SN3053

Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A 3000

by R. D. Hooton, M. Nokken, and M. D. A. Thomas

350 Sparks Street, Suite 502
Ottawa, Ontario K1R 7S8
Canada
613.236.9471 Fax: 613.563.4498
www.cement.ca

Limestone Cements: State-of-the-Art and Recommendations for Further Study

Table of Contents — Page

1.0 Introduction

This literature review on the properties of Portland-limestone cements was requested by St. Lawrence Cement after the presentation made to the CSA A3000 committee in 2006. The St. Lawrence presentation was based on allowing up to 15% limestone, as opposed to the current 5% limit. The mandate for this review was: (a) to look at what is known about effects of such limestone cements on fresh, hardened, and durability properties of concrete, (b) to determine the gaps in the literature, and (c) to recommend issues requiring further research.

1.1 History of the Use of Limestone Additions

1.1.1 Europe

In Europe, a number of countries allowed different percentages of limestone prior to adoption of EN 197-1. For example, Schmidt (1992) states that large quantities of 20% limestone cements were produced by Heidelberg Cement as early as 1965 for specialty applications. Its use in France dates back to at least the 1970's. In the 1987 draft of EN 197, a cement designated as PKZ was composed of 85+/-5% clinker and 15+/-5% limestone Schmidt (1992). By 1990, 15+/-5% limestone blended cements were reported to be commonly used in Germany. In the UK, BS 7583 allowed up to 20% limestone cement in 1992.

The current EN 197-1 (2000) allows all of the 27 common types of cement to contained 5% Minor Additional Components (MAC), which most typically are either limestone or cement raw meal. The 27 EN common cements are listed in Table 1.1. As well, 4 types of cement allow higher amounts of limestone in two replacement level ranges, CEM II/A-L and CEM II/A-LL (6-20% limestone), as well as CEM II/B-L and CEM II/B-LL (21-35% limestone) in addition to the 5% MAC. The difference between the –L and the –LL designations are based on different qualities of the limestone used. For both L and LL, CaCO3 $\geq$ 75% and clay content $\leq$ 1.20g/100g. The difference is in the allowable total organic carbon content: Type LL restricts TOC $\leq$ 0.20% by mass while Type L restricts TOC $\leq$ 0.50% by mass. Both restrictions on the quality of limestone are more stringent than either CSA A3001 (no restriction other than LOI limit of 3.0% at 550C) or ASTM C 150 ("The limestone shall be naturally occurring, consisting of at least 70% by mass of one or more of the mineral forms of calcium carbonate."). According to CEN, the use of CEM II limestone cements has grown from 15% in 1999 to 31.4% in 2004 and is now the single largest type of cement produced (Figure 1.1).

1.1.2 North America

In Canada, CSA A5 has allowed up to 5% limestone in Type 10 cement (now Type GU in A3001) since 1983. This was preceded by presentation of data to show that 5% limestone had no detrimental effect on concrete properties.

In the US, after 3 attempts over a 20 year period, in 2004 ASTM C150 finally allowed up to 5% limestone to be used in Portland cements. However, many state highway agencies use American Association of State Highway Officials (AASHTO) standards rather than ASTM, and

Table 1.1 Types of Common Cement in EN 197-1

Main Type	Notation of the 27 products (types of common cement)		Composition (percentage by mass[a])										
			Main contituents										Minor additional constituents
			Clinker	Blast-furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						Natural	Natural calcined	siliceous	Calca-reous				
			K	S	D[b]	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM 1	95-100	-	-	-	-	-	-	-	-	-	0-5
CEM II	Portland-slag cement	CEM 11/A-S	80-94	6-20	-	-	-	-	-	-	-	-	0-5
		CEM II/B-S	65-79	21-35	-	-	-	-	-	-	-	-	0-5
	Portland-silica fume cement	CEM II/A-D	90-94	-	6-10	-	-	-	-	-	-	-	0-5
	Portland-pozzolana cement	CEM II/A-P	80-94	-	-	6-20	-	-	-	-	-	-	0-5
		CEM II/B-O	65-79	-	-	21-35	-	-	-	-	-	-	0-5
		CEN II/A-Q	80-94	-	-	-	6-20	-	-	-	-	-	0-5
		CEM II/B-Q	65-79	-	-	-	21-35	-	-	-	-	-	0-5
	Portland-fly ash cement	CEM II/A-V	80-94	-	-	-	-	6-20	-	-	-	-	0-5
		CEM IIB-V	65-90	-	-	-	-	21-35	-	-	-	-	0-5
		CEM II/A-W	80-94	-	-	-	-	-	6-20	-	-	-	0-5
		CEM II/B-W	65-79	-	-	-	-	-	21-35	-	-	-	0-5
	Portland-burnt shale cement	CIM II/A-T	80-94	-	-	-	-	-	-	6-20	-	-	0-5
		CEM II/B0T	65-79	-	-	-	-	-	-	21-35	-	-	0-5
	Portland-limestone cement	CEM II./A-L	80-94	-	-	-	-	-	-	-	6-20	-	0-5
		CEM II/B-L	65-79	-	-	-	-	-	-	-	21-35	-	0-5
		CEM II/A-LL	80-94	-	-	-	-	-	-	-	-	6-20	0-5
		CEM II/B-LL	65-79									21-35	0-5
	Portland-composite cement[c]	CEM II/SA-M	80-94	←--11-35--→									0-5
		CEM IIB-M	65-79	←--11-35--→									0-5
CEM III	Blastfurnace cement	CEM III/A	35-64	36-65	-	-	-	-	-	-	-	-	0-5
		CEM III/B	20-34	66-80	-	-	-	-	-	-	-	-	0-5
		CEM III/C	5-19	81-95	-	-	-	-	-	-	-	-	0-5
CEM IV	Pozzolanic cement[c]	CEM IV/A	65-89	←-- 11-35--→						-	-	-	0-5
		CEM IV/B	45-64	←-- 11-35 --→						-	-	-	0-5
CEM V	Composite cement[c]	CEM V/A	40-64	18-30	-	←---- 18-30 ----→			-	-	-	-	0-5
		CEM V/B	20-38	31.50	-	←---- 31-50 ----→			-	-	-	-	0-5

a The value in the table refer to the sum of the main and minor additional constituents.
b The proportion of silica fume is limited to 10%.
c In Portland-composite cements CEM II/A-M and CEM II/B-M and in composite cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

the members who govern the AASHTO M85 cement specification (AASHTO cements use the same basic numbering system as in ASTM C 150 for cement types) is expected to adopt 5% limestone in 2007 after significant work by a joint ASTM-AASHTO harmonization task group since 2005 to minimize differences in these cement standards including the limestone issue.

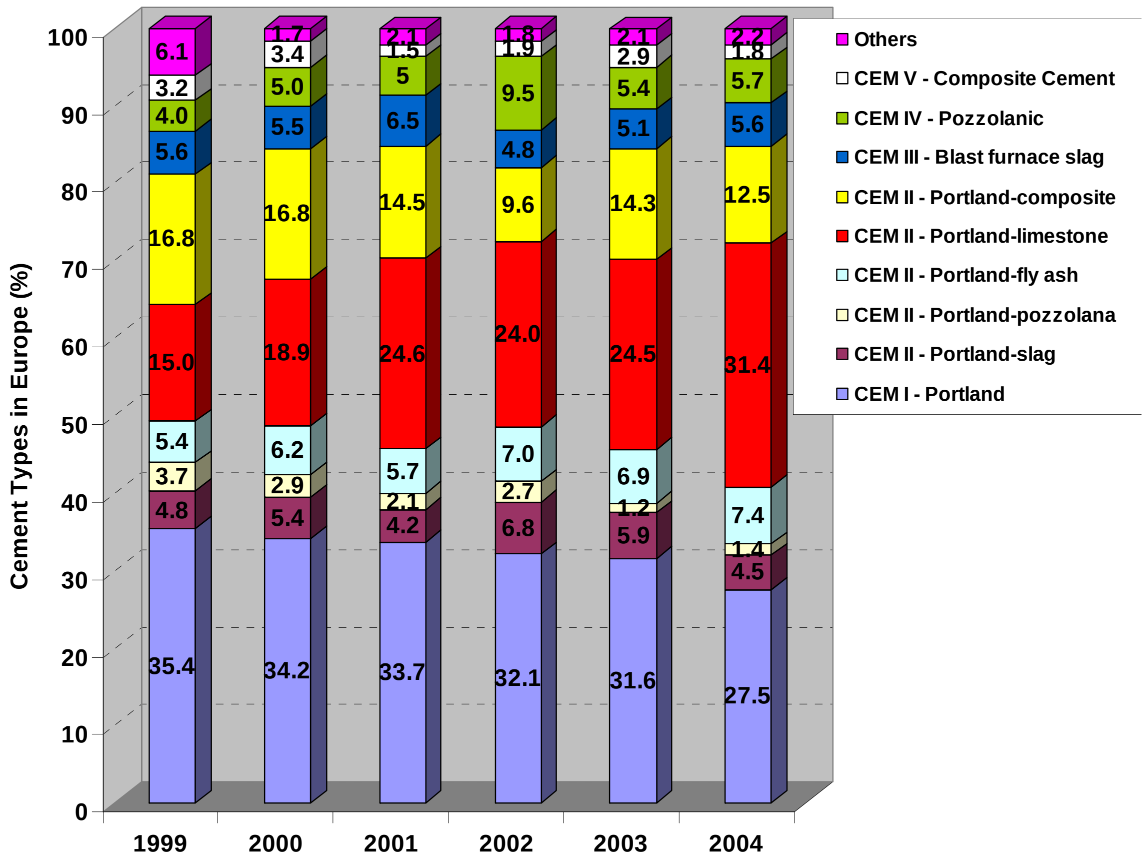


Figure 1.1 CEN Data on Types of Cement Produced in Europe

2.0 Production and Reactions of Limestone Cemnt

2.1 Intergrinding of Limestone cement

Limestone cement can be produced by intergrinding, blending or by addition at the time of mixing concrete. Intergrinding of limestone has several benefits. Limestone is a softer material than clinker and therefore takes less energy to grind to the same fineness. Figure 2.1 shows the energy required to grind each of the two materials to various specific surface areas. As the content of limestone increases, the energy required to produce the same fineness decreases as shown in Figure 2.2.

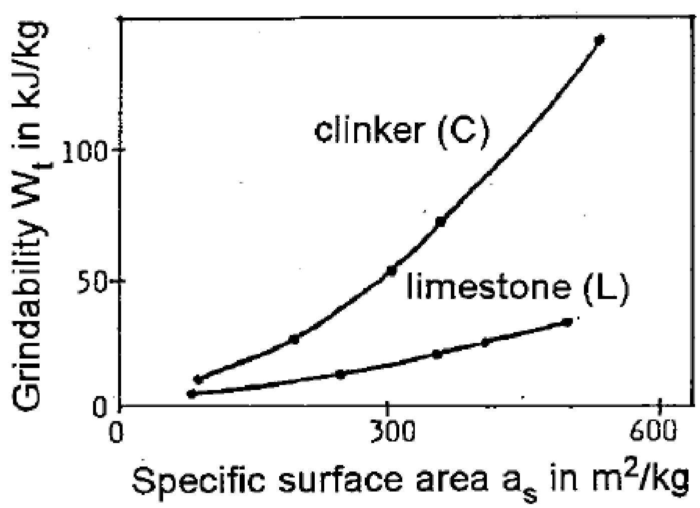


Figure 2.1: Grindability of clinker and limestone (Opoczky, 1992)

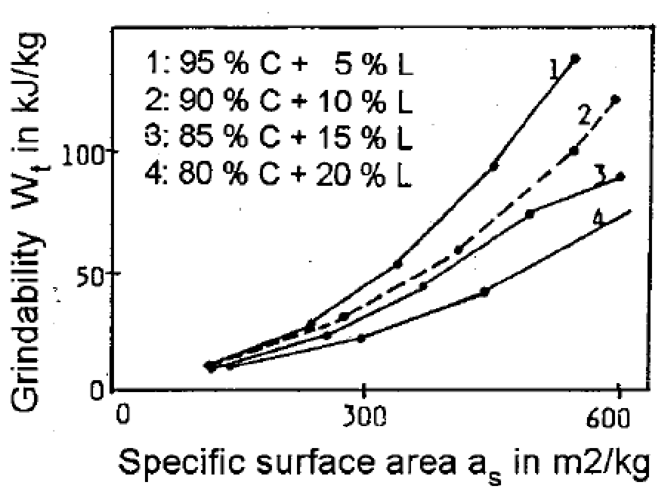


Figure 2.2: Grindability of limestone cement mixtures (Opoczky, 1992)

The particle size distribution of any one constituent is affected by grindability of others (Schiller and Ellerbrock 1992). Voglis et al (2005) found that Portland limestone cement (PLC) gave a wider particle size distribution than that of cement interground with fly ash (PFC) or natural pozzolana (PPC) as shown in Figure 2. when designed to give equivalent compressive strengths. In addition, limestone increased the grinding time required to obtain the target compressive strength (40MPa), but also increased the fineness considerably. Vuk et al (2001) have found that Blaine surface area increased with 5% of limestone addition, for the same residue on the 90µm sieve.

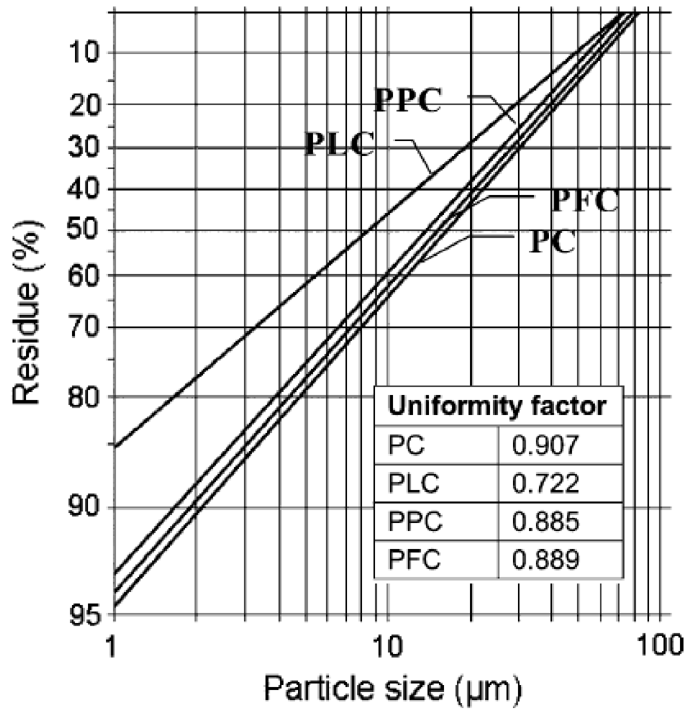


Figure 2.3: Particle size distributions of interground cement mixtures (Voglis et al, 2005)

Tsivilis et al (2002) investigated the fineness of both the clinker and limestone constituents after intergrinding for various times. Particle size distribution was determined by sedimentation in ethyl alcohol followed by loss of ignition. In general, clinker is concentrated in the coarser fraction and limestone in the finer. As the limestone content and grinding time increase, the particle size distribution becomes wider and finer. Figure 2.4 shows the distributions for cement and limestone at two replacement levels and two grinding times. Longer grinding times significantly change the amount of coarsest particles for lower limestone contents, but affect the entire size distribution at higher limestone contents.

