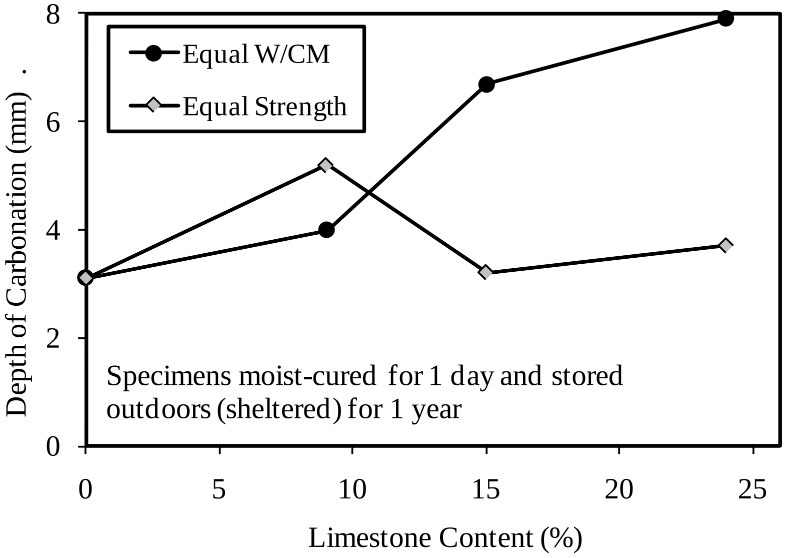
Similar findings were recently reported by Dhir et al. (2007) using blended PLC containing up to 45% limestone. Even concrete produced with a PLC containing 45% limestone showed similar resistance to carbonation when compared with PC concrete of the same strength grade. Concrete produced with a PLC with 15% limestone showed little increase in carbonation over the control, especially at the lower w/cm (0.52) used in the tests.

Collepardi et al. (2004) showed that substitution of 15% or 25% of the portland cement by ground limestone, fly ash or slag (added at the concrete mixer) led to an increase in carbonation rate when concrete was compared at equal w/cm, but that the rate was similar for concretes of equal strength. The data from this study confirmed that, for a given degree of moist curing and exposure conditions, the rate of carbonation is a function of the strength of the concrete and appears to be relatively independent of the type of cement.

Schmidt (1992b) reported data for concrete produced with PLC (containing 13% to 17% limestone) from three cement plants in Germany. The use of PLC increased the rate of carbonation of concrete compared with PC from the same plant, but the depth of carbonation over 3 years was generally less than that of concrete produced with composite cements containing 13% to 17% slag. Twenty-eight day strengths were in the same range (45 MPa to 55 MPa using DIN 1048, 15 cm cubes) for these concretes.

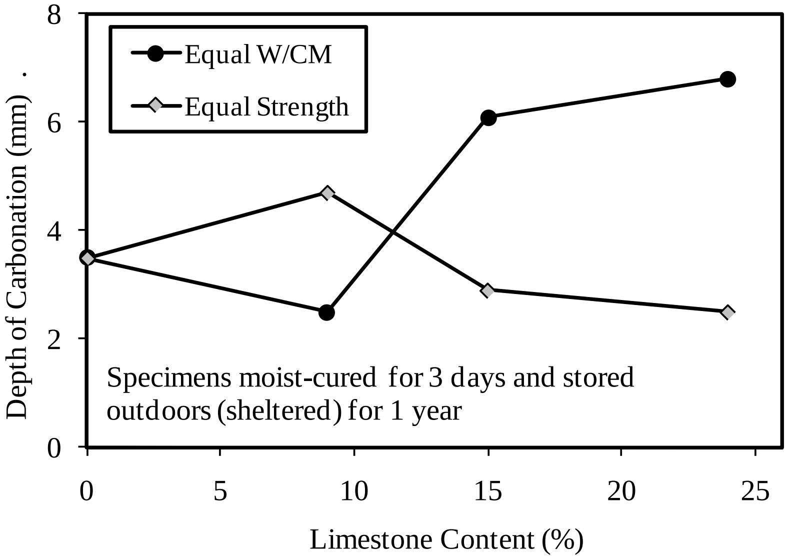
Alunno-Rossetti and Curcio (1997) compared the performance of concretes containing a PC and PLC (20% limestone) produced at each of two plants (see Table 4.3 for details of cements and concrete mixes). Their data indicate that there is no consistent effect of limestone additions on the carbonation of concrete.

The balance of data indicates that concrete produced with PLC will carbonate at a similar rate as concrete produced with PC, provided the concretes are designed to achieve the same 28-day compressive strength.



(a)

Fig. 4.7 (cont.)



(b)

Figure 4.7 Effect of the limestone content of PLC on the carbonation of concrete mixes produced at equal w/cm or equal 28-day strength for specimens cured (a) 1 day or (b) 3 days (Barker and Matthews 1994).

4.2.3 Freeze/Thaw and Deicer Salt Scaling

Much of the data on the effect of limestone on freeze-thaw and deicer-salt scaling resistance of concrete comes from European studies on non-air-entrained concretes. Some of these studies indicate that the freeze-thaw resistance is decreased by the incorporation of limestone (Matthews 1994; Barker and Matthews 1994; Dhir et al. 2007) and others indicate that PLC concrete can achieve equivalent performance to PC concrete provided equal strength is obtained, the limestone content is limited, and the clay and organic content of the limestone are limited (Sprung and Siebel 1991; Siebel and Sprung 1991; Albeck and Sutej 1991; Schmidt et al. 1993).

The limited data available from Europe for air-entrained concrete show that the freeze-thaw and scaling resistance of PLC concrete is comparable to that of equivalent PC concrete (Matthews 1994; Dhir et al. 2007). Figure 4.8 (Matthews 1994) shows that the freeze-thaw resistance of PLC concrete is reduced compared to PC concrete in non-air-entrained concrete, but increased in air-entrained concrete. Table 4.10 (from Dhir et al. 2007) shows that the salt scaling resistance of non-air-entrained concrete decreases with increasing limestone in the cement, but that for air-entrained concrete there is no significant difference between the performance of PC and PLC concrete, even for PLC with up to 45% limestone.

Table 4.10 Deicer Salt Scaling Resistance of PLC Concrete with Varying Amounts of Limestone (Dhir et al. 2007)

Limestone in cement (%)	Mass of scaled-off material (kg/m^2) after 56 freeze/thaw cycles		
	Non-air-entrained		Air-entrained
	w/cm = 0.52	w/cm = 0.65	w/cm = 0.58
0	0.15	0.24	0.05
15	0.18	0.31	0.04
25	0.22	0.43	0.05
35	0.29	0.60	0.05
45	0.44	0.91	0.06

Table 4.2 shows strength and durability data for three series of concrete mixtures (w/cm = 0.78-0.80, 0.45 and 0.40) produced with PC (4% limestone and 380 m^2/kg Blaine) and PLC (12% limestone and 500 m^2/kg Blaine). The results from cyclic freeze-thaw (ASTM C666 Procedure A) and deicer salt scaling (ASTM C672) are shown in Fig. 4.9. All of the concrete tested showed excellent resistance to cyclic freeze-thaw tests. Some scaling was observed for concrete with fly ash or slag in the accelerated laboratory salt scaling tests, however, mass losses were less than maximum values specified by state transportation departments (e.g. typically mass loss ≤ 800 g/m^2 to 1000 g/m^2). There is no consistent difference between the behavior of equivalent mixes with PC or PLC.

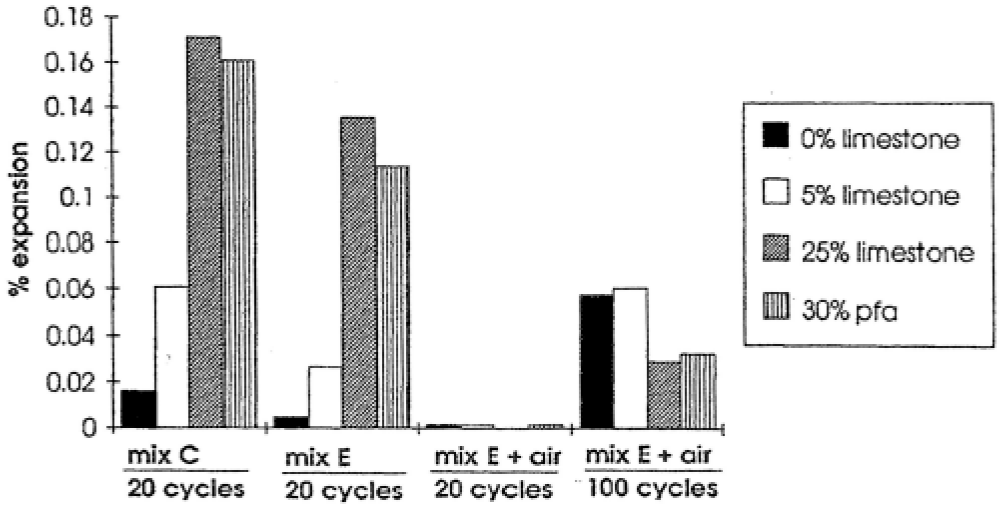


Figure 4.8 Effect of air entrainment on the freeze-thaw resistance of PC and PLC concrete (Matthews 1994).

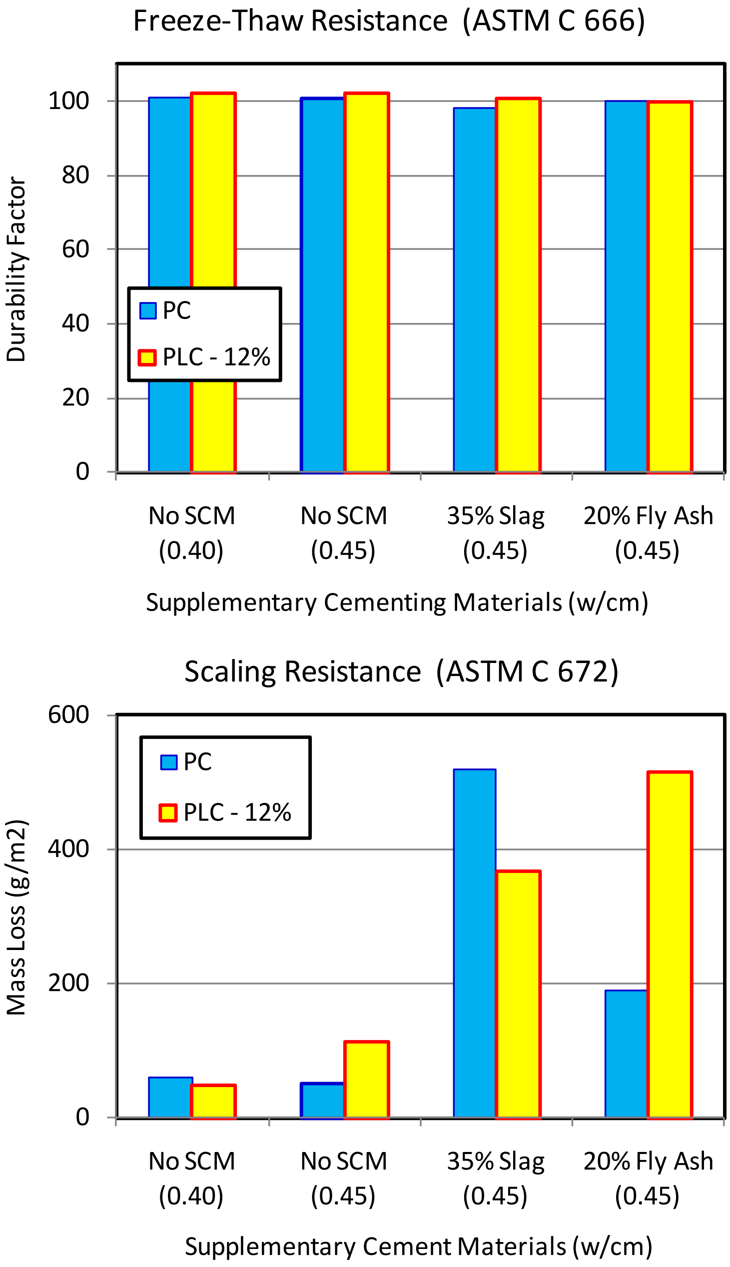


Figure 4.9 Results of freeze-thaw (top) and deicer-salt scaling tests for PC and PLC concretes with and without SCM (Thomas et al. 2010b).

4.2.4 Sulfate Resistance

Soroka and Stern (1976) studied the effect of reagent-grade $CaCO_3$ and CaF_2 (used as an inert filler) on the sulfate resistance of portland cement mortars having a water-to-cement ratio of 0.75. Specimens 25 mm × 25 mm × 160 mm in size were immersed in a 5% Na_2SO_4 solution and the time to cracking is shown in Table 4.11. These data indicate that $CaCO_3$ has a beneficial effect beyond the reduction of the C_3A content of the cement. Soroka and Setter (1980) followed up this preliminary study by examining the expansion and deterioration of mortars containing various amounts of ground limestone immersed in 5% Na_2SO_4 solution for up to 11 months. The additive contents were 10%, 20%, 30%, and 40% by mass. They found that the limestone imparted some improvement in sulfate resistance as compared with the control (and to other fillers tested at similar finenesses: dolomite or basalt). The fineness of the additive was also significant, as can be seen in Table 4.12 (for mortars with 30% filler). However, they found that after long periods of exposure the intensity of cracking of the limestone-filled mortars was essentially the same as for the others. Thus they conclude that the use of limestone improves the sulfate resistance of mortars, but not to such an extent as to produce sulfate-resistant mortars.

Table 4.11 Time to Cracking for Mortar Prisms Exposed to 5% Na_2SO_4 (Soroka and Stern 1976)

Mortar	Onset of cracking (weeks)	Compressive strength at 28 days (MPa)
Reference mortar	6	25.3
With $CaCO_3$ filler (mass %)		
10	10	27.0
20	12	27.3
30	14	29.7
40	16	30.9
With CaF_2 filler (mass %)		
10	6	23.7
20	6	28.2
30	6	32.6
40	6	28.9

Table 4.12 Time to Cracking for Mortar Prisms with 30% Limestone Exposed to 5% Na_2SO_4 (Soroka and Setter 1980)

Fineness (m^2/kg)	Age, weeks
115 – 130	12
300 – 370	10
660 – 710	10
960 - 1120	18
Reference (no limestone)	6

Matthews (1994) exposed 100-mm concrete cubes (w/cm = 0.62 to 0.66) to three sulfate solutions consisting of either Na_2SO_4 (1.5% SO_3) or $MgSO_4$ (0.35% or 1.5% SO_3) for up to 5 years. Portland cement from five different sources was blended or interground (in one case) with 5% or 25% limestone. The sulfate resistance of the concrete was strongly dependent on the C_3A content of the cement with no consistent difference in performance being attributed to the level of the limestone (Fig. 4.10).

Irassar and coworkers (Gonzales and Irassar 1998; Irassar et al. 2000, 2005) compared the performance of three cements with varying C_3A and C_3S levels, and limestone contents of 0%, 10% and 20%. Generally the presence of 10% limestone had little impact on the performance of mortars stored in 5% Na_2SO_4 compared with control mortars without limestone, but 20% limestone resulted in increased expansion. Figure 4.11 shows the expansion results for mortars with 0% and 20% limestone.

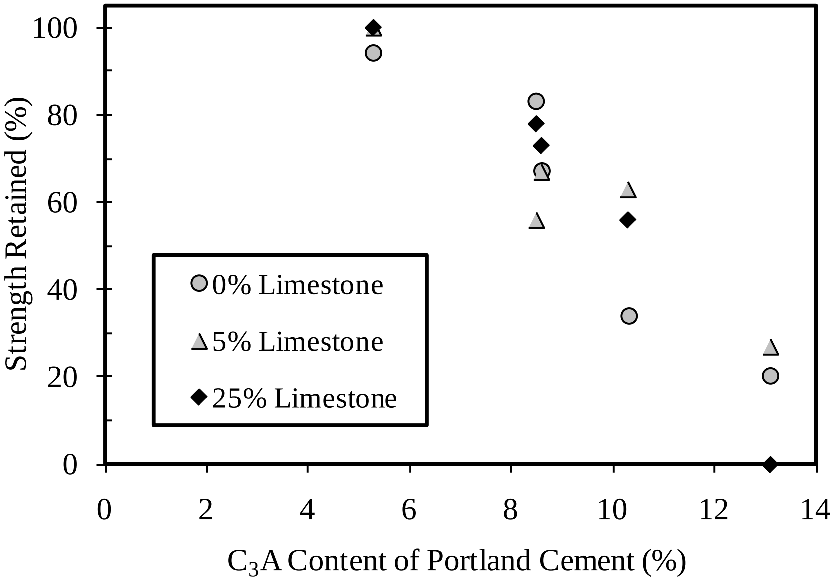
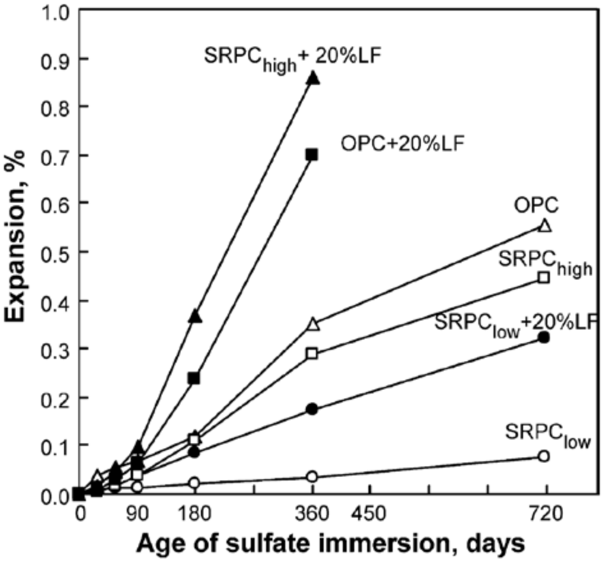


Figure 4.10 Strength retained after 2 years in $MgSO_4$ (1.5% SO_3) solution (Matthews 1994).



	C_3A	C_3S
$SRPC_{low}$	0	40
$SRPC_{high}$	1	74
OPC	6	51

Figure 4.11 Effect of limestone on the expansion of mortars stored in 5% Na_2SO_4 (Irassar et al. 2005).

4.2.4.1 Thaumasite form of sulfate attack (TSA). The sulfate resistance data discussed above were generated by studies conducted at normal laboratory temperature (e.g. 20°C to 23°C). There has been increased concern in the last decade or so about the performance of concrete exposed to sulfates at lower temperatures which favors the thaumasite form of sulfate attack (TSA) especially when the concrete contains a source of carbonate ions.

Thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) is structurally similar to ettringite but differs in that it forms from the calcium silicate hydrate (C-S-H) in concrete rather than the calcium aluminate phases and thus can result in a complete loss of cohesion of the binder. Because thaumasite formation requires a source of carbonate ions, there are concerns that concrete produced with PLC will be more susceptible to TSA than concrete produced with PC (Crammond 2003). To be noted however, is that there have been few cases of TSA in Europe in the 25 or more years that portland-limestone cements have been in use (Irassar 2009).

In a study at the Building Research Establishment (BRE) in the U.K., Barker and Hobbs (1999) tested mortars (40 mm × 40 mm × 160 mm) with w/cm = 0.50 and 0.75 produced with either a sulfate resisting portland cement (SRPC) or an ordinary portland cement (OPC). The OPC was blended with 15% oolitic limestone or 15% carboniferous limestone. The mortars were immersed in either Na_2SO_4 or $MgSO_4$ solution; both solutions contained 0.35% SO_3 and were maintained at 5°C. After 1 year the authors concluded that the sulfate resistance of OPC mortars with and without 15% limestone was broadly similar. It should be noted that no data are available from this study beyond 1 year. However, in a more recent paper summarizing BRE research Crammond (2003) stated that "… portland limestone cement can contain between 6% and 35% limestone filler and is more susceptible to TSA the greater the amount of filler. This is the least TSA-resistant binder type investigated by BRE."

In 1998 BRE initiated a combined field and laboratory trial to investigate the performance of concrete containing limestone aggregates in sulfate-bearing ground (Crammond et al. 2003). Concrete specimens were buried in sulfate-bearing clay at a site in Central England (Shipston on Stour). Concretes cast with high-C_3A portland cement with and without 15%

limestone all showed some surface deterioration when half the samples were retrieved after 3 years. Concretes with carbonate aggregates showed more deterioration than concretes with siliceous aggregates; however, the results reported give no indication of the comparative performance of the equivalent concrete with and without limestone as an ingredient in cement. The remaining samples were scheduled to be retrieved in 2008 (10 years), but no data are available at this time.