2.2 Reactions in limestone cement

The reactivity of limestone was been debated, while most researchers have previously believed the limestone serves as an inert filler, research shows that limestone does react to a limited extent. As the limestone particles become finer, this reaction is more likely (Soroka and Setter, 1977). Matschei et al (2007) found that at low concentrations limestone (calcite) reacts completely to form various carboaluminate phases. The extent of limestone's reactivity is controlled by the amount of sulphate in the system (Figure 2.5). As the sulphate content increases, the likelihood of unreacted calcite increases. Campiteli and Florindo (1990) found that increased limestone addtions decreased the optimum SO_3 content (ASTM C 593) in both fine and coarse cements as shown in Figure 2.6. However, the decreases in sulphate would not be sufficient for complete reaction at high limestone replacement levels. Significant amounts of limestone remain unreacted even after extended moist curing (Klemm and Adams, 1990).

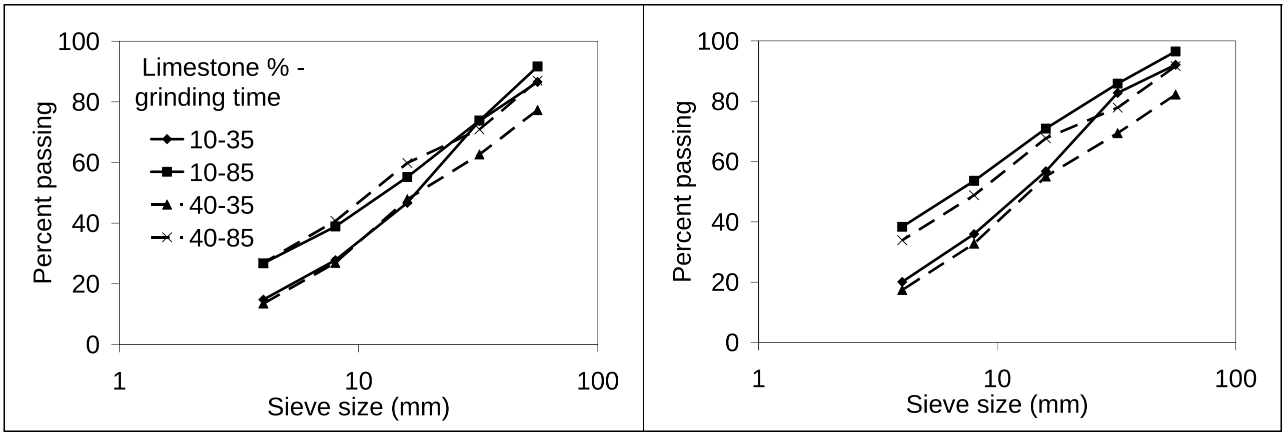


Figure 2.4: Particle size distributions a) cement b) limestone (Tsivilis et al., 2002)

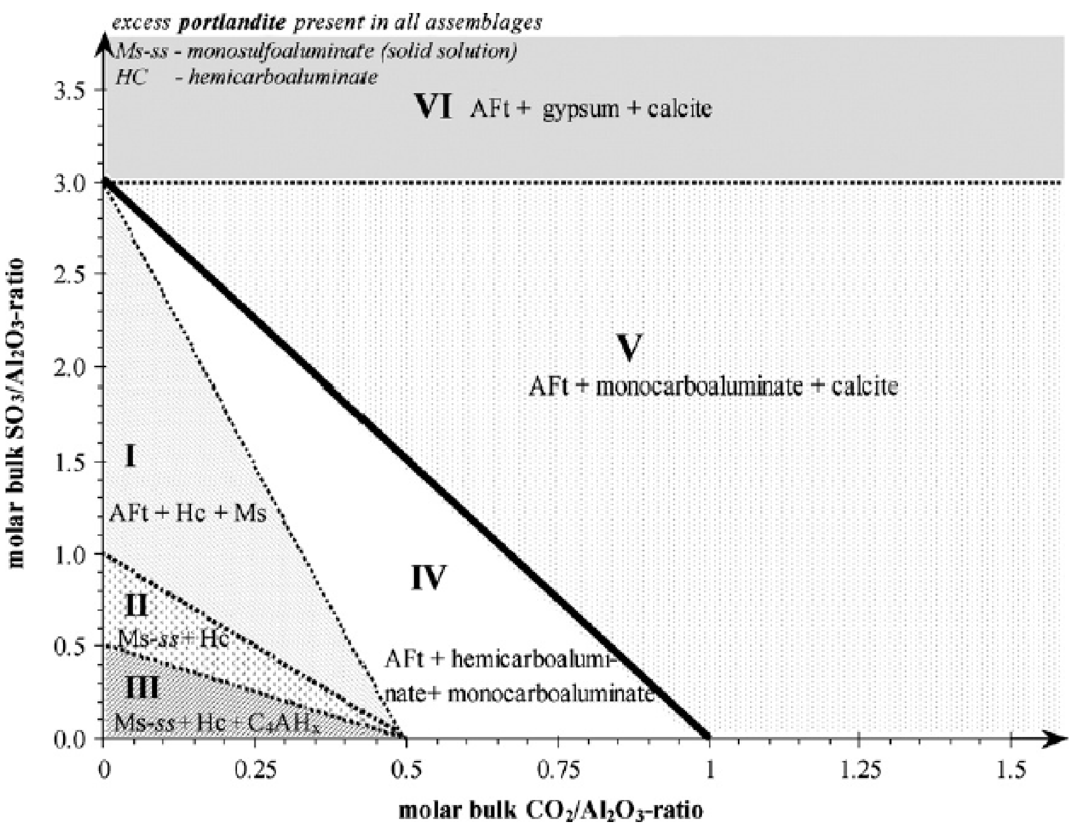


Figure 2.5: Phase equilibrium of limestone (Matschei et al, 2007)

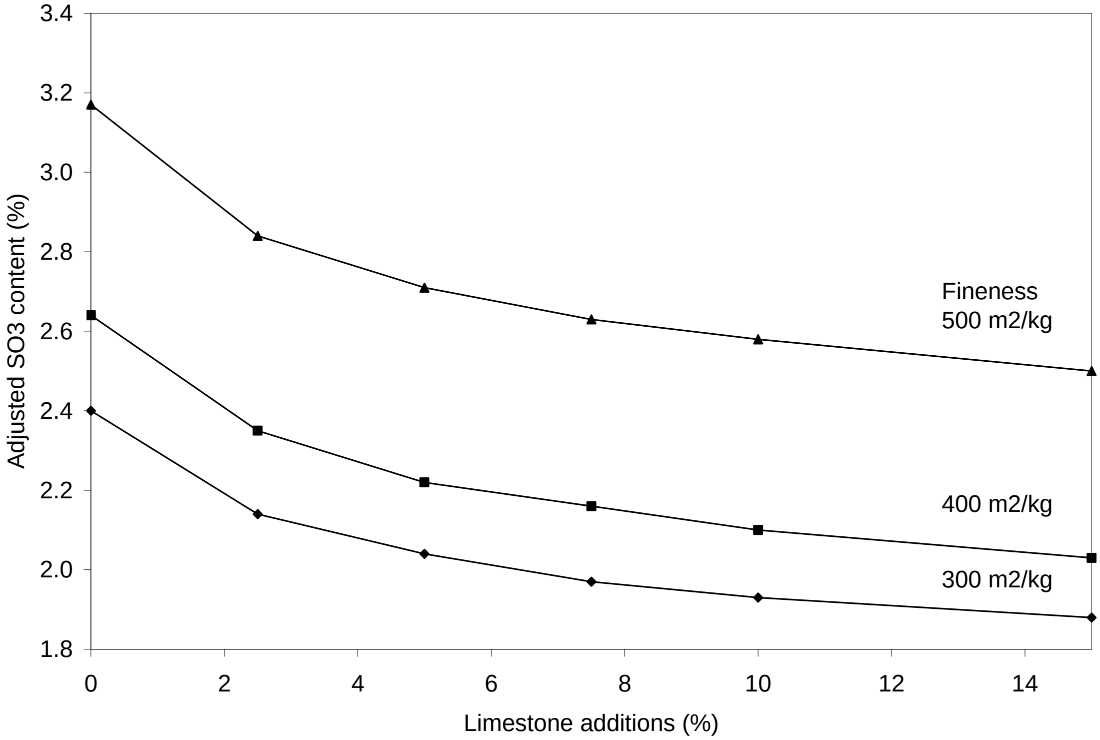


Figure 2.6: Optimum gypsum requirements (after Campiteli and Florindo, 1990)

Differences in the types and amounts of hydration products have been observed between Portland and limestone cements. There is much agreement that limestone reacts primarily with the C_3A component of the cement to form carboaluminates at the expense of hydrates. Tsivilis et al (1999) determined the effect of reactivity with cements of varying C_3A compositions as observed by measuring compressive strength. Clinker with lower C_3A (7.54%) and higher C_3S (65.15%) gave lower compressive strengths at all ages, grinding times and replacement levels than limestone with higher C_3A (11.74%) and lower C_3S (57.99%). However, these results must be interpreted with caution as the latter cement required less water for standard consistency.

It has been suggested that some $CaCO_3$ can be incorporated in CSH formed by C_3S (Ramachandran, 1988 in Moir and Kelham 1997). However, the formation of ettringite is under debate. Tsivilis et al (1998) and Kakali et al (2000) found its formation delayed, while Ingram et al (1990) found that ettringite formation proceeded normally. Other researchers (Ramachandran and Zhang, 1986; Ramachandran, 1988) found acceleration in the formation of ettringite. Production of CH seems to be enhanced at early ages partially due to dissolution of limestone and also due to limestone's ability to act as nucleation sites (Turker and Erdoğdu, 2000). These authors found that the CH crystals forming in limestone cements to have different morphology than those in Portland cements. The crystals were found to be well-dispersed, smaller in size and have a tubular structure (Turker and Erdoğdu, 2000). However, beyond the first 2 to 3 days, calcium hydroxide concentrations decrease as seen in Figure 2.7. The CH concentrations can decrease below the levels of control mixtures at 28 days (Kakali et al, 2000). Barker and Cory (1991) found enhanced formation of calcium hydroxide at early ages with 5% and 25% limestone.

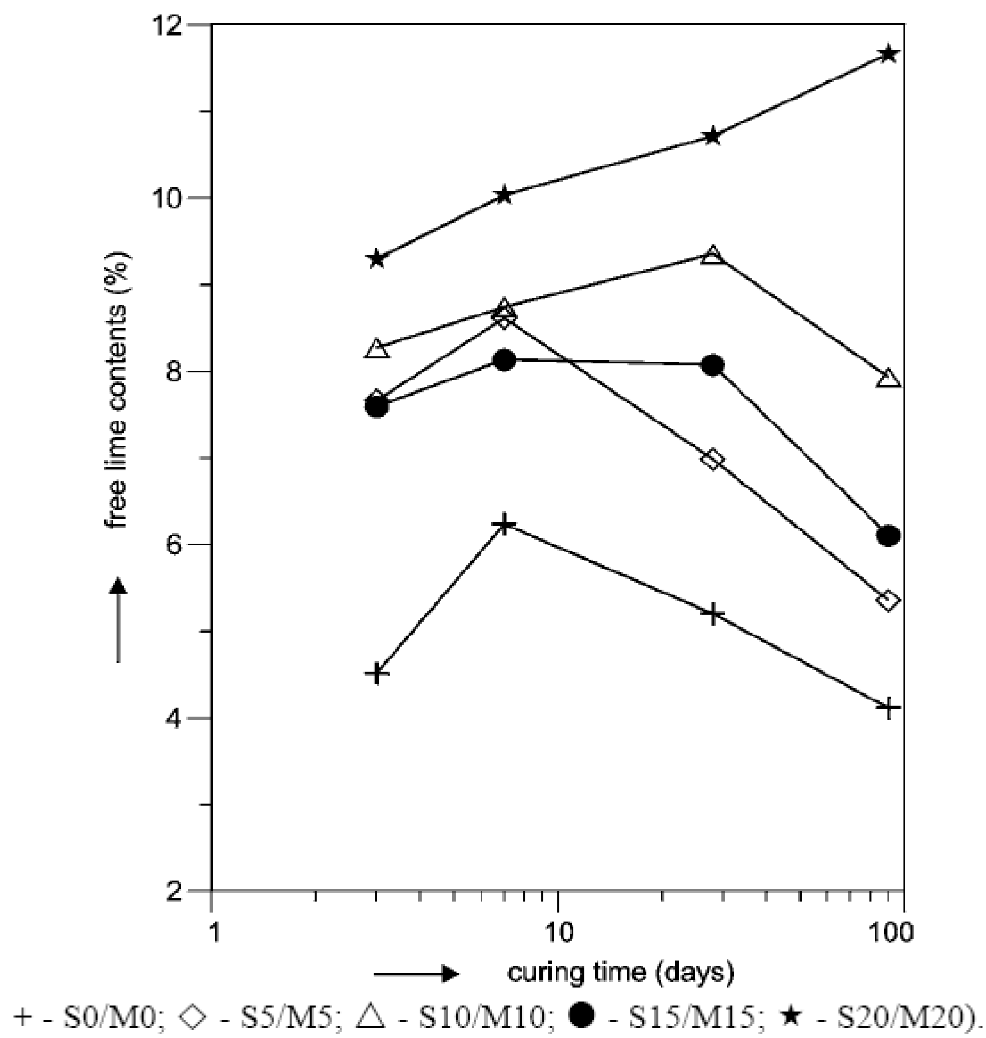


Figure 2.7: Free lime production of limestone cement pastes (Heikal et al, 2004)

3.0 Effects of Limestone on Fresh Concrete Properties

3.1 Workability

In regards to the effect of limestone additions on water demand and workability, there are conflicting results in the published literature. Much of these effects can be related to the particle size distribution of the limestone in relation to the cement. Generally, fine limestone particles can enhance the overall particle packing of the binder materials resulting in less space for water between the solid grains.

Nedhi et al (1998) found that decreasing the average particle size of limestone used as a partial replacement for cement gave better early-age rheological properties (Figure 3.1). These authors measured torque viscosity (h) and flow resistance (g) in high-performance concretes (w/cm = 0.33) with 0.7 micron and 3 micron average size limestone particles (up to 20%) blended with OPC and varying amounts of silica fume. The superplasticizer dosage did not significantly increase with decreasing particle size diameter of the limestone. The amount of limestone replacement did not significantly affect the HRWR dosage or the flow resistance; however, the torque decreased with increasing limestone additions (Figure 3.1). Although the finer limestone particles approach the size of silica fume particles (0.26 microns), Nedhi et al (1998) postulated that the absorption of admixtures is notably higher for silica fume than for limestone. Vuk et al (2001) found that increasing the fineness, as measured residue on 90μm sieve, decreased water demand by approximately 1.5% in cement paste mixtures containing 5% limestone.

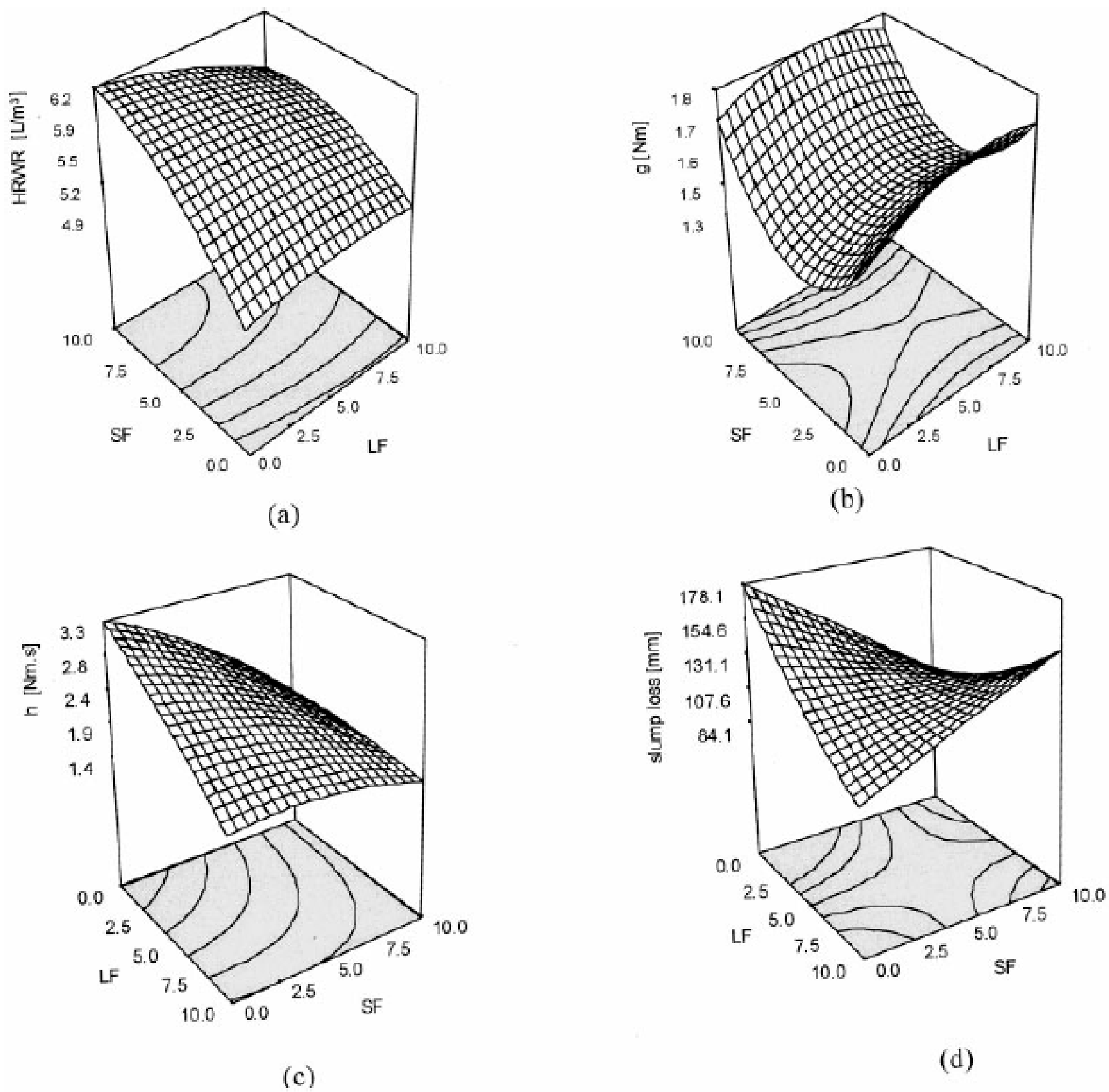


Figure 3.1: Rheological responses for OPC-LF-SF triple-blended composite (Nedhi et al, 1998)

Other researchers have investigated the effect of limestone content on consistency of cement pastes. Tsivilis et al (1999) investigated two types of cement and 3 types of limestone. It was found that lower C_3A (7.54%) cements required more water for standard consistency than those with higher C_3A (11.74%) regardless of limestone type. In the same study, increased limestone replacement and increasing fineness decreased water demand. Limestone with high calcite and dolomite content affect water demand more than limestone with high quartz/clay content. Conflicting results were observed by El-Didamony et al (1995) showing that increased water is needed to maintain consistency of cement pastes as the limestone content increases (Figure 3.2). These researchers interground cement clinker and limestone (0-20%) in a laboratory steel ball mill until reaching a fineness of 3000 ± 50 cm^2/g. Heikal et al (2004) found similar results with ternary blends of either OPC or sulphate resistant cement, fly ash and limestone. In these experiments the fly ash plus limestone was kept constant at 20%, but the individual materials varied from 0 to 20%; however, no data was included on the fineness of the blends or the relative particle sizes of the constituents. However, Guemmadi et al (2005) found that the consistency of low w/c cement pastes (w/c 0.24 - 0.26) varied with both the fineness and replacement level of limestone, but no clear trend was observed (Figure 3.3). Ghezal (1999) found that SCC mixtures containing limestone exhibited rapid slump losses that caused rejection on site. Nedhi (2000) postulated that increased MgO content of limestone gave decreased workability of superplasticized concretes due to admixture interactions. He measured the decreased workability by rheology measurements of the limestone and chemical admixtures (no cement).

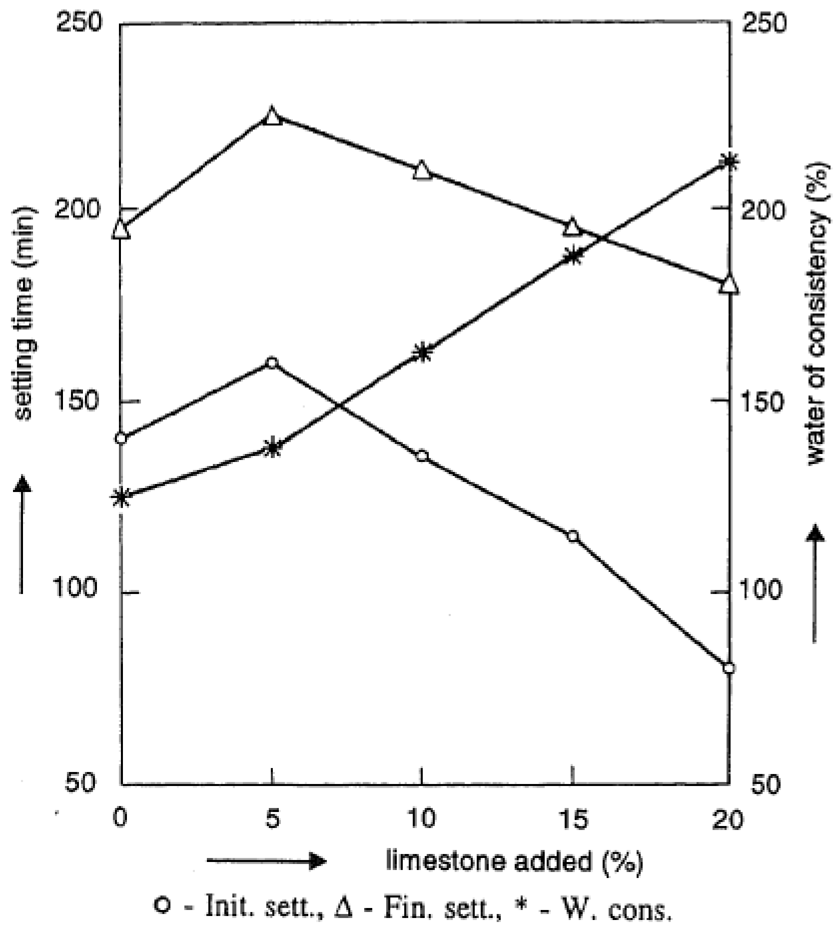


Figure 3.2: Water demand and setting of limestone cement pastes (El-Didamony et al, 1995)

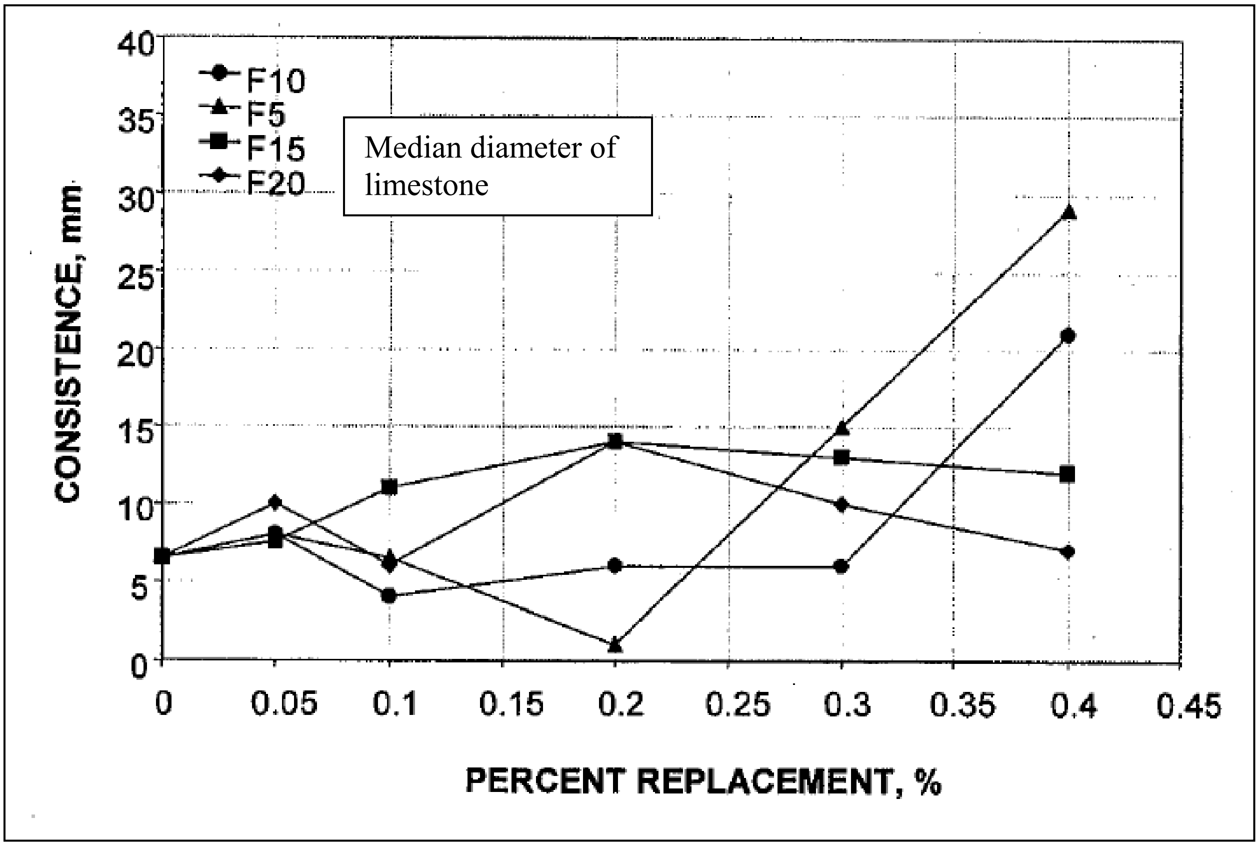


Figure 3.3: Consistency of limestone cement pastes (Guemmadi et al, 2005)

Less research has been carried out on the effects of limestone additions in concrete concerning water demand. Moir and Kelham (1997) found that concrete slump decreased (less workable) with coarser limestone than with finer particles. Decreased workability was also observed with increasing limestone additions by increased admixture dosages to achieve the target slump (Bonavetti et al, 2003). Matthews (1994) determined that an 0.01 increase in w/c was required to achieve the same slump from 0% to 5% limestone and another 0.01 increase for limestone from 5% to 25%. However, Schmidt et al (1993) observed that the water content could be reduced for limestone cement concretes. It must be recognized that modern concretes almost always include a water reducer. Sprung and Siebel (1991) found that water requirement is primarily related to interparticle space once surface forces are counteracted by the chemical admixture.

3.2 Bleeding

Particles absorb water onto their surfaces. Therefore, it is not surprising that bleeding is highly dependant on the surface area of the binder particles. As the surface area increases, the affinity for water absorption increases. As shown in Figure 3.4, tests carried out at BRE (1993) showed that bleeding rate was highly correlated to the overall specific area of the binders, but independent of the amount of limestone addition. Increasing fineness of limestone fillers would decrease tendency for bleeding.

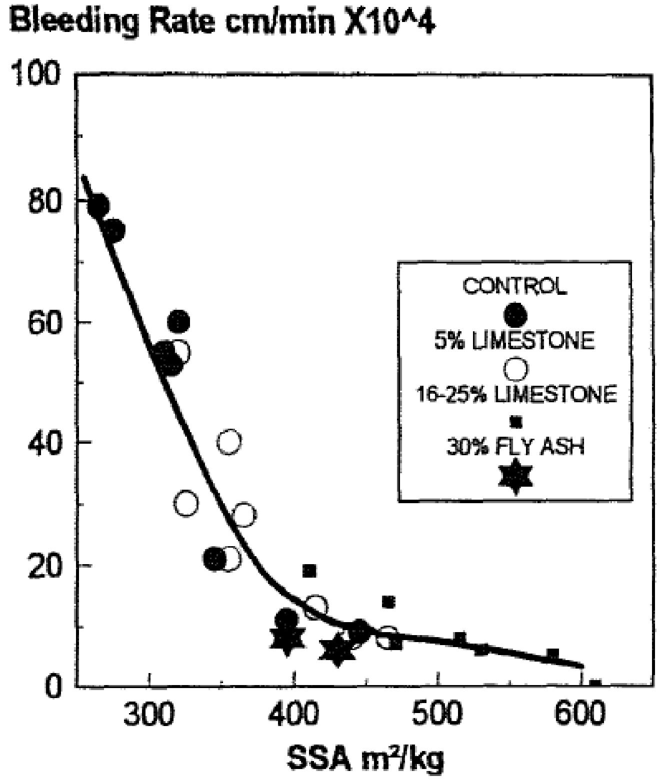


Figure 3.4: Bleeding rate vs. specific surface area (BRE, 1993)

3.3 Setting time

The general consensus is that the fineness of the limestone is a factor influencing set time of cement pastes. However, the magnitude of this effect differs among various studies. Vuk et al (2001) investigated cement pastes of different fineness and C_3S contents at 0% and 5% limestone replacements. Initial and final set times were found to decrease as fineness increased. The decrease was more pronounced in cements with low C_3S. El-Didamony et al (1995) found that increasing limestone additons decreased the set time of cement pastes (as also shown in Figure 3.2). To a lesser extent, Tsivilis et al (1999) found that limestone affected both initial and final set to a minor degree generally decreasing as fineness increased. Guemmadi et al (2005) found that the setting time of pastes varied with the fineness, but no clear trend was observed. On the other hand, Moir and Kelham (1997) found that increased fineness gave longer initial set times at 20% limestone replacement.

In regards to limestone content, Tsivilis et al (1999) found a minor decrease in set times as replacement increases while Guemmadi et al (2005) found little correlation. Heikal et al (2000) determined that for mixtures containing a total of 20% Homra (ground brick) and limestone, initial set time was not significantly affected. Final set in these mixtures slightly decreased as limestone percentages increased.

3.4 Influence on hydration:

Hydration of cement in low water to cement ratio systems is a space limitation problem. At less than 0.36 – 0.38 w/c, the originally water-filled space is not sufficient to accommodate the cement hydration products in sealed conditions. In these systems, a portion of the cement remains unhydrated. If extra water is available for curing, the w/c ratio below which unhydrated cement remains increases to 0.42. As cement is a major cost factor in concrete, significant cost savings could be realized by replacing a portion of the cement with a relatively inert filler such as limestone.

As limestone acts as nucleation sites for hydration products (Soroka and Stern, 1977), it is not surprising that the inclusion of limestone increases the rate of hydration. Bonavetti et al. (2003) investigated hydration of cement pastes at various w/c ratios (0.25 to 0.50) with approximately 10% and 20% limestone replacements. It was found that the degree of hydration was markedly more rapid during the first 7 days in the higher w/c pastes containing limestone. At lower w/c (~0.30), the differences were not as noticeable. However, it must be noted these pastes were designed to have similar strength. The fineness increased with additional limestone, so it is difficult to separate the effects of the fineness from the influence of the limestone content. Increases in hydration with increasing limestone contents (up to 35%) were determined by non-evaporable water contents of 0.30 w/c cement pastes (Kakali et al, 2000). Similar results were observed in concrete mixtures at 0.34 and 0.50 w/c containing approximately 10 and 20% limestone (Bonavetti et al, 1999, 2000) For both water to cement ratios investigated, the addition of limestone increased the degree of hydration at all ages as can be seen in Figure 3.5. Again, cement was interground with limestone at a cement plant to obtain equivalent strength class; the fineness of the mixture increased as the limestone content increased.