Tsivilis and coworkers (Tsivilis et al. 2007; Kakali et al. 2003; Skaropoulou et al. 2009a) ran a series of tests using cement with 6.7% C_3A interground with 15% and 30% limestone and reported separately on the effect of various supplementary cementitious materials (SCM) on the performance of the cement with 15% limestone (Tsivilis et al. 2003; Skaropoulou et al. 2009b). Mortar bars (40 mm × 40 mm × 53 mm) were produced at w/cm = 0.50 and after 28 days curing were placed in a solution of 1.8% $MgSO_4$ at both 5°C and 25°C. Mortars were produced both with a siliceous sand and a calcareous sand. After 11 months visual inspection showed no cracking of the mortar without limestone, expansion and cracking of the mortar with 15% limestone, and expansion and spalling of the mortar with 30% limestone (Tsivilis et al. 2007). After 60 months both mortars with 15% and 30% limestone were reported (Skaropoulou et al. 2009a) to have completely disintegrated (damage rating 9) and the mortar with no limestone in the cement was exhibiting cracking and spalling (damage rating 5 and 6). Figure 4.12 shows the changes in mass of the mortars over 5 years. Thaumasite was found in all the specimens at 5 years, even the specimen produced without limestone in the cement and with siliceous sand.

Specimens produced with the cement with 15% limestone plus SCM showed variable performance and the changes in mass are shown in Figure 4.13 (Skaropoulou et al. 2009b). The use of 20% natural pozzolan increased the rate of deterioration with visible deterioration occurring after just 7 months compared with 8 months for the specimens without SCM. Signs of deterioration appeared at 11 months for specimens containing 30% fly ash, 16 to 30 months for specimens with 10% metakaolin and 30 months for specimens with 50% slag. Generally, the performance of the mortar with 15% limestone in the cement plus 50% slag was similar or slightly better than the mortar produced with cement without limestone or SCM (compare data in Skaropoulou et al. 2009a with Skaropoulou et al. 2009b).

It is interesting to note in these studies (Tsivilis et al. 2003; 2007; Kakali et al. 2003; Skaropoulou et al. 2009a; 2009b) that mortars with calcareous sand generally deteriorated faster than equivalent mortars with siliceous sand, but the differences were small. Also, none of the mortars stored at 25°C showed any deterioration after 5 years.

Tests were conducted at the University of Sheffield on pastes (Hartshorn et al. 1999) and mortars (Hartshorn et al. 2002; Torres et al. 2002, 2005) produced with portland cement with 8.5% C_3A. Paste samples (10 mm diameter × 10 mm) with w/cm = 0.5 were produced with 0%, 5%, 15% and 30% of carboniferous limestone. After curing for 28 days paste samples were stored in one of eight solutions: boiled tap water, distilled water, 0.4% $MgSO_4$, 1.8% $MgSO_4$, 0.4% Na_2SO_4, 1.8% Na_2SO_4, 0.4% $MgSO_4$ + 0.4% Na_2SO_4, and 1.8% $MgSO_4$ + 1.8% Na_2SO_4.

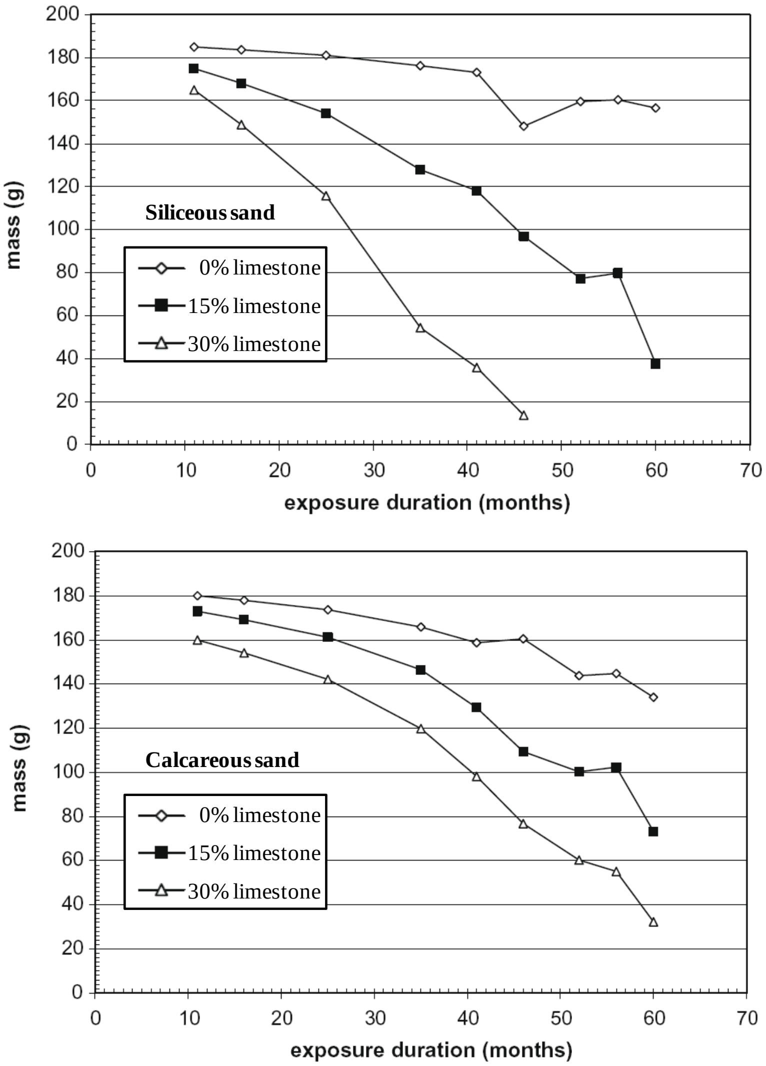


Figure 4.12 Change in mass of mortars with siliceous sand (top) or calcareous sand (bottom) stored in 1.8% $MgSO_4$ solution at 5°C (Skaropoulou et al. 2009a).

The temperature of storage was 5°C. The neat portland cement paste specimens (no limestone) started to show signs of deterioration after 252 days storage in the 1.8% $MgSO_4$ and 1.8% $MgSO_4$ + 1.8% Na_2SO_4 solutions (which produced the fastest rate of deterioration for all pastes) with severe distress in form of grey-white mush forming at the surface being observed after 1 year. Pastes with limestone deteriorated more rapidly and the extent of deterioration increased with limestone content. After 1 year the cylinders with 35% limestone stored in either 1.8% $MgSO_4$ or 1.8% $MgSO_4$ + 1.8% Na_2SO_4 solutions had almost completely deteriorated and turned into a grey mush. Thaumasite was found in all the specimens containing limestone even the mix with just 5% limestone.

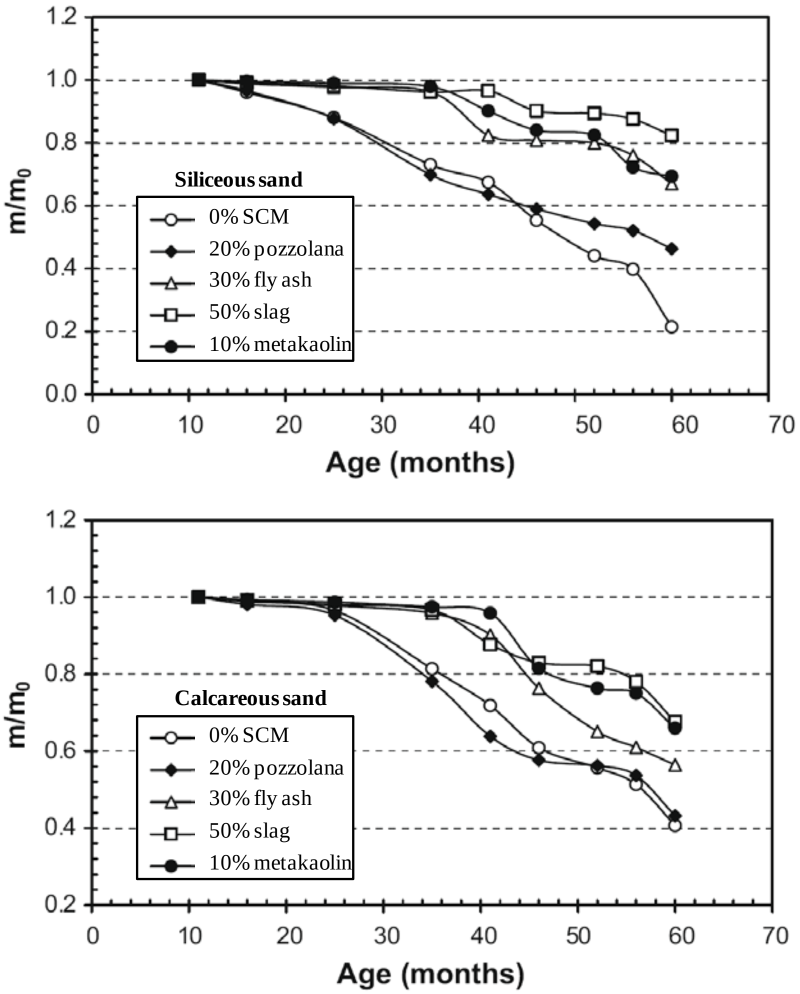


Figure 4.13 Relative mass change of mortars with siliceous sand (top) or calcareous sand (bottom) and SCM stored in 1.8% $MgSO_4$ solution at 5°C (Skaropoulou et al. 2009b).

Mortar samples (40 mm × 40 mm × 160 mm) with w/cm = 0.5 were produced with quartz sand and were stored, after 28 days curing, in 1.8% $MgSO_4$ solution at 5°C and 20°C. Thaumasite was detected in the mortars with 35% limestone after just 126 days storage at 5°C (Hartshorn et al. 2002). The mortars were reexamined at an age of 5 years (Torres et al. 2002, 2005). The samples had been maintained in the magnesium sulfate solution at 5°C for 4 years, but had been allowed to dry out during the fifth year. The extent of damage was observed to increase with increasing limestone and there was evidence of more deterioration for the mortar produced with cement containing 5% limestone compared with the mortar produced with plain portland cement. Thaumasite was found in all of the mortars, even those produced without limestone. It was conjectured that the source of carbonate in the mortar without limestone may have been atmospheric CO_2 (Torres et al. 2002).

Research in Germany (Kipus and Puntke 2003), evaluated a suite of mortars (w:c 0.60) or concrete (w:c 0.50) made with cements with C_3A contents of 11% ("normal") or 3% ("sulfate resisting") stored in a range of Na_2SO_4 solutions of 1500 mg/L to 29800 mg/L sulfate at either 20°C or 8°C. In all cases, specimens made with 11% C_3A contents performed poorly while cements with 3% C_3A contents performed well in those environments whether or not they contained 5% or 15% limestone (blended not interground).