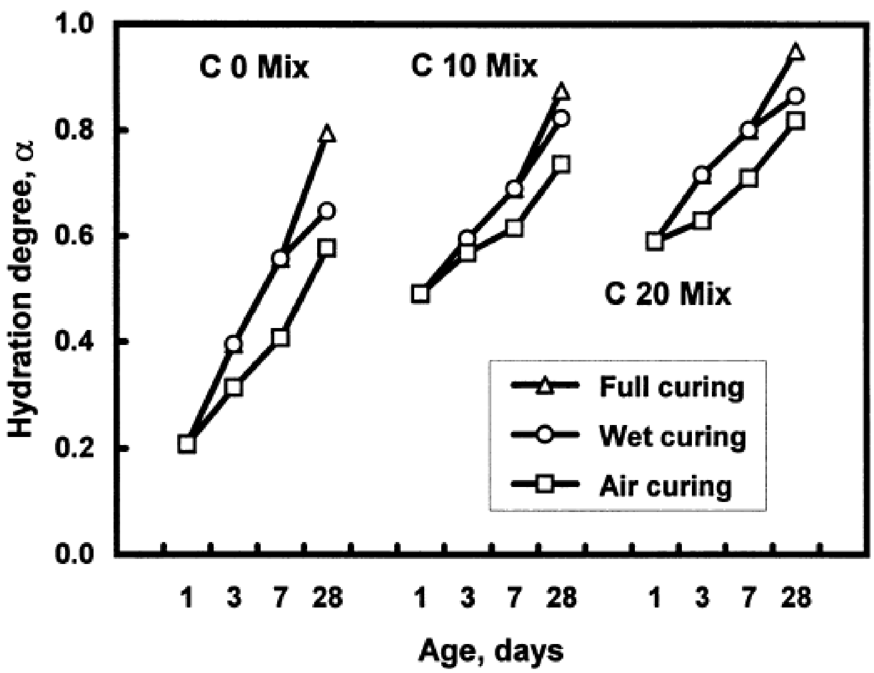


Figure 3.5: Degree of hydration for limestone concretes under various curing conditions (Bonavetti et al, 2000)

A schematic representation of the effect of limestone fillers can be seen in Figure 3.6. The early age hydration is increased, but at some point falls below that of mixtures without limestone. At the line B-B where the degree of hydration is the same, it is expected that compressive strength would be equal in all systems. This is effect is similar to curing at different temperatures; increased temperatures give more rapid hydration but lower strengths at later ages. The increased rate of hydration may in fact be detrimental to both mechanical and durability properties. More research is needed in this area.

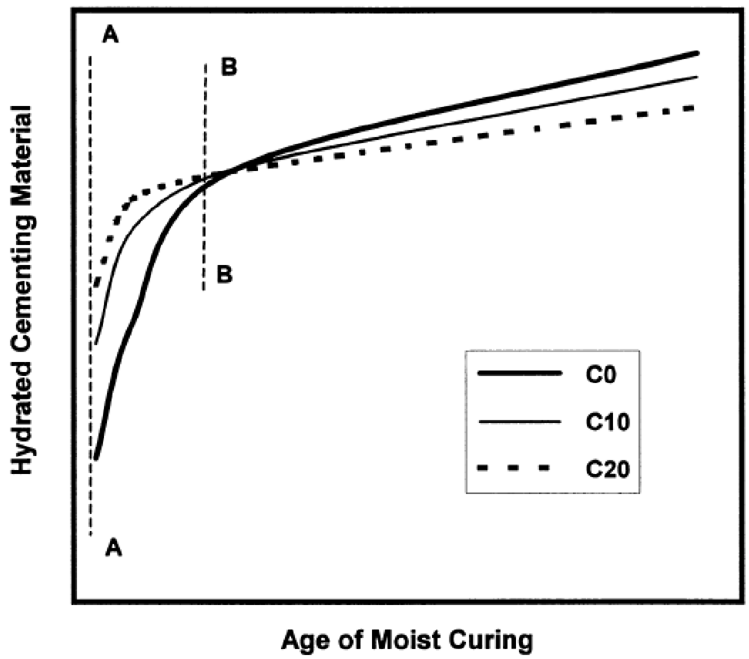


Figure 3.6: Schematic of hydrating materials with time for limestone mixtures (Bonavetti et al, 2000)

For ternary blends of cement, fly ash and limestone, chemically combined water was found to increase with increasing amount of limestone (decreasing fly ash, as total of these was kept at constant 20% replacement) in OPC pastes (Heikal et al, 2004). However, for sulphate resistant cements, increased hydration was observed up to 10% limestone with minimal differences at higher amounts of limestone.

Bentz and Conway (2001) used computer modeling to predict the hydration and strength development of low w/c cement pastes with limestone substitutions. Limestone was used to replace 20.5% and 30.8% of the coarsest cement particles at 0.25 w/c and 14.5% and 22.3% at 0.30 w/c. The simulations showed that the degree of hydration of the pastes containing limestone were significantly higher than the control sample at all ages without unduly sacrificing strength. Unlike Bonavetti et al (2000) in Figure 3.6, the cross-over of the degree of hydration between the control and limestone mixtures was not observed when modeling to one year age. However, as the coarse cement particles hydrate slower due to the large volume to surface area, the increased hydration observed in the model may be primarily due to the cement size differences. It is suggested that the model be used to not only simulate the control pastes with similar particle size distributions as that with the limestone filler, but it also be used to estimate performance of typical interground and blended systems currently produced.

In later work, Bentz (2006) determined that 20% limestone increased the degree of hydration low w/c pastes but did not significantly affect hydration at high w/c (0.435). This result conflicts with that found by Bonavetti et al. (2003). Similar strength and hydration at 15% replacement as those of the control cement paste were found with modeling the replacement of coarse cement particles (> 30 microns) with coarse limestone filler (~100 micron median size) (Bentz, 2005).

3.5 Heat of hydration

As limestone acts as nucleation sites for hydration, it is expected that the heat of hydration will be increased. Moir and Kelham (1997) investigated heat generated by Portland cement blended with various materials at 20% replacement levels. Figure 3.7 presents the additional (excess) heat produced compared to 80% of heat measured for Portland cement. In this manner, positive values show an increase in heat of hydration compared to the control mixture. The results show that limestone blends had higher excess heat of hydration than OPC and fly ash, slag or pozzolanic blends. (Stone M26, Stone M8 and Chalk are all limestone blends of decreasing fineness.) Péra et al (1999) also observed significant increased heat generation for 50% limestone replacement over than of OPC up to 1000 hours of hydration.

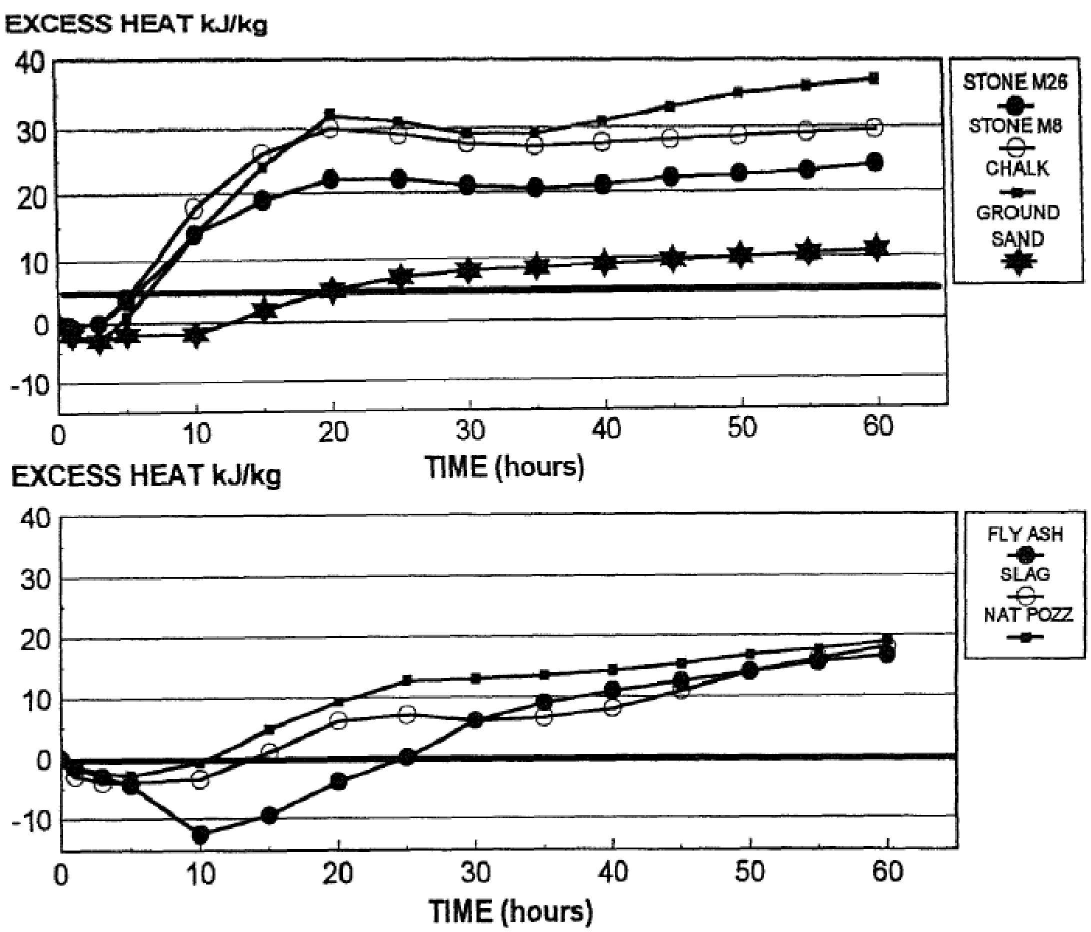
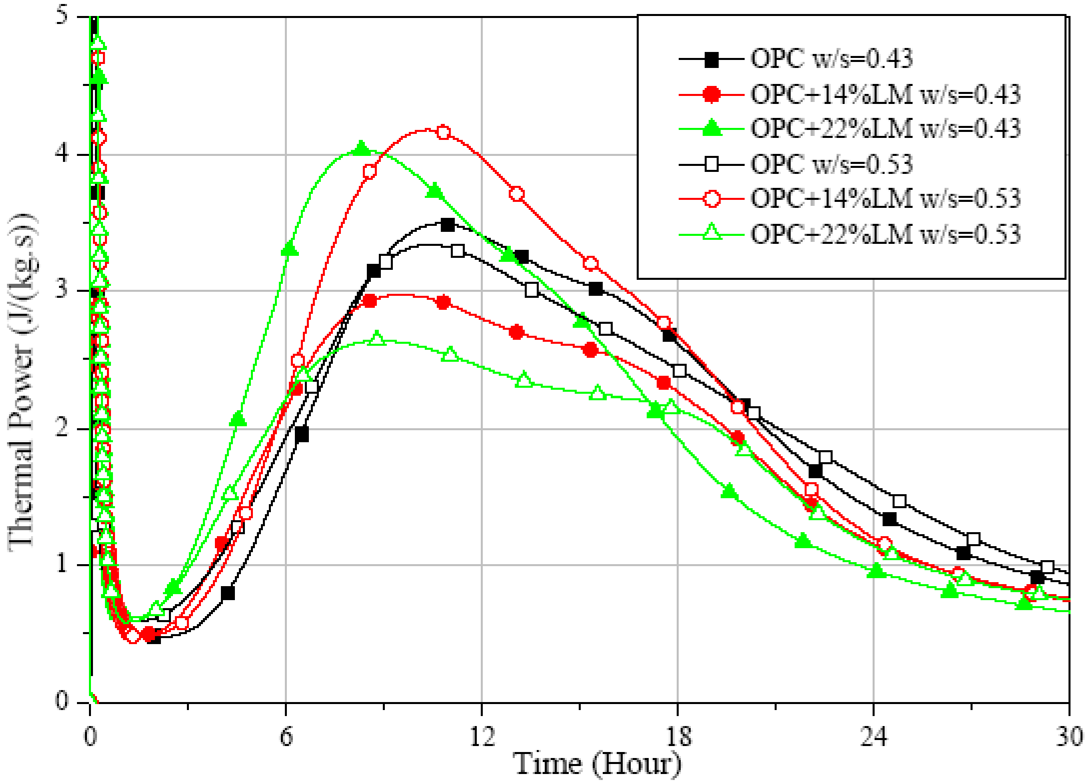


Figure 3.7: Heat of hydration (Moir and Kelham, 1997)

Vuk et al (2001) found that clinker chemistry had a significant effect of the heat of hydration of cements containing 5% limestone. As expected, higher amounts of C_3S gave increased energy output. Measurements at 3 days revealed that limestone with high fineness (2% residue on 90μm sieve) had insignificant effect on the heat of hydration for both clinkers, while mixed results were observed with limestone of lower fineness (5% retained). At 14 days, both clinker types and limestone fineness gave lower measured heat than the control mixtures.

Xiong and van Breugel (2003) found that limestone additions gave an earlier peak and faster rates of hydration as measured with isothermal calorimetry at 20ºC than those of control paste at water to solid ratio of 0.43. At higher w/s (0.53), the hydration began marginally earlier, but did not produce the same levels of heat as the control mixture. At higher temperatures, 30ºC and 40ºC, similar effects were observed with the expected increase in hydration due to increased temperature (Figure 3.8).



.

Figure 3.8: Energy release of limestone cements (Xiong and van Breugel, 2003)

4.0 Mechanical Properties

4.1 Compressive Strength

The strength of concrete produced with limestone cement is strongly influenced by the quality of the limestone used, the manufacturing process (blending versus intergrinding) and the final particle size distribution of the cement. Limestone is softer than portland cement clinker and will, therefore, be finer than the clinker if the two products are ground together. For cements of equal surface area (Blaine), the clinker particles in portland limestone cement (PLC) will be coarser than those in portland cement (PC). To compensate for this, limestone cements are ground finer. Typical particle size distributions for PC and PLC from German cement works (Cilas) are shown in Figure 4.1 (Schmidt, 1992a).

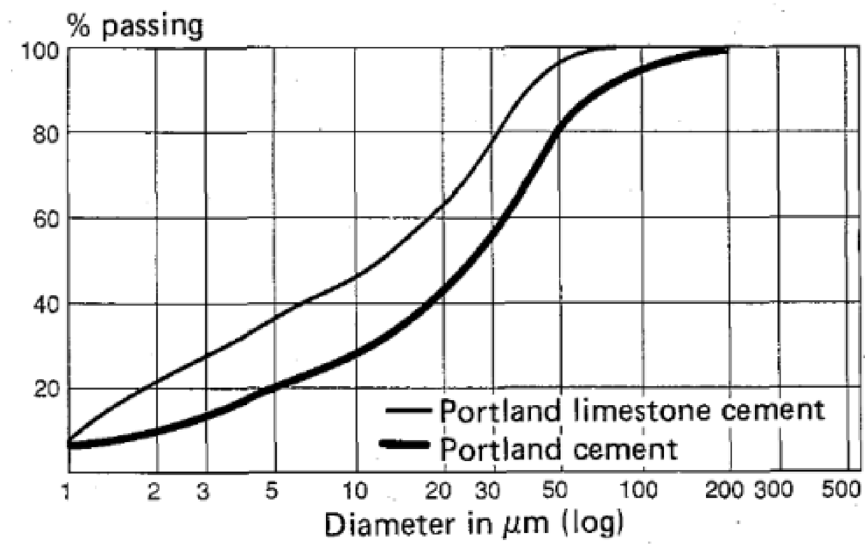


Figure 4.1 Particle Size Distribution for PC and PLC from a German Cement Works (Schmidt, 1992a)

It is more appropriate to compare PC and PLC cements on the basis of equal 45 microns (# 325) sieve retention values. Hawkins et al (2005) compared a series of cements with limestone contents of 0, 3, 5.5 and 8% prepared at equal Blaine versus at equal sub-45 micron (# 325) value. In these tests a limestone with 85% $CaCO_3$ was used together with a Type II low-alkali clinker with a C_3A content of 5.1% and the clinker, gypsum (all cements contained 2.5% SO_3) and limestone were ground together in a laboratory ball mill. These data show that comparable strengths can be obtained provided that the PLC is ground to a higher surface area or equal sub-45 micron (# 325) sieve value. (Figure 4.2)

Limestone additions up to 5% 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 early production of calcium carbo-aluminate (Voglis et al. 2005). Even when ground limestone is blended with PC (as opposed to intergrinding), the strength is relatively unaffected up to 5% limestone (Livesey, 1991; Matthews, 1994).

At higher replacement levels the loss of strength due to dilution must be compensated for by finer grinding. For example, Voglis et al (2005) showed comparable strengths for PC and PLC with 15% limestone, when the PLC was ground to 511 m^2/kg compared with 303 m^2/kg for the PC. Bonavetti et al (2000) compared three cements from the same plant with 0, 8.3 and 18.1% interground limestone having Blaines of 317, 372 and 420 m2/kg, respectively. Concretes (W/CM = 0.5) produced with these cements achieved 28-day, water-cured compressive strengths of 40.2, 38.1 and 36.3 MPa (for 0, 8.3 and 18.1% limestone, respectively). Early-age strengths were increased in the concretes produced with the limestone cements and, as a result, the 28-day strengths of concretes that were air-cured after 1 day, were greater for the mixes with PLC.

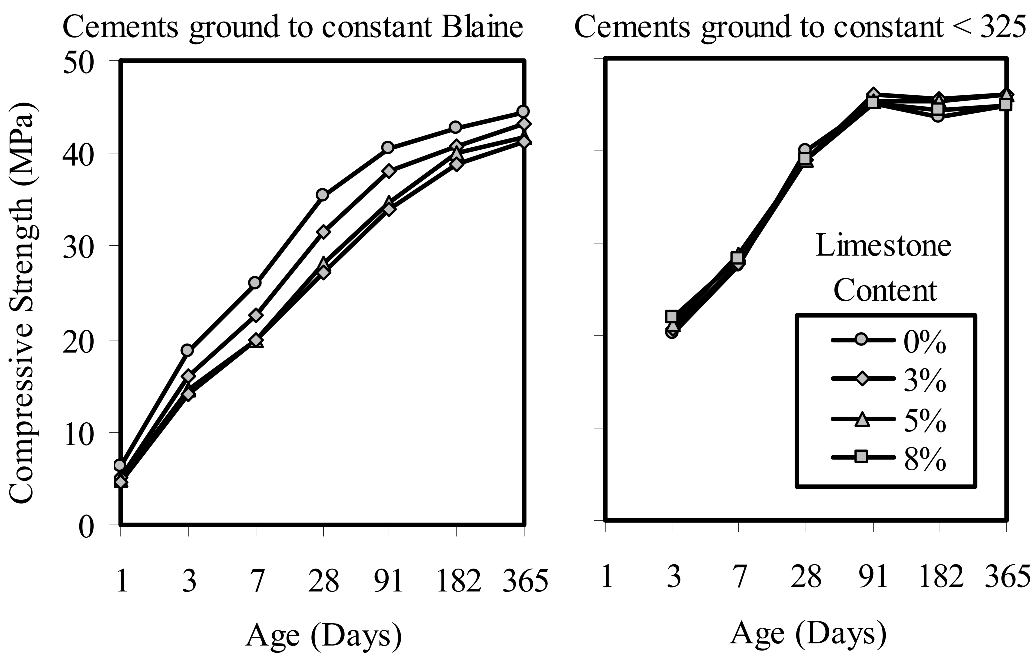


Figure 4.2 Strength Development of Mortars Produced with PC and PLC Ground to Constant Blaine or < 325 Mesh (Hawkins et al 2005)

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 4.1 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.

Table 4.1 Strength of Concrete Produced with PLC from Italian Cement Plants (Alunno-Rossetti and Curcio, 1997)

	Plant B		Plant G	
	PC	PLC	PC	PLC
Limestone in cement (%)	0	20	0	20
Fineness of cement (m^2/kg)	345.0	482.5	362.0	489.5
Strength of concrete with 270 kg/m^3 cement at 28 days (MPa)	30.7	30.0	31.6	29.1
Strength of concrete with 330 kg/m^3 cement at 28 days (MPa)	39.7	38.0	37.5	36.5

Both Matthews (1994) and Dhir et al (2007) have shown that the strength of concrete is reduced significantly when high levels (≥ 25%) of ground limestone are blended with Portland cement (as opposed to intergrinding the limestone with clinker and gypsum). Matthews (1994) concluded that the performance of concrete produced with a cement with 25% limestone (blended) was equivalent to what would be expected due to a 25% replacement of the portland cement with an inert diluent. Dhir et al (2007) concluded that there was only minor differences in the performance of concrete with PC and PLC containing 15% limestone, but that above 15% limestone the W/CM of the concrete should be reduced by 0.08 for every 10% limestone to achieve the same 28-day compressive strength.

In summary, with regards to the impact of PLC on the compressive strength of concrete, the published data would seem to 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*" at least for cements with up to 15% limestone.

4.2 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; Irasser et al. 2001; Dhir et al. 2007). Generally the trend in behaviour 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.

4.3 Creep and Shrinkage

In their study of PL and PLC cements produced from two Italian cement plants (see Section 4.1), Alunno-Rossetti and Curcio (1997) measured creep and shrinkage of two series of concrete mixtures produced using the four cements (eight mixes in all). The results are shown in Table 4.2. 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 reduced shrinkage and similar creep for concretes produced with cements containing up to 45% ground limestone (blended not interground). The data are shown in Figure 4.3. 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 24 hours after casting.

Table 4.2 Creep and Shrinkage of Concrete Produced with PLC from Italian Cement Plants (Alunno-Rossetti and Curcio, 1997)

	Plant B		Plant G	
	PC	PLC	PC	PLC
Limestone in cement (%)	0	20	0	20
Fineness of cement (m^2/kg)	345.0	482.5	362.0	489.5
Shrinkage of concrete with 270 kg/m^3 cement at 1 year (μm/m)	635	640	540	560
Shrinkage of concrete with 330 kg/m^3 cement at 1 year (μm/m)	680	690	615	595
Creep of concrete with 270 kg/m^3 cement at 360 days (μm/m)	718	1102	824	972
Creep of concrete with 330 kg/m^3 cement at 360 days (μm/m)	778	914	756	869

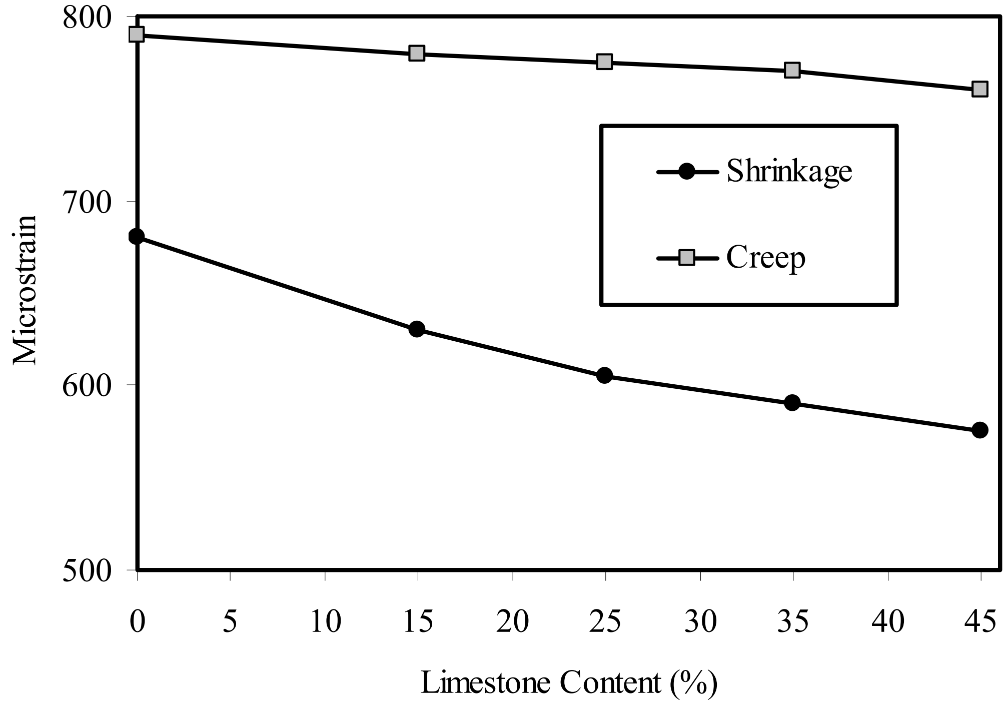


Figure 4.3 Effect of Limestone Content in PLC on the Creep and Shrinkage of Concrete (Dhir et al, 2007)

It is not clear why there is such a marked difference in the effect of limestone filler 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.

5.0 Durability

5.1 Permeability and Chloride Resistance

Many test methods have been developed to the measure the resistance of concrete to the movement or penetration of fluids (such as water, oxygen or carbon dioxide) or aggressive species (such as chlorides or sulfates). Some of these tests involve the measure of fluid flow in response to a hydraulic pressure gradient or moisture gradient, or they involve the measure of ionic movement in response to a concentration gradient, whereas other tests measure another property, such as electrical conductivity or resistivity, and relate this parameter to penetration resistance. Regardless of the test method applied, it is generally considered that the durability of concrete improves with its ability to resist the movement of fluids and ionic species.

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 interground 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 mixes and the results of the tests are shown in Table 5.1.

Table 5.1 Permeability Test Results for Concretes Produced with PLC
(Tsivilis et al. 2003)

Cement Properties			Concrete Properties					
Lime-stone (%)	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

In general, the concretes produced with PLC have higher gas permeability coefficients 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 and lower water sorptivity values. The porosity 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. 1999) reported that the quality and composition of both the clinker and the limestone had a significant impact on the permeability of concrete.

Matthews (1994) conducted oxygen permeability tests on concretes (W/CM = 0.60) produced with a range of different cements. Five different portland cements were used in this program. One of these was interground with 5 and 25% limestone, the remainder were blended with 5 or 25% ground limestone. One of the cements was blended with 30% fly ash and another was interground with 28% fly ash. After stripping at 24 hours, concrete samples were stored either in water or air until 28 days, after which all samples were further conditioned in air at 20^{o}C and 65% RH until test at 100 days. The results of the oxygen permeability are shown in Figure 5.1; the results have been averaged for all mixes produced with the same limestone content. It is evident that the permeability decreases with increasing limestone in the cement, however, differences are relatively small compared with the reductions due to extended curing (note different scales for the water-cured and air-cured concretes).

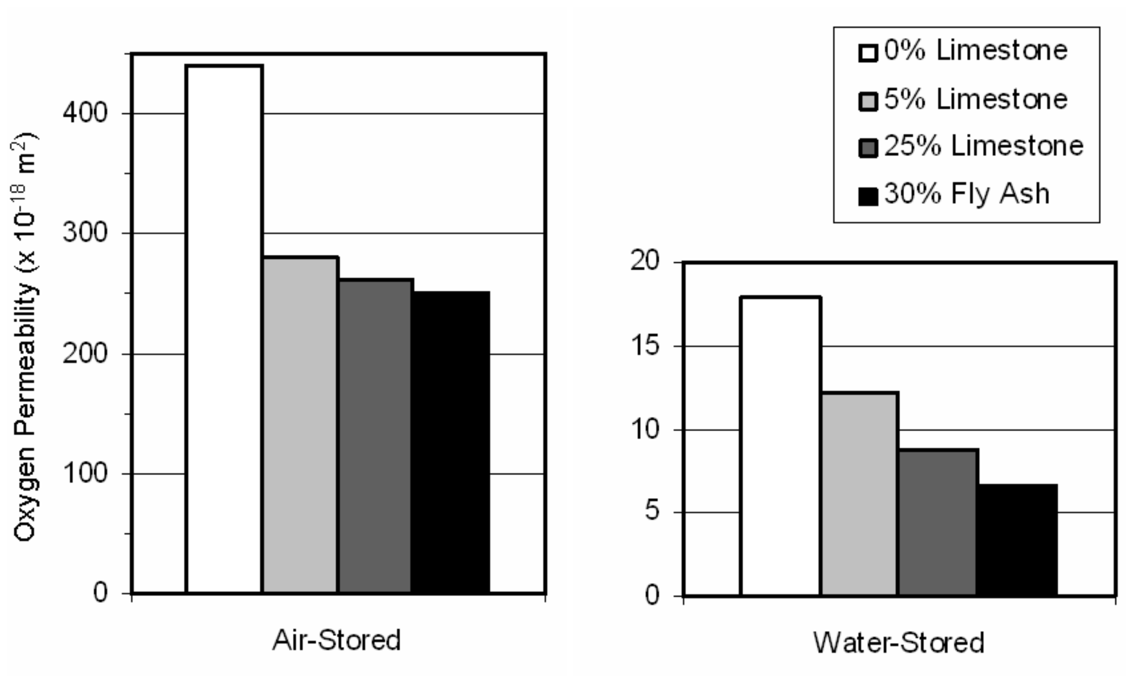


Figure 5.1 Effect of Limestone Additions on the Permeability of Concrete (Matthews, 1994)

In this same study (Matthews, 1994) reinforced concrete prisms were placed in the tidal zone of a marine exposure site. Figure 5.2 shows the chloride concentration profiles measured after 5 years' exposure; the results have been averaged for all mixes produced with the same limestone content. Concretes produced with PLC with 5% limestone showed slightly improved resistance compared with PC concretes, whereas those produced with PLC with 25% limestone showed slightly reduced resistance. The impact of the limestone was small compared to that of fly ash, the use of which led to very substantial improvements in the chloride resistance.

Dhir et al (2007) produced 5 series of concretes with W/CM ranging from 0.45 to 0.80 and, within each series, concretes were produced with a PC and the same PC blended with 15, 25, 35 or 45% ground limestone. 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). The results are shown in Figures 5.3 and 5.4. 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 it can be seen that there is no difference in the performance of PC or PLC concretes of the same 28-day strength.