In an extensive review of research into thaumasite, Irassar (2009) concluded that risk of TSA is minimized with low water-to-cement ratios, sulfate resistant (low C_3A content) cements, and sufficient cement contents; referring to ACI 201 guidelines. In other words, following established sulfate resistant concrete practice will minimize risk of TSA. Currently the evidence available would indicate that the PLC is more vulnerable to TSA than PC concretes. However, it is also evident that SCMs may be able to reduce the risk of TSA when combined with PLC. More work is needed to determine whether sulfate-resistant concrete can be produced with PLC/SCM blends.

4.2.5 Alkali-Silica Reaction

Hobbs (1983) reported that the use of 5% limestone extended the time to cracking, but did not eliminate it, in mortar bars made with high-alkali cement and highly-reactive Beltane opal sand.

Figure 4.14 (from Thomas et al. 2010b) shows the expansion of mortar bars and concrete prisms containing an alkali-silica reactive aggregate (siliceous limestone from the Spratt quarry in Ontario). Expansion results are reported at 14 days for the accelerated mortar bar test (AMBT) (ASTM C1260), 1 year for the concrete prism test (CPT) (ASTM C1293) and 3 months for the accelerated concrete prism test (ACPT) (this test is similar to the CPT except specimens are stored at 60°C (140°F)). The data show that there is no consistent difference between expansions produced with PC compared with PLC.

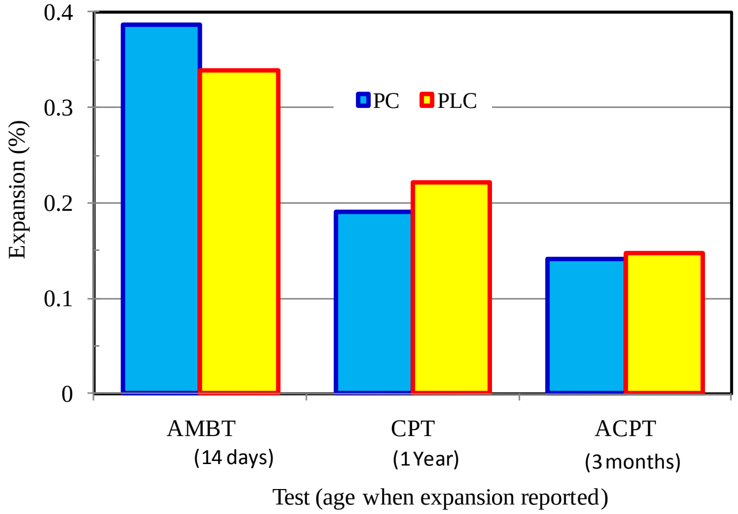


Figure 4.14 Expansion of mortar and concrete containing an alkali-silica reactive aggregate (Thomas et al. 2010b).

4.2.6 Abrasion Resistance

Dhir et al. (2007) conducted abrasion tests on two series of concrete mixtures (w/cm = 0.52 and 0.65) produced with cements containing between 0% and 45% limestone. The results, shown in Figure 4.15, indicate that for concrete compared at equal w/cm the depth of abrasion increases with increasing limestone content although the difference between concretes with 0% and 15% limestone is small. Concretes of the same 28-day strength have similar abrasion resistance irrespective of the limestone content of the cement.

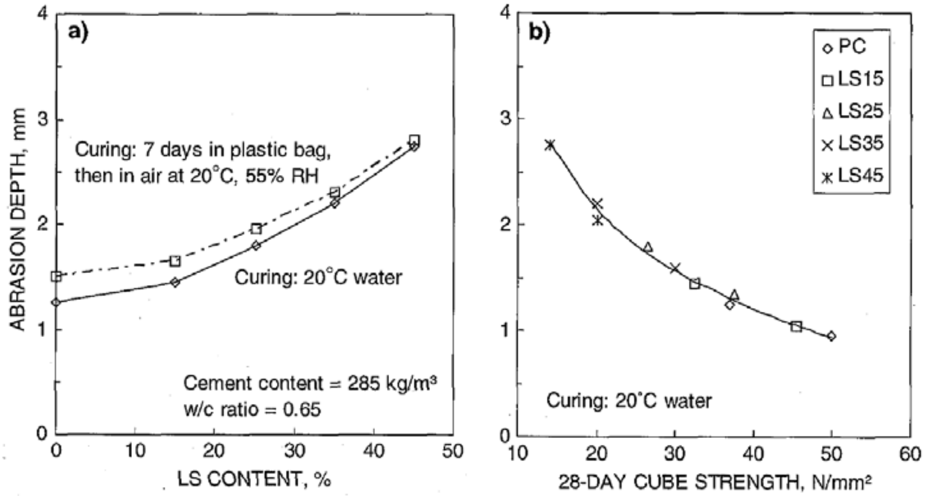


Figure 4.15 Effect of the limestone (LS) content of portland-limestone cement on the abrasion resistance of concrete (Dhir et al. 2007).

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CHAPTER 5 SPECIFYING AND MONITORING QUALITY

This section reviews specification requirements for cements with more than 5% limestone in Canada and Europe. Provisions for limestone characteristics and finished cement are reviewed.

5.1 LIMESTONE REQUIREMENTS

For limestone used in amounts of greater than 5%, EN 197-1 and CSA A3001 both identify three characteristics for limestone to be used as an ingredient in cement: 1) a minimum $CaCO_3$ content of 75% by mass; 2) a maximum methylene blue index of 1.2 g/100 g; and 3) a maximum total organic carbon content of 0.2% or 0.5% by mass. The requirements reportedly are to ensure concrete performance, particularly freeze-thaw durability (Sprung and Siebel 1991). This section provides information on each of these requirements.

5.1.1 Minimum $CaCO_3$ Content

EN 197-1 and CSA A3001 require that limestone used in portland-limestone cements have a minimum $CaCO_3$ content of 75% by mass. As noted in Chapter 1, the European standard permits limestone to be used in amounts up to 35% by mass and the Canadian standard permits up to 15% by mass to be used. The European standard does not limit the $CaCO_3$ content of limestone when it is used at levels less than 5% by mass. The Canadian standard requires that a limestone used in amounts of less than 5% be of “a quality suitable for the manufacture of portland cement clinker.” ASTM C150 and AASHTO M 85 require limestone used in portland cements (maximum 5% by mass) to have a minimum $CaCO_3$ content of 70% and stipulates that it be naturally occurring. The CSA, EN and ASTM limits on $CaCO_3$ content are all somewhat arbitrary.

Procedures for determining CaO are provided in ASTM C114/AASHTO T 105 and in ASTM C25, as are procedures for determining CO_2 content. A CO_2-based determination was selected for limestone used in C150 and M 85 portland cement to enable user verification of limestone content using a CO_2 determination on the finished cement and information provided by the manufacturer on $CaCO_3$ of limestone. Interferences from CaO contained in portland cement clinker, calcium sulfate, and possible inorganic processing additions preclude the use of CaO to determine limestone content of portland cement. However, a CO_2-based measurement on limestone will not necessarily distinguish between $CaCO_3$ and $MgCO_3$, which may be the reason that EN 197-1 and subsequently CSA A3001 require that $CaCO_3$ content of limestone be based on measured CaO content.

The requirement to determine $CaCO_3$ content for limestone used in CSA A3001 portland-limestone cements and EN197-1 CEM II is a manufacturer’s responsibility. These standards do not have provisions for user testing of limestone quality parameters. This is consistent with provisions for qualifying pozzolan and slag for use in C595 and M 240 blended cements. The standards include qualification tests and criteria for pozzolan and slag that the manufacturer must meet, but user acceptance tests and criteria are conducted on the finished product, not component materials.

5.1.2 Methylene Blue Index

The methylene blue index (MBI) is a chemical characterization technique. Test procedures are provided in EN 933-9 and CSA A3004-D1. The MBI procedure determines the amount of methylene blue dye absorbed by a limestone sample ground to a fineness of about 500 m^2/kg

(Blaine). Bensted (1985) provides a comparison of results on various materials using the MBI procedure. The dye is preferentially adsorbed by clay minerals and thus the index provides an indication of the clay content of the limestone, although not a direct measure, as different clays adsorb the dye at different rates. However, Sprung and Siebel (1991) point out that the clay minerals in the limestones in their study were, similar and predominantly illitic. Referring to Bensted (1985), they note that montmorillonitic clays adsorb about 8 times as much dye and kaolinitic clays adsorb about half as much. However, they also indicate a correlation between the MBI of limestones used in cements in their study and several properties: BET specific surface area, the water demand of a limestone powder, and the water required to achieve a standard consistency for a limestone paste. In addition the MBI was related to the impact of limestone in cement on concrete frost resistance (see below).

5.1.3 Total Organic Carbon

The total organic carbon content, as the name implies, is a measure of the amount organic carbon compounds present in the limestone. These arise naturally from soils and sediments in limestone quarries or during formation of limestone in geologic processes. The TOC is determined either by subtracting the inorganic carbon content from the total carbon content, or by determining the carbon content on a sample that has had the inorganic carbon content removed by acidification. CSA A3004-D2 provides detailed methodology, as does EN 13639.

Organic carbon compounds *in aggregates* used in concrete are known to affect setting time and strength development, and it is presumed that similar effects may occur if they are present in limestone used in cement (above some level: a TOC of 0.2% or 0.5% by mass is referred to in EN 197-1). The organic carbon content may also influence the performance of admixtures, as does unburnt carbon in fly ash, and thus it may impact frost performance by reducing the air-entrainment ability of certain admixtures. Schneider et al. (2007) indicate that “No significant correlation between TOC and the scaling of concrete in laboratory investigations was established, but concretes using Portland-limestone cements with TOC ≤ 0.20 wt-% always showed high frost resistance.”

5.1.4 Impact of Limestone Composition on Freeze-Thaw Resistance (Basis for Limestone Requirements)

Research from the early 1990s (Sprung and Siebel 1991) on frost resistance of PLC concretes appears to have been used by European standards bodies to justify CaO content, MBI and TOC limits. In their study, limestones from 33 European sources were analyzed for a range of characteristics and then tested in pastes, mortars and concretes. The $CaCO_3$ content ranged from 58% to 98%, the MBI ranged from 0.07% to 2.53%, and the TOC ranged from 0.04% to 0.37%. Some concretes made with cements with limestone outside of one or more of the EN197-1 limits (MBI, TOC, $CaCO_3$) performed poorly in standardized freeze-thaw testing. The testing protocol subjected 10-cm concrete cubes, with a water-to-cement ratio of 0.60, without entrained air, to 100 freeze-thaw cycles between -15°C and 20°C, 1 cycle per day. These concretes would not meet building code requirements for freeze-thaw durability (ACI 318 2008). Data provided in Table 5.1, are reproduced from Sprung and Siebel (1991) and Fig. 5.1 is reproduced from Siebel and Sprung (1991). The concretes were made using cements with 15% limestone, ground to a fineness of about 550 m^2/kg Blaine.

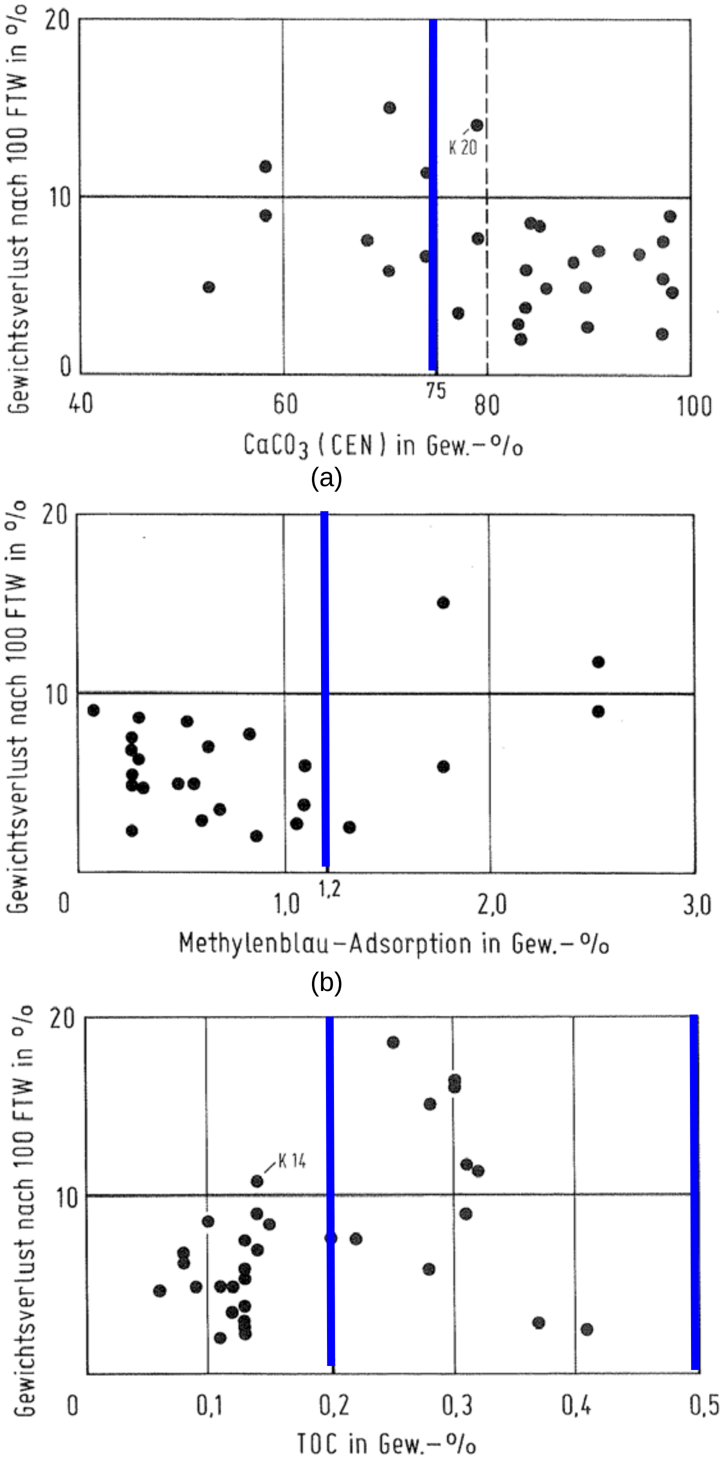
Table 5.1 Summary of non-air-entrained concrete freeze-thaw testing of 33 portland-limestone cements.*

Limestone number	Requirements of limestone				Concrete frost resistance
	$CaCO_3$ (CEN) % by mass		Methylene blue adsorption % by mass	Total organic carbon % by mass	Weight loss in 100 freeze-thaw cycles % by mass
	<75%	<80%	>1.20	>0.20	>10
K0					
K1	•		•	•	•
K2	•		•	•	•
K7					
K10					
K11					
K13				•	•
K14					
K15					
K16				•	•
K17					
K18					
K20		(•)			•
K21					
K22				•	
K23	•			•	
K24	•				
K25	•			•	•
K26					
K27					
K28					
K29					
K30					
K31				•	
K32		(•)			
K33			•	•	
K34					

* • indicates requirements not met. (•) Indicates borderline results.
Source: Sprung and Siebel 1991.

The data indicate that these limits should be considered conservative in classifying limestones for use in cement. Almost all limestones that meet the prescriptive limits also meet performance criteria. However, in each case a number of limestones (50% or more) that fail one or more of the prescriptive limits perform well in the German performance test. Other factors are apparently impacting the concrete freeze/thaw performance. There appears to be only limited research on these criteria since the early 1990s.

The two sets of EN197-1 TOC limits of 0.2% (-LL) or 0.5% (-L) are apparently a compromise between limits advocated based on German tests and experience using limestone deposits in other European countries. CSA reviewed EN197-1 limestone quality limits based on the history of their use in Europe, and adopted the less restrictive 0.5% TOC limit.



(a)

(b)

(c)

Figure 5.1 Freeze-thaw performance of non-air-entrained concretes made using cements with multiple limestone sources with a range of (a) $CaCO_3$ contents, (b) MBI values, and (c) TOC contents. Vertical axis is weight loss after 100 freeze-thaw cycles. Horizontal line at 10% is the maximum limit selected for classifying acceptable concrete performance. Heavy blue lines are limits in EN197 (Note: EN197-1 has limits on TOC of 0.2% for -LL and 0.5% for –L). *Source*: Siebel and Sprung (1991).

US cement producers have noted that the CSA MBI or TOC requirements would preclude some limestone deposits that have been successfully used in ASTM C1157 cements at 10% limestone content and at higher levels in masonry cement formulations. Given that limestone quality criteria should provide an acceptable level of confidence for producers and users that limestone does not compromise concrete durability, and should also avoid disqualifying limestones that perform well in service, consideration should be given to developing alternative criteria for acceptance of limestone used in portland-limestone cement.

5.2 REQUIREMENTS FOR CEMENT

EN197-1 outlines requirements for 27 basic cement types based on composition. These are also classified into three ranges of 28-d compressive strength (each of these has two further divisions of normal strength gain or rapid strength gain). CEM II/A-L or CEM II/A-LL cements with between 6% and 20% limestone under EN197-1 have the same physical requirements (compressive strength, initial setting time, and soundness) within each class as other cement types. Sulfate contents for CEM II cements are 3.5% or 4.0% maximum, depending on the strength class, and all cements have an additional requirement of 0.10% maximum chloride content. Although CEM I and CEM III cements have loss-on-ignition requirements and insoluble residue requirements, CEM II cements do not.

As described in Section 1.2 (Table 1.3), portland-limestone cements in CSA A3001 have designations similar to portland cement types except an “L” is appended to the designation. Thus, Type GUL (general use), Type MHL (moderate heat), Type LHL (low heat of hydration), and Type HEL (high early strength) are the four portland-limestone cement types defined. Sulfate resistant portland cement types (MS and HS) do not have corresponding portland-limestone cements (see Section 5.2.1). Blended cements based on portland cement and SCMs are designated with a suffix of “b;” for example Type GUb is a blended cement intended for general concrete construction. Blended cements that include SCMs as well as between 5% and 15% limestone are denoted with both suffixes: for example GULb.

Identical requirements for minimum compressive strengths, maximum autoclave expansion (soundness) test, range of initial setting times, and maximum fineness (% retained on 45-µm sieve) apply to both portland and portland-limestone cements (see Table 1.4) in CSA A3001. The maximum heat of hydration requirements for Type MH or Type MHL and Type LH or Type LHL cements are also the same.

Chemical requirements for cements with between 5% and 15% limestone are somewhat different for portland and portland-limestone cements in CSA A3001 (Table 5.2). All four types of portland-limestone cements have maximum loss-on-ignition (LOI) limits of 10.0% by mass, whereas portland cements are limited to a maximum LOI of 3.0% (3.5% for GU and HE if additional testing indicates the maximum loss from limestone is 3.0%). The higher LOI limit is specifically to accommodate the higher loss due to the presence of limestone, which loses on the order of half its mass at ignition temperatures (approximately 1000°C).

Portland-limestone cements in CSA A3001 have 3.0% maximum SO_3 content limits, or must demonstrate mortar expansion (CSA A3004-C5, similar to ASTM C1038) less than 0.020% at 14 days. For portland cements, the maximum sulfate content in CSA A3001 (as in ASTM C150 and AASHTO M85) depends on the C_3A content of the cement and the cement type, with a default maximum that ranges from 2.5% to 4.5%; however, higher amounts of sulfate can be used if mortar expansion test results are less than 0.020% at 14 days.

CSA A3001 portland cements also have requirements on maximum MgO content (5.0%) and Types MH, LH, MS, and HS, have limits on C_3A content. These limits do not apply to portland-limestone cements. Portland-limestone cements in CSA A3001 are required to be interground.

5.2.1 Sulfate resistance

CSA specification A3001 only contains provisions for sulfate resistant portland-limestone *blended* cements that are required to contain pozzolans or slag cement (Tables 1.3 and 1.4). These cements are designated Types MSLb and HSLb for moderately- and highly-sulfate resistant, respectively.

The restriction on portland-limestone cements (without SCMs) is based on laboratory test results indicating decreased sulfate resistance performance of some portland-limestone cements at low temperatures due to thaumasite formation (Hooton et al. 2010; Thomas et al. 2010). The same preliminary testing has shown that SCMs can improve sulfate resistance of cements with up to 15% limestone at low temperatures and provisions are have been adopted in CSA A3001to define sulfate resisting blended cements with limestone, with additional performance testing required (Tables 5.3 and 5.4).