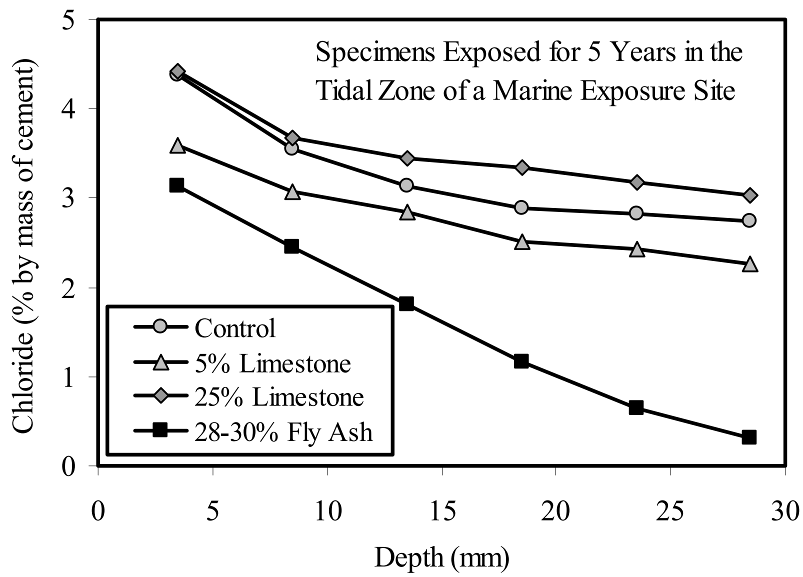


Figure 5.2 Effect of Limestone Additions on Chloride Penetration into Concrete (Matthews, 1994)

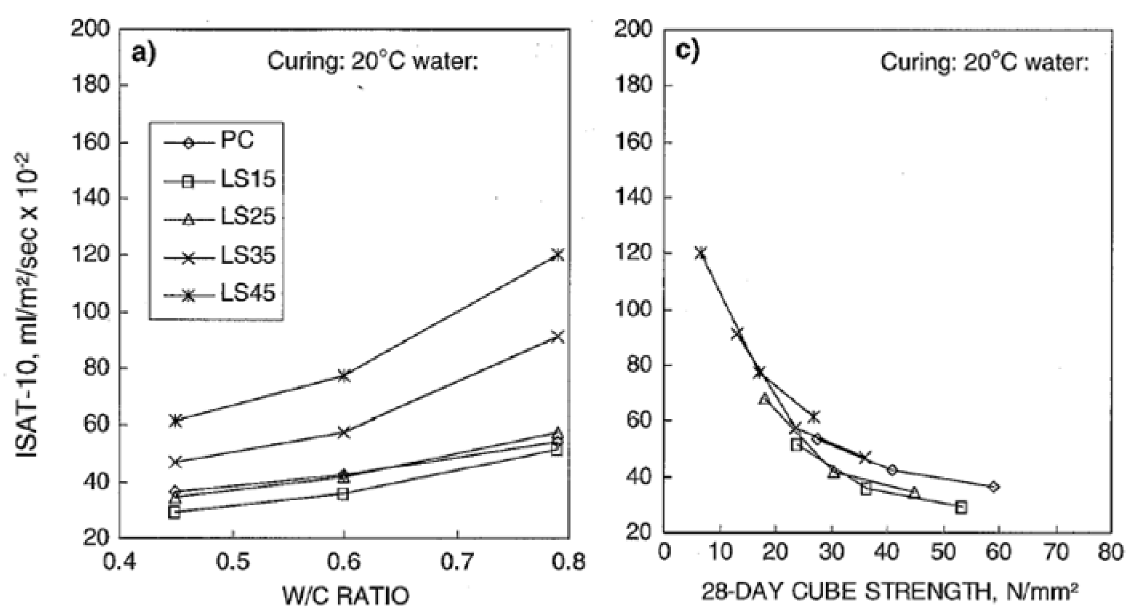


Figure 5.3 Effect of Limestone Addition on the Initial Surface Absorption of Water into Concrete (Dhir et al. 2007)

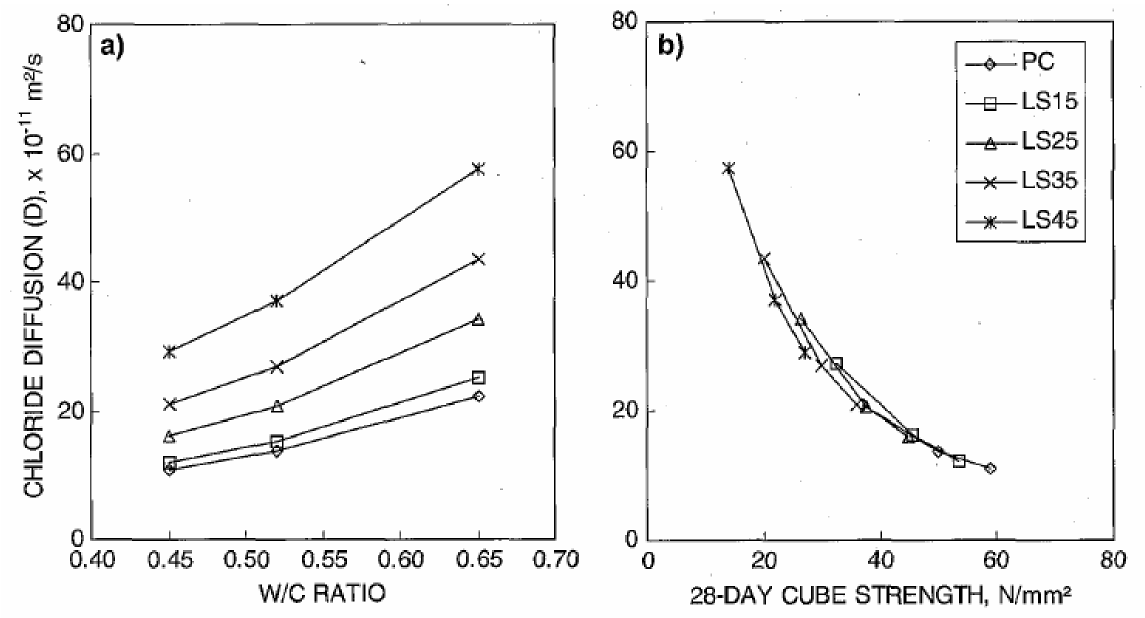


Figure 5.4 Effect of Limestone Addition on the Chloride Diffusion Coefficient of Concrete (Dhir et al. 2007)

Tsivilis et al (2000) produced concretes with 5 cements with limestone contents ranging from 0 to 35%, and conducted the "Rapid Chloride Permeability Test, RCPT" (ASTM C 1202) after 28 days of moist curing. Table 5.2 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 RCP value despite being cast with a lower W/CM, indicating that permeability may be expected to increase at this level of limestone. However, at the high coulomb levels reported, these differences may not be significant.

Table 5.2 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

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.

Irasser 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 5.3. 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.

Table 5.3 Diffusion Coefficients (x 10^{-12} m^2/s) for Concrete Determined after 360 Days Immersion in 3% NaCl Solution (Irasser et al. 2001)

	W/CM		
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

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.

The balance of evidence would seem to indicate concrete produced with PLC up to 15% will produce concrete with similar resistance to the penetration of fluids. However, there is evidence that increased chloride ion penetration will 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.

5.2 Resistance to Carbonation

Matthews (1994) reported carbonation data for concrete mixes (W/CM ~ 0.60) produced with five series of cements as discussed in section 5.1. Within each series cements were produced with 0, 5 or 25% limestone. In one series (E) the limestone was interground with the portland cement clinker and in the other four series ground limestone was blended with the portland cement. However, for three of the blended cements (F, G and H), rapid-hardening portland cement (RHPC) was used for the production of the PLC. One of the series of cements (F) was also used in the production of concrete mixes with lower (W/CM ~ 0.50) and higher (W/CM ~ 0.80) water-to-cementing-materials ratios. Concrete specimens were moist-cured for either 1 or 3 days prior to placement in one of two exposure conditions, these being indoors at 20°C and 65% RH or outdoors but sheltered from direct precipitation. Only the data from the specimens stored outdoors will be discussed here as this exposure condition is the most conducive to carbonation-induced corrosion[1].

[1] Concrete carbonates more rapidly indoors, but there is insufficient moisture available in this exposure condition to sustain the corrosion process once the carbonation front reaches the embedded steel. The depth of carbonation of specimens stored indoors was approximately 50% greater than that of similar specimens stored outdoors, however, the same general trends were observed in both exposure conditions.

The depth of carbonation of after 5 years storage on the outdoor-sheltered exposure site is shown in Figures 5.5 and 5.6 for concrete (W/CM ~ 0.60) that received 1 and 3 days initial curing, respectively. Concretes produced with PLC with 25% limestone showed a significantly greater depth of carbonation compared with concretes produced with cement from the same source, but without limestone.

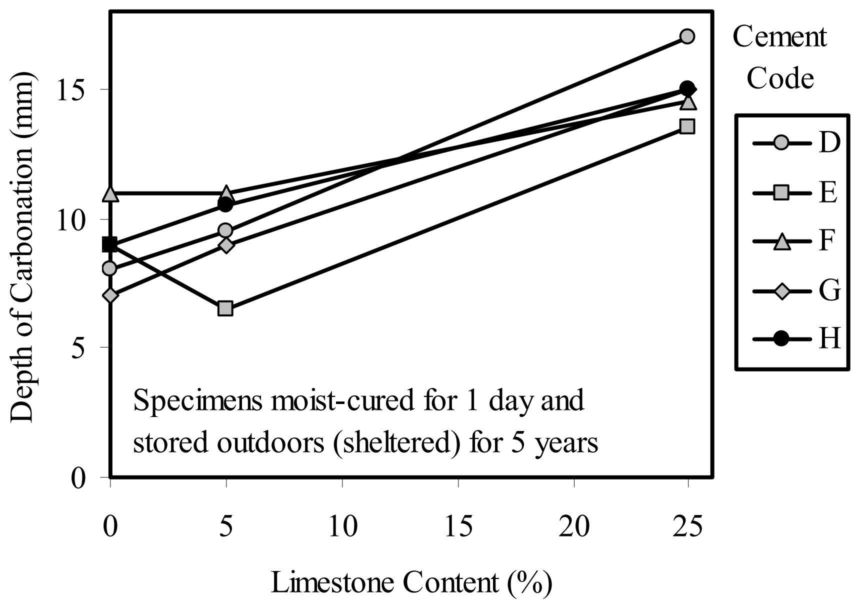


Figure 5.5 Effect of Limestone Addition on the Carbonation of Concrete (W/CM ~ 0.60) Moist-Cured for 1 Day and then Stored Outdoors-Sheltered for 5 Years (modified from Matthews, 1994)

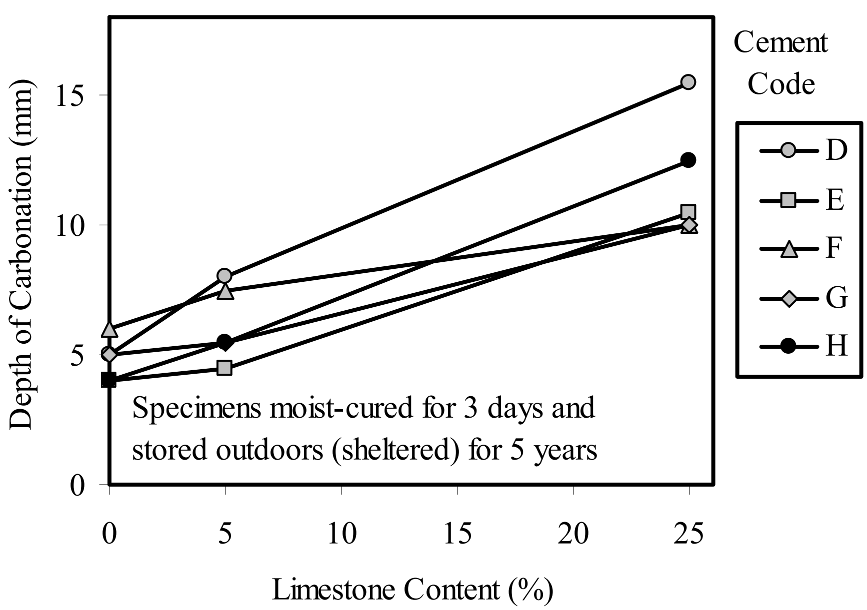


Figure 5.6 Effect of Limestone Addition on the Carbonation of Concrete (W/CM ~ 0.60) Moist-Cured for 3 Days and then Stored Outdoors-Sheltered for 5 Years (modified from Matthews, 1994)

Figure 5.7 shows the depth of carbonation for PC and PLC concretes of varying W/CM. For a given W/CM the depth of carbonation of concrete produced with PLC containing 25% limestone is considerably greater than that for the concrete produced with PC. It is interesting to note that concrete produced with PC combined with 28 or 30% fly ash also exhibited much increased carbonation compared with the 100% PC concrete, although the increases due to fly ash were not quite as great as those due 25% limestone.

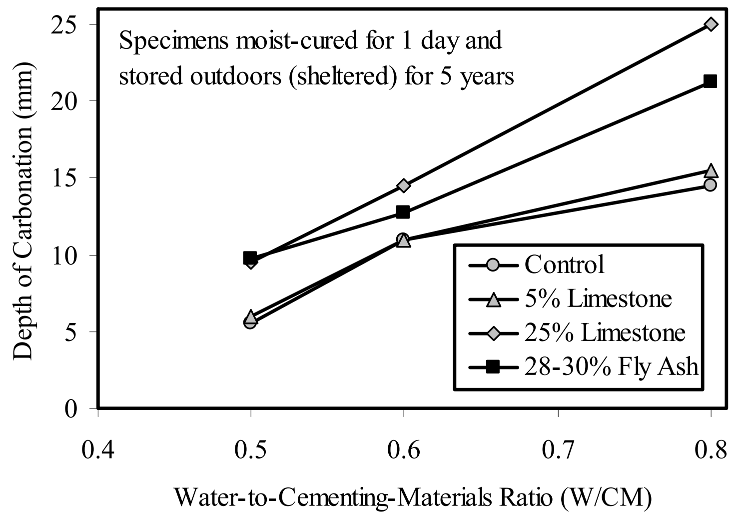


Figure 5.7 Depth of Carbonation as a Function of W/CM for Concrete Produced with Cements with Varying Levels Limestone (modified from Matthews, 1994)

Figure 5.8 shows the depth of carbonation at 5 years plotted against the water-to-Portland-cement ratio (P/C) of the concrete mix. The good relationship between these parameters indicates that the limestone component of the cement does not contribute towards the carbonation resistance of the concrete.

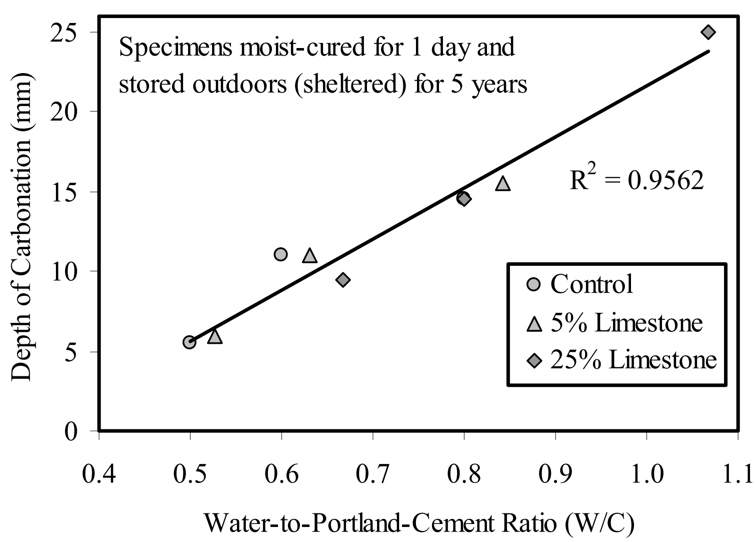


Figure 5.8 Depth of Carbonation as a Function of W/C for Concrete Produced with Cements with Varying Levels Limestone (modified from Matthews, 1994)

Figure 5.9 shows the depth of carbonation at 5 years plotted against the 28-day standard-cured compressive strength of the concrete. This relationship indicates that provided the concrete is produced to the same 28-day strength its resistance will be the same regardless of the quantity of limestone in the cement.