The requirements for CSA sulfate resistant portland-limestone blended cements are complex. Moderate sulfate resistance for Type MSLb would be assured by a maximum limit of 0.10% expansion at 6 months for mortar bars immersed in $NaSO_4$ solutions (50 g/L, similar to ASTM C1012) for specimens stored at 23°C and similarly a maximum of 0.10% expansion at 18 months for bars stored at 5°C. Type HSLb cements would have a maximum limit of 0.05% expansion at 6 months at 23°C, and a limit of 0.10% expansion at 18 months at 5°C. In addition, for testing both cement types at 5°C, if the expansion is above 0.03% between 12 and 18 months, the testing is extended to 24 months with the same 0.10% expansion limit. There are also prescriptive limits for minimum SCM content requirements for these cements: 25% Class F fly ash, 40% slag cement, 15% metakaolin (Class N pozzolan), 5% silica fume and 25% slag cement, or 5% silica fume and 20% Class F fly ash.

At the time this report is being published, EN197-1 does not contain provisions for sulfate resistant cements. However, this area is actively being researched and preliminary recommendations for optional sulfate resistance requirements (denoted by an “SR” suffix) have been made by the technical committee, CEN TC 51. Research is also underway on performance test methods for sulfate resistance.

Table 5.2 Summary of Compositional Requirements in CSA A3001 (% by mass)

Requirement	Types	Limit (maximum)	Notes
MgO	GU, MS, MH, HE, LH, HS	5.0	
Sulfate, SO_3*	LH, HS	2.5	
	GU, MS, MH, GUb, MSb, MHb, HEb, HSb, LHb, GUL, MHL, HEL, LHL	3.0	3.5 for Type GU if C_3A content is >8.0%
	HE	3.5	4.5 for Type HE if C_3A content is >8.0%
Sulfide, S^{2-}	GUb, MSb, MHb, HEb, HSb, LHb,	2.0	Only applies to blended cements made with slag cement if SO_3 limit exceeded.
Loss on ignition (LOI)	GU, MS, MH, HE, LH, HS	3.0	An LOI of 3.5% maximum is allowed for Types GU and HE, provided that additional testing at 550±25°C does not exceed 3.0%. Also applies to binary blended cements with slag
	GUb, MSb, MHb, HEb, HSb, LHb	3.5	For blended cements produced with silica fume
	GUb, MSb, MHb, HEb, HSb, LHb	6.0	For blended cements produced with fly ash
	GUL, MHL, HEL, LHL GUb, MSb, MHb, HEb, HSb, LHb GULb, MSLb, MHLb, HELb, HSLb, LHLb	10.0	For blended cements produced with natural pozzolans. For blended limestone cements produced with slag.
	GULb, MSLb, MHLb, HELb, HSLb, LHLb	10.5	For blended limestone cements produced with silica fume
	GULb, MSLb, MHLb, HELb, HSLb, LHLb	13.0	For blended limestone cements produced with fly ash
	GULb, MSLb, MHLb, HELb, HSLb, LHLb	17.0	For blended limestone cements produced with natural pozzolan
Insoluble residue (IR)	MS, MH, LH, HS	0.75	
	GU, HE	1.5	
Tricalcium aluminate, C_3A	MS, MH	8	
	LH	6	
	HS	5	

Key: For complete details, review the relevant standards. See text for primary cement types.
*SO_3 limits can be exceeded if CSA A3004-C5 expansion test results are less than 0.020% at 14 days.
**This is an optional requirement that applies only when specifically requested.

Table 5.3 Physical Requirements in CSA A3001, % by mass unless otherwise stated
(excluding sulfate resistance requirement, see Table 5.4)

CSA A3004 Test method	Types	Limit	Notes
A3, Fineness, maximum 45 µm sieve	GU, MS, MH, HS, GUL, MHL	28	
	GUb, MSb, MHb, HEb, LHb, HSb, GULb, MSLb, MHLb, HELb, LHLb, HSLb	24	
B5, Autoclave expansion, maximum %	GU, MS, MH, HE, LH, HS, GUL, MHL, HEL, LHL	1.0	
	GUb, MSb, MHb, HEb, LHb, HSb GULb, MSLb, MHLb, HELb, LHLb, HSLb	0.8	
C6, Sulfate resistance, maximum % expansion at 14 days	MS	0.050	A3004-C6 is similar to ASTM C452
	HS	0.035	
C8, Sulfate resistance, Maximum % expansion at 6 months	MSb	0.10	C8 is similar to ASTM C1012.
	HSb	0.05	If expansion is greater than 0.05% at 6 months, limit is 0.10% at 1 year.
B2, Initial time of set, minutes	GU, MS, MH, HE, LH, HS, GUL, MHL, HEL, LHL	minimum 45	
	GUb, MSb, MHb, HEb, HSb GULb, MSLb, MHLb, HELb, HSLb	minimum 60	
	LHb, LHLb	minimum 90	
	HE, HEL, HEb, HELb	maximum 250	
	GU, MS, MH, LH, HS, GUL, MHL, LHL	maximum 375	
	GUb, MSb, MHb, LHb, HSb GULb, MSLb, MHLb, LHLb, HSLb	maximum 480	
B7, Heat of hydration, Maximum kJ/kg at 7 days	MH, MHb, MHL, MHLb	300	
	LH, LHb, LHL, LHLb	275	
C2, Compressive strength, minimum MPa*at:			Strength at any age shall not be less than that of the preceding age.
1 day	HE, HEL, HEb, HELb	13.5	
3 days	LH, LHL	8.5	
	GU, MS, MH, HS, GUb, MSb, MHb, HSb, GUL, MHL GULb, MSLb, MHLb, HSLb	14.5	
	HE, HEb, HEL, HELb	24.0	
7 days	LHb, LHLb	8.5	
	GU, MS, MH, HS, GUb, MSb, MHb, HSb GUL, MHL	20.0	
28 days	LH, LHb, LHL, LHLb	25.0	
	GU, MS, MH, HS, GUb, MSb, MHb, HSb, GUL, MHL GULb, MSLb, MHLb, HSLb	26.5	

For complete details, review the relevant standards.
*1 MPa = 145.0377 psi.

Table 5.4 Additional Requirements for Sulfate Resistant Cements in CSA A3001

Cement type	MS	MSb	MSLb***	HS	HSb	HSLb***
Sulfate resistance,* maximum % expansion at 14 days*	0.050	--	--	0.035	--	--
Sulfate resistance,** maximum % expansion at:						
6 months	--	0.10 (A)	--	--	0.05 (A)	--
12 months	--	--	0.10 (A)(B)	--	--	--
18 months	--	--	--	--	--	0.10 (A)(B)

*Per CSA A3004-C6, which is similar to ASTM C452.

**Per CSA A3004-C8, which is similar to ASTM C1012; however A3004-C8 has two procedures: Procedure A [indicated in the table by “(A)”], in which specimens are stored at 23°C, and Procedure B in which testing is also conducted at 5°C [Indicated in the table by “(B)”]. “–“ indicates no requirement.

***MSLb and HSLb cements shall contain a minimum of 25% Class F fly ash or 40% slag cement.

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CSA A3004-C8, Test methods for determination of expansion of blended hydraulic cement mortar bars due to external sulphate attack

CSA A3004-D1, Methylene blue adsorption test of limestone for use in portland-limestone cement

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CHAPTER 6 CASE HISTORIES

This chapter provides data from two series of field studies in which cements with up to 15% limestone have been used. The first series is comprised of three sets of pavements placed in different Canadian provinces and covers a wide range of both fresh and hardened concrete properties. The second series summarizes several test pavements in two US states that used ASTM C1157 cements with 10% limestone as an ingredient.

6.1 CANADIAN STUDIES

Three trial paving projects using portland-limestone cements (PLC) have been constructed in Canada and these are located in Quebec, Alberta and Nova Scotia. Details of the cementitious materials used at the three sites are presented in Table 6.1 Table 6.2 provides details of the mixture proportions used for each project. In all cases the PLC was produced as a full-scale industrial trial grind with the limestone being interground with the clinker and gypsum at the cement plant. In the Nova Scotia trial, 15% ground, granulated blast-furnace slag was also interground with the clinker, gypsum and limestone to produce a ternary blended cement (in US terminology, or a portland-limestone blended cement in Canadian usage). The performance of the PLC was compared directly with the portland cement (PC) by producing concrete with the same mixture proportions. Supplementary cementitious materials (SCM) were also used in each trial at varying proportions; the SCMs were introduced at the ready-mixed concrete plant.

Table 6.1 Chemical Composition of Cementitious Materials used in Field Trials, % by mass

Location of trial	Cement type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2Oeq.	SO_3	LOI	Blaine (m^2/kg)
Quebec[1]	PC[2]	20.53	4.63	2.77	62.7	2.48	0.21	3.23	2.26	373
	PLC[3]	19.23	4.4	2.64	61.45	2.41	0.20	3.4	5.25	453
	Fly ash	36.53	19.39	5.27	18.62	4.92	5.69	2.06	0.30	
	Slag	35.75	9.72	0.50	35.66	13.05	0.33	2.93	-	
Alberta	PC[2]	20.17	4.31	2.65	61.48	4.48	0.62	2.79	2.86	399
	PLC[3]	18.76	4.04	2.47	61.05	4.29	0.55	2.58	5.77	510
	Fly ash	56.4	24.1	3.5	10.0	1.1	3.14	0.2	0.26	
Nova Scotia	PC-slag[4]	22.9	5.9	1.9	59.3	3.2	0.89	4.10	0.6	453
	PLC-slag[5]	22.4	5.7	1.8	57.1	3.4	0.85	3.96	6.15	532
	Fly ash	48.02	20.65	7.92	6.68		1.48*	3.08	1.43	

[1] In the Quebec trial the SCM used was a pre-blended SCM consisting of two parts Type S slag with one part Type CI fly ash.

[2] Type PC cement used in Quebec and Alberta contains 3% to 4% limestone and 91% clinker

[3] Type PLC cement used in Quebec and Alberta contains 12% limestone and 83% clinker

[4] Type PC-Slag cement used in Nova Scotia contains 3% to 4% limestone, 15% slag and 76% clinker

[5] Type PLC-Slag cement used in Nova Scotia contains 12% limestone, 15% slag and 68% clinker

All proportions expressed in notes above are approximate and are based on gypsum content of 5%

*Available alkali reported (ASTM C311) not total alkali

Table 6.2 Details of Concrete Mixtures used in Field Trials

Location of trial	SCM[*] (%, type)	Cement type	W/CM	Slump (mm)	Air (%)	Set time (mins)	Cementitious material[**] (kg/m^3)	Clinker content (kg/m^3)
Quebec	0	PC	0.45	100	6.8	–	355	323
		PLC	0.44	80	6.0	–	355	295
	25 CI/S	PC	0.44	75	6.2	–	355	242
		PLC	0.45	100	6.6	–	355	221
	40 CI/S	PC	0.44	95	6.8	–	355	194
		PLC	0.44	80	6.0	–	355	177
	50 CI/S	PC	0.44	95	6.8	–	355	162
		PLC	0.44	95	6.5	–	355	147
Alberta	0	PC	0.42	125	7.8	330	410	373
		PLC	0.42	120	6.8	345	410	340
	15 CI	PC	0.40	135	6.2	396	410	321
		PLC	0.40	100	6.0	378	410	289
	25 CI	PC	0.38	115	6.4	451	410	280
		PLC	0.38	95	6.3	403	410	255
	30 CI	PC	0.37	120	6.1	468	410	261
		PLC	0.37	115	6.4	442	410	238
Nova Scotia	0	PC-Slag	0.42	75	5.8	–	392	298
		PLC-Slag	0.44	60	6.6	–	384	261
	15 F	PC-Slag	0.43	80	6.1	–	384	248
		PLC-Slag	0.43	65	6.2	–	385	222
	20 F	PC-Slag	0.44	65	6.6	–	385	234
		PLC-Slag	0.43	75	6.5	–	386	210

[*] F=Type F fly ash, CI=Type CI fly ash, CI/S=Type CI fly ash blended with slag cement.
** Note: 1 kg/m^3 = 1.686 lb/yd^3)

6.1.1 Paving at Ready-Mixed Concrete Plant, Quebec

The first field trial was conducted using PLC with 12% interground limestone produced at a cement plant in Ontario. A total of eight concrete mixtures were produced, four with PLC and four with PC from the same plant. Details of the mixture proportions are given in Table 6.2. The total cementitious materials content of all mixtures was 355 kg/m^3 (598 lb/yd^3) and the water-to-cementitious -materials ratio was w/cm = 0.44 to 0.45. A blended SCM (2 parts slag and 1 part fly ash) was added at the ready-mixed concrete plant at cement replacement levels of 0%, 25%, 40% and 50%. The concrete was used to construct a parking slab (4500 ft^2, 450 m^2) at the concrete plant (Fig. 6.1). The concrete was placed in October, 2008. Extensive laboratory testing was conducted on specimens cast during the placing of the concrete and the results were recently reported in a paper by Thomas et al. (2010). In the PLC mix with 50% SCM, the clinker only constituted approximately 41% to 42% of the total mass of cementitious materials. This compares with about 91% to 92% clinker for the control mix produced with PC and no SCM (PC contains approximately 3% to 4% limestone and 5% gypsum).

The test data for concrete specimens cast during the trial are presented in Table 6.3. As expected, the inclusion of SCM significantly influenced concrete properties and generally an increase in the SCM content reduced the early-age strength but increased the resistance to chloride ingress. The SCM content did not impact the freeze-thaw durability as measured by ASTM C 666, but increased mass losses were observed for concrete with 40% or 50% SCM when tested in deicer-salt scaling tests. However, the scaling mass losses were significantly below the acceptance limits specified by provincial agencies in Canada (e.g. 800 g/m^2 to 1000 g/m^2).

For concrete produced at a given level of SCM there was no consistent difference between the performance that could be attributed to the portland cement type; in other words, concrete produced with PLC showed equivalent performance to concrete produced with PC.

Figure 6.1 Paving at a ready mixed concrete plant in Quebec.

Table 6.3 Details and Test Results for Concrete Mixtures for the Quebec Field Trial

	No SCM		25% SCM		40% SCM		50% SCM	
	PC	PLC	PC	PLC	PC	PLC	PC	PLC
W/CM	0.45	0.44	0.44	0.45	0.44	0.44	0.44	0.44
Plastic air content, %	6.8	6.0	6.2	6.6	6.8	6.0	6.8	6.5
Slump, mm	100	80	75	100	95	80	95	95
Slump, in.	3.9	3.1	3.0	3.9	3.7	3.1	3.7	3.7
Hardened air content								
Air content, %	5.3	5.6	4.9	5.4	5.6	5.3	5.6	6.6
Spacing factor, μm	173	187	148	149	164	165	150	147
Spacing factor, in.	0.068	0.074	0.058	0.059	0.065	0.065	0.059	0.058
Strength, MPa								
1 day	24.2	25.2	21.7	20.7	18.9	19.2	15.3	15.6
7 days	30.2	30.5	29.8	29.6	30.3	31.1	29.4	28.8
28 days	37.7	38.2	41.3	39.8	43.5	43.5	43.0	42.5
56 days	41.3	40.9	45.4	44.7	48.6	48.3	48.7	46.5
Cores at 35 days	39.7	35.3	35.7	35.5	42.3	43.2	37.6	39.4
Strength, psi								
1 day	3510	3650	3150	3000	2740	2780	2220	2260
7 days	4380	4420	4320	4290	4390	4510	4260	4180
28 days	5470	5540	5990	5770	6310	6310	6240	6160
56 days	5990	5930	6580	6480	7050	7000	7060	6740
Cores at 35 days	5760	5120	5180	5150	6130	6260	5450	5710
[1]Durability factor, %	101	100	101	104	101	103	102	100
[2]Scaling mass C 672, g/m^2	40	10	30	50	80	230	400	320
[2]Scaling mass C 672, oz/yd^2	1.17	0.29	0.88	1.46	2.34	6.73	11.71	9.36
[3]Scaling mass BNQ, g/m^2	39	114	273	127	106	142	380	497
[3]Scaling mass BNQ, oz/yd^2	1.14	3.34	7.99	3.72	3.10	4.16	11.12	14.54
[4]RCPT,Coulombs								
28 days	3446	3734	2004	1765	1145	1056	1052	932
56 days	2781	2964	1233	1317	733	666	548	474
Cores at 35 days	2395	2345	1410	1308	570	617	491	520
[5]Diff. coeff., D_a, × 10^{-12} m^2/s	15.0	11.9	3.77	2.91	1.51	1.22	1.25	1.81

[1] Durability factor after 300 freeze-thaw cycles - ASTM C666 Procedure A

[2] Mass loss after 50 freeze-thaw cycles ponded with salt solution - ASTM C672 “Salt Scaling Test”

[3] Mass loss after 56 freeze-thaw cycles ponded with salt solution - BNQ “Salt Scaling Test”

[4] Charged passed after 6 hours - ASTM C1202 “Rapid Chloride Permeability Test”

[5] Chloride diffusion coefficient, D_a, determined on 35-day-old cores using ASTM C1556 “Bulk Diffusion Test”

6.1.2 Paving at Cement Plant, Alberta

The second field trial was conducted using PC and PLC produced at a cement plant in Alberta; the PLC contained 12% interground limestone. This trial incorporated four concrete mixes with PLC and four with PC, with fly ash being added at the ready mix plant at levels of 0%, 15%, 25%, and 30%. The total cementitious materials content of all mixtures was 410 kg/m^3 (691 lb/yd^3) and the water-to-cementitious-materials ratio was w/cm = 0.37 to 0.42. Approximately 260 m^3 (340 yd^3) concrete was used for 850 m^2 (9150 ft^2) of paving (see Fig. 6.2) and additional PC and PLC mixtures were also produced for two retaining walls and 50 lineal meters (164 ft) of slip formed curb. The concrete was placed in September, 2009. The pavement was 0.30 m to 0.45 m (12 in. to 18 in.) thick and was reinforced with a single mat of reinforcement. The concrete was placed by pump, struck off, bull floated and tined. After finishing the surface was treated with an evaporation retarder as it was windy. Finally, a curing membrane was applied.

Figure 6.2 Paving at a cement plant in Alberta.

Table 6.4 Details and Test Results for Concrete Mixtures for the Alberta Field Trial

	No SCM		15% Fly ash		25% Fly ash		30% Fly ash	
	PC	PLC	PC	PLC	PC	PLC	PC	PLC
W/CM	0.42	0.42	0.40	0.40	0.38	0.38	0.38	0.38
Air content, %	7.8	6.8	6.2	6.0	6.4	6.3	6.1	6.4
Slump, mm	125	120	135	100	115	95	120	115
Slump, in.	5.00	4.75	5.25	4.00	4.50	3.75	4.75	4.50
Set time, mins	330	345	396	378	451	403	468	442
Strength, MPa								
1 day	13.9	17.5	14.3	17.3	13.6	14.2	11.4	11.9
7 days	24.6	28.9	27.3	29.0	27.1	25.1	25.3	24.0
28 days	29.7	34.7	35.6	35.6	38.9	34.4	36.3	35.2
56 days	33.3	37.9	42.0	41.8	40.9	39.4	43.6	38.2
Strength, psi								
1 day	2020	2540	2070	2510	1970	2060	1650	1730
7 days	3570	4190	3960	4210	3930	3640	3670	3480
28 days	4310	5030	5160	5160	5640	4990	5260	5100
56 days	4830	5500	6090	6060	5930	5710	6320	5540
[1]Scaling mass loss, g/m^2	177	199	112	106	180	135	170	125
[1]Scaling mass loss, oz/yd^2	5.18	5.83	3.27	3.10	5.27	3.94	4.96	3.67
[2]RCPT, Coulombs, at 56 days	1894	2016	1822	1389	1182	1009	839	791

[1] Mass loss after 50 freeze-thaw cycles ponded with salt solution - ASTM C672 “Salt Scaling Test”

[2] Charged passed after 6 hours - ASTM C1202 “Rapid Chloride Permeability Test”

Results of tests performed on test specimens produced on site are presented in Table 6.4. Generally increasing levels of fly ash were found to decrease the early-age strength but increase the later-age strength, increase the set time, and increase the resistance to chloride ion penetration (as evidenced by a decrease in the electrical conductivity in ASTM C1202). For concrete with a given level of fly ash, the use of PLC decreased the set time (for mixes with fly ash) and increased the early-age strength compared with PC; otherwise the PLC concrete gave equivalent performance as the PC concrete.

6.1.3 Paving at Cement Plant, Nova Scotia

The third field trial was conducted using a blended portland cement containing 3% to 4% limestone and 15% slag and a blended portland-limestone cement containing 12% limestone and 15% slag; in both cases the cements were produced by intergrinding portland cement clinker, gypsum, limestone and ground granulated blast-furnace slag. In October 2009, six concrete mixtures were produced at a nearby ready-mixed concrete plant, and were delivered to the cement plant to construct a length of pavement just outside the main entrance to the plant (see Fig. 6.3). The total volume of concrete placed was about 230 m^3 (300 yd^3). Details of the six concrete mixtures are given in Table 6.2; fly ash was added at the concrete plant.