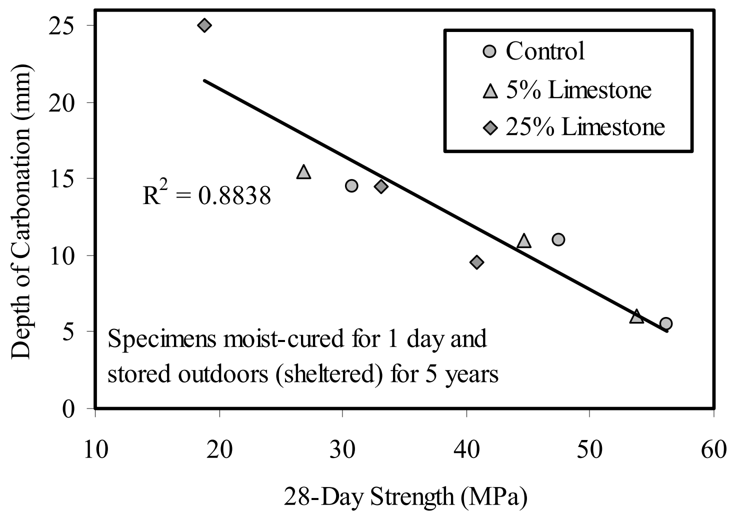


Figure 5.9 Depth of Carbonation as a Function of Strength for Concrete Produced with Cements with Varying Levels Limestone (modified from Matthews, 1994)

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 5.10 confirms the findings of Matthews (1994) that concretes of equal strength will carbonate at similar rates even when the concretes are produced with PLC with varying limestone contents.

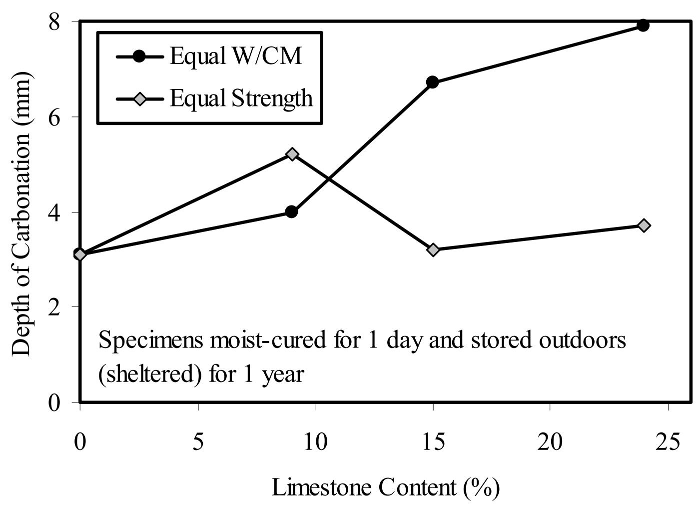


Figure 5.10 Effect of the Limestone Content of PLC on the Carbonation of Concrete Mixes Produced at Equal W/CM or Equal 28-Day Strength (from Barker and Matthews, 1994)

Similar findings were recently reported by Dhir et al (2007) using blended PLC containing up to 45% limestone as shown in Figure 5.11. 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% showed little increase in carbonation over the control, especially at the lower W/CM (0.52) used in the carbonation tests.

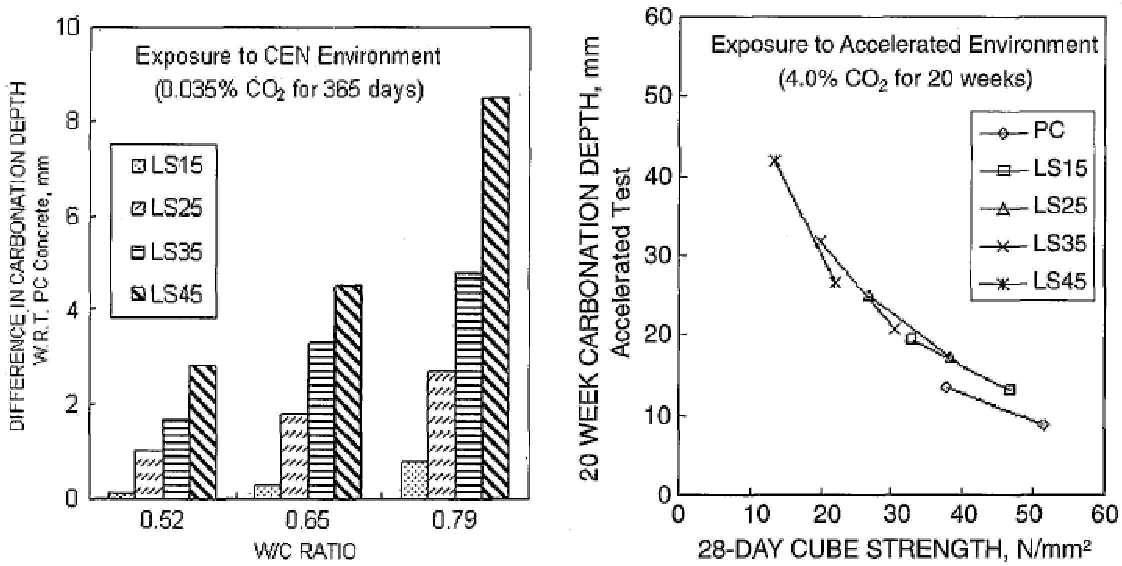


Figure 5.11 Effect of W/CM Ratio and Strength on the Carbonation of Concrete with Varying Levels of Limestone Exposed to Normal (Left) and Elevated (Right) Levels of Carbon Dioxide (Dhir et al. 2007)

Collepardi et al (2005) showed that substitution of portland cement for ground limestone (15% and 25% blended at the concrete mixer) led to an increase in carbonation rate when concrete was compared at equal W/CM (Figure 5.12). However, as shown in Figure 5.12, replacing portland cement with 25% fly ash led to a similar increase in carbonation as that observed for 25% limestone. 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. Figure 5.13 shows the relationship between carbonation rate and strength for concretes produced with cements containing varying levels of limestone (15% and 25%), fly ash (25%) and slag (15% and 50%).

Schmidt (1992b) reported data for concrete produced with PLC (containing 13 to 17% limestone) from 3 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 was generally less than that of concrete produced with composite cements containing a combination of 13-17% fly ash and 13-17% slag.

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 4.1 for details of cements and concrete mixes). Their data indicate that there is no consistent effect of limestone additions on the carbonation of concrete.

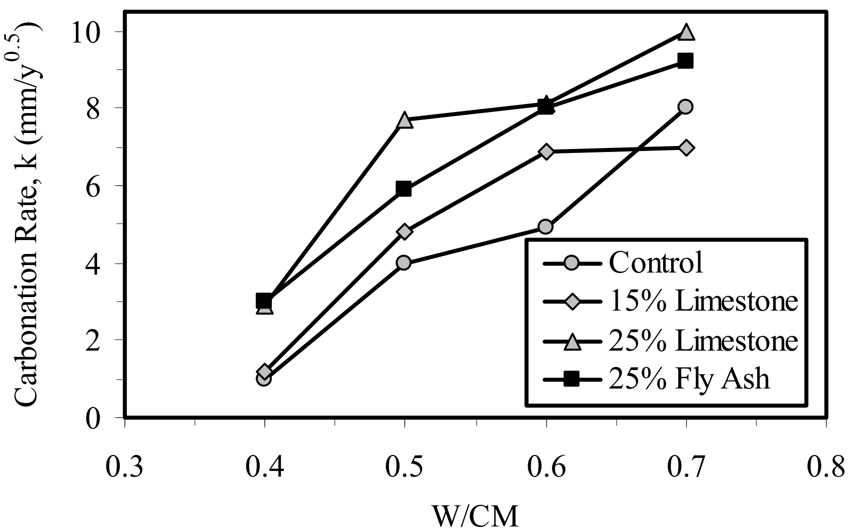


Figure 5.12 Effect of W/CM Ratio on the Carbonation Rate of Concrete with Varying Levels of Ground Limestone Used to Replace Portland Cement (Collepardi et al. 2004)

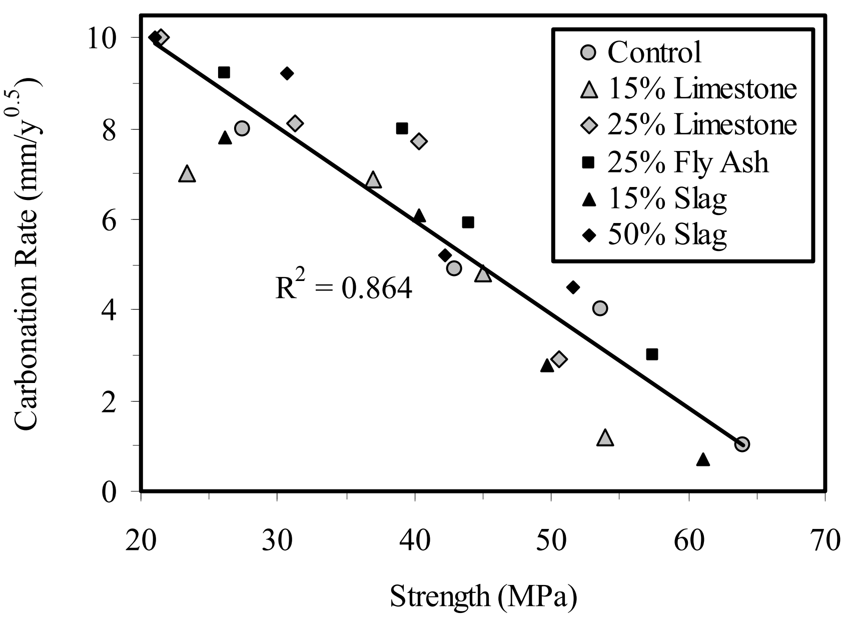


Figure 5.13 Effect of Strength on the Carbonation Rate of Concrete with Varying Levels of Limestone, Fly Ash and Slag Used to Replace Portland Cement (Collepardi et al. 2004

The balance of data indicates that the use of PLC will lead to an increase in carbonation for concretes produced at a constant water-to-cementing-materials ratio (W/CM), but that the rate of carbonation is similar in concretes produced to equal strength. The partial replacement of Portland cement with fly ash and slag also results in an increase in the rate of carbonation of concrete. The increased rate of carbonation due to the use of limestone appears to be only slightly greater than that due to the use of similar amounts of fly ash. It is expected that the use of PLC in combination with fly ash and slag will lead to further increases in carbonation although there are few data in the literature to show this.

5.3 Resistance to Alkali-Silica Reaction

Hobbs (1983) reported that the use of 5% limestone extended the time to but did not eliminate cracking in mortar bars made with high-alkali cement and highly-reactive Beltane opal sand. To the authors' knowledge there are no other published data on this subject. However, intuitively one would expect the risk of damage due to ASR to be reduced slightly with PLC merely because of the dilution of the portland cement alkalis.

5.4 Resistance to Freeze-Thaw and Deicer Salt Scaling

Much of the data on the effect of limestone on the 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 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 5.14 (from 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 5.4 (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 5.4 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

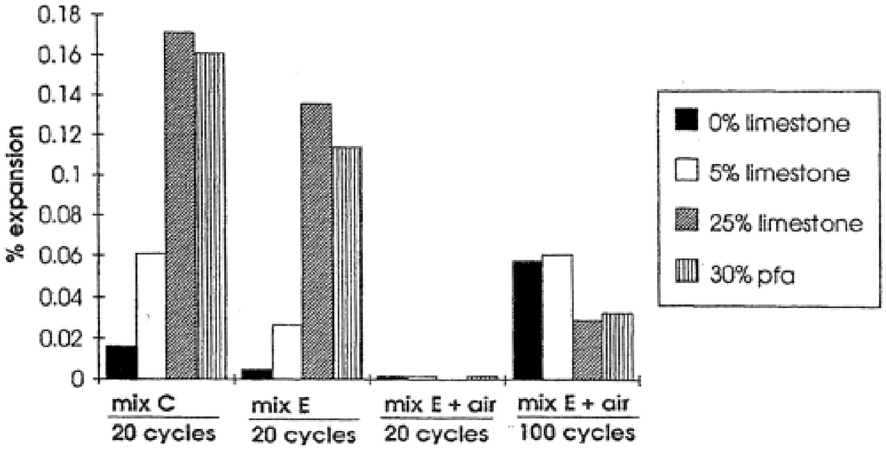


Figure 5.14 Effect of Air Entrainment on the Freeze-Thaw Resistance of PC and PLC Concrete (Matthews, 1994)

There are few data available on the performance of PLC concrete in severe environments with exposure to deicing salts and multiple freeze-thaw cycles. To the authors' knowledge there are no data on the performance on PLC-SCM combinations in these environments.

5.5 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 5.15, 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.

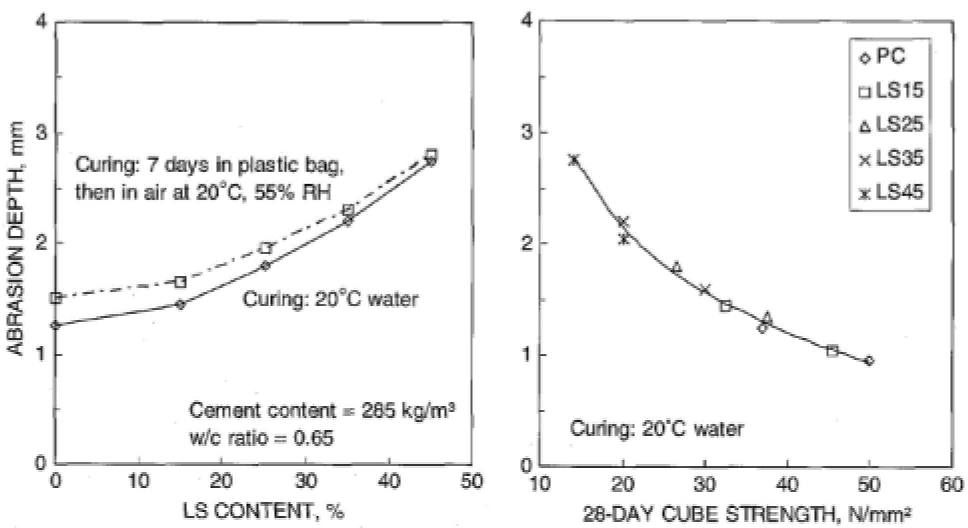


Figure 5.15 Effect of the Limestone Content of PLC on the Abrasion Resistance of Concrete (Dhir et al. 2007)

5.6 Sulfate Resistance

General Issues

In general, the use of limestone in cements should act to dilute the C_3A and other active aluminate content of cements and or cementitious systems. As well, any formation of carbo-aluminates from reaction of the calcium carbonate with calcium aluminates would tend to reduce the available alumina to participate in deleterious sulfate reactions. On the other hand, if use of limestone cements result in lower strength or more permeable concretes, it could allow faster ingress of external sulfates. Finally, while there is no evidence of deleterious effects of up to 5% limestone in cements (Hooton, 1990; Hooton and Thomas, 2002) as currently allowed in both CSA A3001 and ASTM C 150 cements, one of the specific concerns is the possibility that increased quantities of finely ground carbonates could increase the potential for thaumasite sulfate attack (TSA). The following is a review of the literature with regard to these issues.