Figure 6.3 Paving at a cement plant in Nova Scotia.

Table 6.5 presents data from tests conducted on specimens cast on site. For concrete mixes with 15% and 20% fly ash, there was no consistent significant difference between the strength of mixes cast with the blended PC-slag versus PLC-slag, except that PC-slag mixes had slightly higher 90-day strengths. For the mixes without fly ash, the strengths were similar at 3 days, but the mix with PLC-slag showed lower strengths (by about 10%) at the later ages. It should be noted that the mix with PLC-slag had a slightly higher w/cm (by 0.02) and significantly higher air content (by 0.8%) compared to the mix with PC-slag and this could partially explain the lower strengths (note a 1% increase in air can reduce the strength by approximately 5.5%). RCPT tests conducted on concrete samples at an age of 90 days show that the partial replacement of either blended cement with fly ash has a profound effect on the charge passed. Mixes without fly ash are classed as concrete with high chloride penetrability by the criteria in ASTM C1202, mixes with 15% fly ash are classed as low to intermediate penetrability, and mixes with 20% fly ash are classed as low penetrability. Comparing mixes with the same fly ash content, those produced with blended PLC-slag showed lower chloride ion penetrability compared with mixes with PC-slag; the differences are considered to be significant.

Table 6.5 Details and Test Results for Concrete Mixtures for the Nova Scotia Field Trial

	No SCM		15% Fly Ash		20% Fly Ash	
	PC	PLC	PC	PLC	PC	PLC
W/CM	0.42	0.44	0.43	0.43	0.44	0.43
Air content, %	5.8	6.6	6.1	6.2	6.6	6.5
Slump, mm	75	60	80	65	65	75
Slump, in.	3.00	2.25	3.25	2.50	2.50	3.00
Strength, MPa						
3 days	21.9	21.8	18.7	19.7	17.7	17.6
7 days	29.2	27.1	23.8	25.0	23.8	23.3
28 days	37.4	33.3	31.5	34.3	32.6	33.0
91 days	41.1	36.8	37.9	41.7	38.1	41.1
Strength, psi						
3 days	3180	3160	2710	2860	2570	2550
7 days	4230	3930	3450	3630	3450	3380
28 days	5420	4830	4570	4970	4730	4790
91 days	5960	5340	5500	6050	5530	5960
[1]Scaling mass loss, g/m^2	101	170	151	285	203	243
[1]Scaling mass loss, oz/yd^2	2.96	4.98	4.43	8.33	5.93	7.10
[2]RCPT, Coulombs at 100 days	4288	3568	1492	635	960	464
[3]Diff. coeff. D_a , × 10^{-12} m^2/s	6.1	6.4			3.9	3.4

[1]Mass loss after 50 freeze-thaw cycles ponded with salt solution - ASTM C672 "Salt Scaling Test"

[2]Charged passed after 6 hours - ASTM C1202 "Rapid Chloride Permeability Test"

[3]Chloride diffusion coefficient, D_a, determined on 2-month-old cores using ASTM C1556 "Bulk Diffusion Test"

Calculated diffusion coefficients indicate that partially replacing 20% of the cement with fly ash increases the resistance of the concrete to chloride ion penetration. However, there is no consistent difference between the chloride resistance of concrete produced with either blended PC-slag or blended PLC-slag cement. Results from deicer scaling tests indicate no consistent difference with fly ash content. At each level of fly ash the scaled mass loss is slightly higher for the blended PLC-slag cement compared with the PC-slag cement. However, differences are small and in all cases the scaled mass loss can be considered very low and well below typical limits used in Canada (e.g. maximum allowable losses from 800 g/m^2 to 1000 g/m^2).

6.2 US STUDIES–C1157 CEMENTS WITH LIMESTONE

Van Dam and Smartz (2010) reported results of three pilot paving projects in Colorado using ASTM C1157 cements with 10% limestone. Included were a section of an interstate highway, a rural highway and a local road. After noting the environmental advantages of using limestone, the report concludes that in each case, "…slip form paving concrete made with ASTM C1157 cement are readily constructible and can easily achieve specified strength requirements." It was further noted that the concretes also contained 20% fly ash (added at the batch plant), which further improved the carbon footprint of the concrete. Van Dam et al. (2010) also report on pilot projects in Utah and refer to laboratory durability testing on C1157 Type GU and Type I/II cements. The laboratory testing included C1012 (sulfate resistance), C1567 (ASR mitigation—using Class F fly ash), C666 (freeze-thaw testing), C672 (deicer scaling resistance), C157 (shrinkage) and C1202 (rapid chloride permeability) and demonstrated acceptable performance in these tests. Tables 6.6 and 6.7 summarize some of the concrete parameters of these pilot projects.

Table 6.6 Concrete in Colorado and Utah Pilot Programs

Pilot Project #1			
Compressive strength , MPa (psi)		Flexural strength	5.7 MPa (825 psi) at 7 d
1-d	13.3 (1930)	20% fly ash	
2-d	26.1 (3790)		
3-d	36.0 (5220)		
7-d	45.4 (6580)		
Pilot Project #2			
Flexural strength	4.8 MPa (695 psi) at 28 d	Water:cement ratio	0.34
		Cementitious materials (including 20% fly ash)	320 kg/m^3 (540 lbs/yd^3)
Pilot Project #3			
Flexural strength	4.9 MPa (710 psi) at 28 d	Water:cement ratio	0.42
		Cementitious materials (including 20% fly ash)	307 kg/m^3 (517 lbs/yd^3)
Pilot Project #4			
Compressive strength	35.3 MPa (5120 psi) at 28 d	20% fly ash	
Flexural strength	5.0 MPa (720) psi at 28 d		
Pilot Project #5			
Compressive strength	>34.5 MPa (>5000 psi) at 28 d	25% fly ash	

Sources: Van Dam and Smartz 2010; and Van Dam et al. 2010.

Table 6.7 Laboratory Strength Results on Portland and C1157 cements from Two Plants

Source	Cement content, kg/m^3 (lb/yd^3)	Cementitious materials	Compressive strength, MPa (psi)	
			7-d	28-d
Plant A	297 (500)	ASTM C150	23.8 (3450)	31.4 (4550)
		ASTM C1157	27.6 (4000)	34.1 (4950)
		ASTM C1157 and fly ash	17.6 (2550)	24.1 (3500)
	341 (575)	ASTM C150	27.9 (4050)	36.2 (5250)
		ASTM C1157	26.9 (3900)	34.5 (5000)
		ASTM C1157 and fly ash	25.5 (3700)	34.5 (5000)
Plant B	297 (500)	ASTM C150	24.5 (3550)	31.7 (4600)
		ASTM C1157	27.6 (4000)	34.1 (4950)
		ASTM C1157 and fly ash	18.3 (2650)	25.2 (3650)
	341 (575)	ASTM C150	30.7 (4450)	39.0 (5650)
		ASTM C1157	36.9 (5350)	41.5 (6025)
		ASTM C1157 and fly ash	25.5 (3700)	34.5 (5000)

Source: Adapted from Van Dam et al. 2010.

6.3 SUMMARY

The data from the three Canadian field trials show that concrete can be produced using PLC containing 12% interground limestone to give equivalent performance to concrete using PC provided that the PLC is ground to a higher fineness. The performance of concrete with PLC-SCM blends is equivalent to that of concrete with a corresponding blend of PC-SCM. In some of the concrete mixtures used in these studies, the clinker content was less than 50% of the total cementitious material content.

Data from US projects also indicates good performance with cements with limestone as a significant ingredient, with strengths generally improved slightly compared to portland cements.

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CHAPTER 7 SUMMARY

This report has reviewed published literature related to use of limestone as an ingredient in portland-limestone cements. Special emphasis was placed on limestone in amounts of up to 15%, although in some instances the effects of higher amounts were reviewed to provide additional information. In addition, several concrete field trials were summarized. The following general statements are supported by the literature:

- Limestone has been commonly used in Europe and other countries for several decades. Since adoption of EN197 in 2000, use of portland-limestone cements in Europe has grown steadily. Canadian specifications have permitted limestone as an ingredient in portland cements 1983 and contained provisions for portland-limestone cements since 2008. Portland cements with limestone as an ingredient in amounts up to 5% have been in common use in the US since 2004 and cements meeting ASTM C1157 with 10% limestone have been successfully used as well. [Masonry cements with limestone as an ingredient have been available since the 1920s.] Experience with these cements has demonstrated that they can provide strong, durable concretes and mortars.

- The environmental benefits of cements with limestone are appreciable. Although more grinding energy can be required, the energy saved by reducing clinker in the finished cement clearly outweighs the extra grinding energy. As well, by not calcining limestone to produce clinker, CO_2 emissions are reduced directly and through lower combustion fuel usage.

- By following well-documented mixture design and control practices, concretes made using cements with limestone can perform similarly to concretes without limestone. Although relatively inert compared to clinker or supplementary cementitious materials (SCMs), limestone appears to contribute directly to properties through three mechanisms:

    1) Particle packing effects, which can reduce water demand (and therefore water-to-cement ratios for equivalent workability) and subsequently increase strengths;
    2) Nucleation effects, in which hydration products of traditional cement reactions are accelerated slightly; and
    3) Chemical reactions, which only occur to a minor extent, to produce carboaluminate phases, which can reduce porosity.

- Laboratory research indicates that sulfate resistance of portland-limestone cements may be somewhat reduced. Preliminary laboratory research results also indicate that use of supplementary cementitious materials (SCMs) can mitigate this effect and provide sulfate resistant concrete.

- Requirements for limestone used as an ingredient in cement, based on methylene blue index, total organic carbon content and calcium carbonate content, have been implemented in

Europe and Canada. They appear to provide conservative assurance that the use of limestone will not adversely impact freeze-thaw durability.[*]

- Evidence that fresh and hardened concrete properties are within normal ranges (compared with concretes without limestone) have been documented in this report. Control of limestone particle size distribution and overall fineness of the cement, along with sulfate content optimization provides for equivalent behavior or even slight benefits when limestone is used in amounts up to 15%.

- Recent case histories of field placements in Canada and the US (up to 10% limestone), in addition to decades of experience in Europe and other countries, demonstrate that cements with up to 15% limestone can be effectively used in concretes and that SCMs can be used with limestone in this range as a component of ternary blended cements.

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[*] Given that European and Canada requirements are based on limited studies of concrete performance, in concretes that would not meet current building code requirements for freeze-thaw durability, consideration should be given to establishing alternate criteria to assure that limestone used in portland-limestone cement will not compromise performance.