Effect on Ettringite-Based Sulphate Attack

The sulfate resistance of limestone cements is more function of C_3A content than limestone content (Moir & Kelham 1997).

As shown previously in Table 1.1, currently in Europe, EN197-1 has four classes of Composite Cements with Limestone filler, CEM II/A-LL or-L (6-20% limestone) and CEMII/B-LL or -L (21-35% limestone), but with exception of Italy and Sweden, they are not allowed to be specified for sulphate-resistant applications CEN (2003). In Sweden, testing for sulphate resistance must be performed (SS134204), and in Italy (under UNI 9158), it is only allowed to be used for moderate sulfate exposures and the C_3A of the clinker fraction must be either <8% with SO_3 <3.5%, or C_3A <10% if SO_3 <3.0%. However, in the European Standard EN197-1, there is currently no test method for evaluating the sulfate resistance of a Portland or blended cement, due to lack of agreement on a common test method, in spite of several European countries previously having had test methods. As a result, in 2006 the CEN committee drafted an amendment A2 to EN197-1: 2000 to simply prescriptively allow a family of seven types of cement for use in sulfate resistant applications (not yet adopted). These types include three CEM I cements with either 0, 3, or 5% Bogue C_3A in the clinker, as well as slag cements CEM III/B (66-80% slag), CEM III/C (81-95% slag), and pozzolan cements CEM IV/A (20-35% pozzolan), CEM IV/B (36-55% pozzolan). The CEM II limestone cements were not considered.

Soroka and Stern (1976) replaced 10, 20, 30, and 40% by mass of cement with ground limestone and compared to the same replacements by inert calcium fluoride. ASTM C 1012 mortar bars (except w/c = 0.75 was used and bars were wet cured for 7d then air-cured at 65%rh to 28d) were exposed to 5% sodium sulphate and length change and time-to-cracking were recorded as shown in Table 5.5.

The results showed that time-to-cracking increased significantly with increased limestone replacements, whereas the calcium fluoride replacements had no effect in spite of both fillers having generally increased strength at time of sulfate exposure. They suggest that the improvement in sulphate resistance is possibly due to the formation of calcium carboaluminates, thus suppressing formation of monosulfate (and therefore reducing the potential for ettringite formation on exposure to sulphate solutions), as had been previously suggested by Chatterji and Jeffery (1963).

Table 5.5: Sulphate Resistance of Cement with Limestone Replacements
(Soroka and Stern, 1976)

Mortar	Onset of cracking (weeks)	Compressive strength at 28 days (kg/cm^2)
Reference mortar	6	253
With $CaCO_3$ filler (wt%)		
10	10	270
20	12	273
30	14	297
40	16	309
With CaF_2 filler (wt%)		
10	6	237
20	6	282
30	6	326
40	6	289

Soroka and Setter (1980) extended their study and found that up to 40% by mass replacement of OPC with reagent grade limestone improved sulphate resistance, with the best improvements occurring with limestone having high fineness (Blaine of 960-1120 m^2/kg) as shown in Table 5.6. They attributed this to the increased likelihood of very fine limestone reacting to form carboaluminate hydrates. However the OPC plus limestone filler mixtures were not equivalent to expected SRPC performance.

Table 5.6: Effect of 30% filler based on type and fineness on Weeks to Failure of Mortar Bars in 5% sodium sulphate (Soroka and Setter, 1980 as presented in Hawkins et al, 2003)

Fineness, m^2/kg	Limestone	Dolomite	Basalt
115-130	12	12(?)	4
370-300	10	6	4
660-710	10	6	4
960-1120	18	6	2
Reference		6 weeks	

Sawicz and Heng (1996) measured expansions of 50x50x150mm concrete prisms exposed to 5% sodium sulphate at room temperature after 28 days curing. The concretes had w/c from 0.50 to 0.70, used a cement with 12.1% C_3A and 7, 14, 21, and 28% powdered limestone (Blaine = 330m^2/kg) in addition to 350kg/m^3 cement (limestone powder replacing some of the limestone coarse aggregate). At w/c <0.60, sulfate expansions were reduced after 150 days exposure when up to 14% limestone was included. There was no effect of limestone at w/c >0.60. Expansions are shown in Figure 5.16.

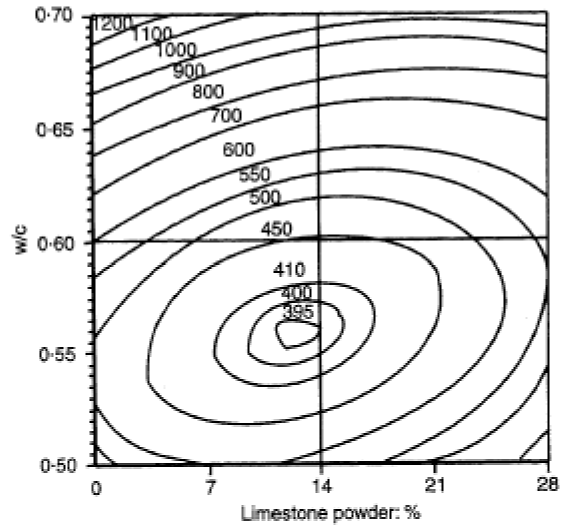


Figure 5.16: Sulphate expansion isobars (microstrain) for different w/c and limestone levels (Sawicz and Heng, 1996)

Using XRD, they attributed the beneficial effects of limestone on sulphate resistance to the reversion of the initially formed ettringite (during curing) to mono and hemi-carbonate rather than mono and hemi-sulphate phases.

Concretes made with cements having high C_3A (13.1%) content were completely disintegrated at 5-years. Concretes had 300kg/m^3 of cement, w/c ~ 0.60 (slump was kept constant = 60 - 70mm). The same occurred with C3A content of 10.3% (partially of completely disintegrated). In contrast, concretes made with cements with C_3A equal to 7.1%, 5.3% and 8.6% performed well. So, for the OPCs there is a clearly relationship between C_3A content and sulfate resistance (Matthews 1994).

With 25% limestone addition: in general, no differences between OPC and LPC performance were observed, but in some mixtures the performance was improved whilst in others, worsened. Overall the effect of 25% limestone addition was to extend the range of performance obtained from OPCs with a wide range of C_3A contents, the OPC with the lowest C_3A content being improved and the rate of deterioration of the highest C_3A OPC being increased (Matthews 1994).

There is little evidence of any systematic effect of 5% of limestone addition, but for rapid hardening cement 5% of limestone improved significantly the performance (this could be due to its high SO_3, resulting in a greater consumption of C_3A to form ettringite during the setting and hardening process, leaving less aluminates to react with sulfate from external sources) (Matthews 1994).

Mortar prisms with 35% of limestone addition (C_3A in clinker around 8%) exposed to magnesium sulphate solution at 5°C suffered extensive damage and deterioration in 1 year. Prisms with 15% of limestone show strong signs of impending damage. Compression member with 35% limestone, exposed to aggressive sulphate environments and temperatures around 5°C can show a loss of almost 75% in compressive strength, while the loss in flexural strength is lower (Harsthorn et al. 2001)

To follow up to the above-cited work by Harsthorn et al, Collepardi et al (2003) exposed cement pastes after 28 days wet curing to 10% sodium sulphate solutions at both 5 and 20°C. Pastes (40x40x160mm) were cast at w/b = 0.40 with 0 (CEM I 52.5), 15 (CEM II/A-LL 42.5), and 30% (CEM II/B-LL 32.5) limestone. After 3 months exposure, no damage was noted so pastes were exposed to wet/dry cycles (1 per week) for 4 months. The drying caused microcracking of the pastes but no sulphate-related damage was observed. Some thaumasite was observed in cracks in all pastes stored at 5°C with slightly more in the 30% limestone cement. This was attributed to the higher w/c in the 30% limestone paste (0.57 at a w/b = 0.40) as opposed to an effect of the cement type.

Barker and Hobbs (1999) exposed mortar prisms (40x40x160mm) to magnesium and sodium sulfate solutions at 5°C. The mixtures utilized two 15% limestone cements, one Portland and one sulfate resistant cement cast at 0.50 and 0.75 w/c. The limestone cements performed similarly to the Portland in most cases, while the SRPC performed better.

Borsoi et al (2000) found that mixtures containing 10% limestone filler exhibited surface damage due to presence of ettringite and thaumasite after 5 years exposure to severe magnesium sulphate solutions (3000 mg/L), but did not show evidence of strength reduction. When the 8.2% C_3A cement was replaced with a 0% C_3A cement, the surface damage with 10% limestone was mitigated. In lower sulphate exposures (300 and 750 mg/L), no damage was observed after 5 years.

González and Irasser (1998) performed ASTM C 1012 tests on both Type II and Type V cements with 10 and 20% limestone filler. The 10% limestone showed no effect on expansion or mass loss of the cements, but for 20% limestone, the sulphate resistance was lower than the control mixtures (see Table 5.7). The only sulphate phases detected by XRD were gypsum and ettringite.

Table 5.7: Sulphate Resistance of Limestone Mixtures (González and Irasser, 1998) as Presented in Hawkins et al (2003)

Cement	Type V			Type V			Type II		
C3A content, % mass C3S content, % by mass	0 40			1 74			6 51		
Limestone replacement	0	10	20	0	10	20	0	10	20
Time to 0.10% Expansion, days	1260	857	208	148	164	92	165	209	108
Reduction in compressive strength (1 year in sulfate solution, %)	3	4	5	29	17	50	8	25	40

Irassar et al (2000) found that 10% limestone gave similar expansion and strength as Type V cements. The blended limestone mixtures performed better with higher C_3S content. For the mixture with 20% limestone addition, the results were higher expansion and lower strength regardless of C_3S content.

Irassar et al (2005) evaluated sulphate resistance of a Type II and two Type V cements, each with and without 20% limestone replacement, using ASTM C 1012 mortar bars. All three Portland cements passed ASTM C 452, using the CSA expansion limits. Expansions are shown in Figure 5.17. The data looks like it might be part of the same data presented in Table 5.7, above. In this paper, with the exception of the SRPC (Type V) with low C_3S content, they observed thaumasite, which had formed after ettringite.

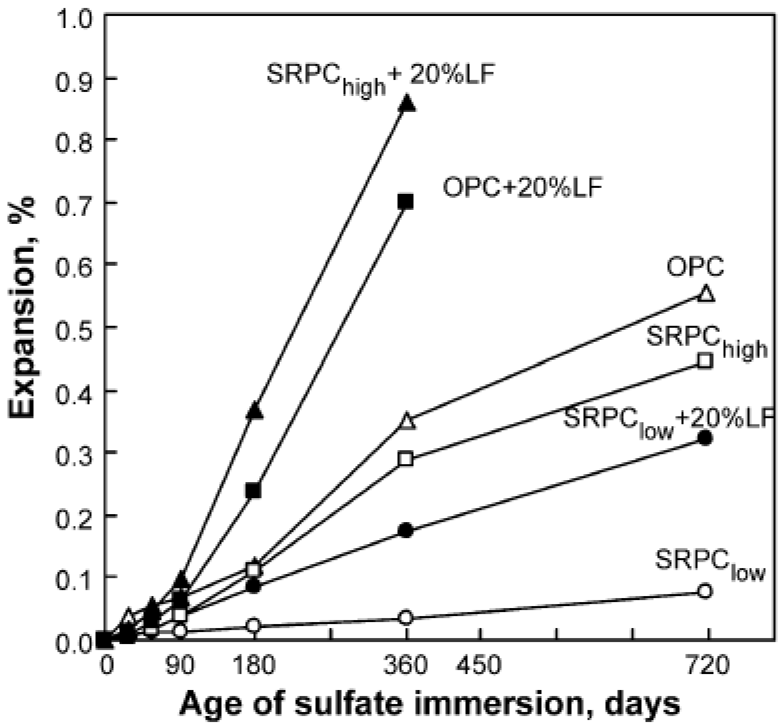


Figure 5.17: ASTM C 1012 Expansions of cements with and without 20% limestone (Irassar et al, 2005)

With all 3 cements, addition of 20% limestone increased expansions, but it should be noted that only the SRPC with 0% C_3A and only 40% C_3S passed the ASTM C 1157 expansion limit of 0.1% at one year.

Hekal et al (2002) noticed that 10% limestone exhibited similar strength loss to that of a control paste mixture (w/b = 0.3, 25mm cubes water cured for 28 days) when subjected to cyclic wetting and drying in a 60°C, 10% magnesium sulphate solution. When immersed in 10% magnesium sulphate at 20 or 60°C, strengths after 180 days were similarly unaffected for 0 and 10% limestone pastes, while 5% limestone showed improved strength performance, similar to that of a 40% slag paste.

Thaumasite formation and TSA

The thaumasite form of sulfate attack has been only identified in a few cases in Canada, and in cold, wet environments (Bickley et al, 1994; Rogers et al, 1997; Thomas et al, 1993;

Thomas et al, 2002), although minor occurrences of thaumasite have been found in decalcified zones of concrete stored in sulphate solutions at room temperature in the laboratory (Brown and Hooton, 2002). However, in none of these cases, were limestone fillers used in the concretes.

The discovery in the U.K. during the 1990's of severe deterioration in a number of buried concrete foundations containing carbonate aggregates has raised concerns about the effect of limestone in cement on the performance of concrete in sulfate environments. In these cases the concrete produced would have satisfied the prevailing recommendations for sulfate resistance at the time (e.g. BRE Digest 363 and BS 5328), but the deterioration was diagnosed as being the result of the thaumasite form of sulfate attack (TSA) rather than "classical" sulfate attack. The vulnerability of the concrete to TSA was ascribed to the presence of carbonate aggregate (Thaumasite Expert Group, 1999; Crammond, 2002a). However, in some of these cases, it must be noted that high levels of sulfates were not detected in the original undisturbed soils, but they did contain sulfides, which oxidized during the construction process to form sulfates. The role of carbonate in portland cement is discussed in greater detail below.

There is evidence that this form of sulfate attack can occur, especially in wet and cold conditions, on concretes with finely divided calcium carbonate, which normally could be considered to be sulfate resistant. There does not appear to be an obvious dependence of thaumasite formation on the level of limestone in cement (Sims and Huntley, 2002), it being detected the same amount in the 5% and 25% limestone cements (Matthews 1994).

Part of the long-term study performed by the U.K. Working Group on limestone in cement included studies on sulfate resistance (Matthews, 1994). Concretes were produced with a range of portland cements, with C_3A contents ranging from 5.3% to 13.1% (by Bogue) and limestone contents of 0, 5 or 25%, and exposed to solutions of sodium sulfate (1.5% SO_3) or magnesium sulfate (0.35% and 1.5% SO_3) at 20°C (68°F). There was no consistent difference in the performance of concrete after 2 and 5 years with the limestone content of the portland cement, but as expected, a strong correlation was found between performance and the C_3A content of the cement. However, because of the poor performance exhibited by the cement with the highest C_3A and at a 25% limestone content, and the detection of thaumasite in most of the concretes produced with so-called "limestone-filled cements" (meaning more than 5% limestone), a recommendation was made that limestone-filled cements not be used beyond Class I sulfate conditions (i.e. when SO_4 content of groundwater exceeds 0.4 g/L or SO_4 content of a 2:1 water-soil extract exceeds 1.2 g/L). There is no such restriction on cements containing up to 5% limestone.

Later studies on mortars (w/c = 0.5 and 0.75) stored in both sodium and magnesium sulfate solutions at 5°C (41°F) indicated reduced expansion of the 15% limestone cements in both sulphate solutions, and little difference in the visual rating performance of mortar produced with high-C_3A (~ 10%) portland cement with and without 15% limestone (Barker and Hobbs, 1999), except when an impure oolitic limestone was used (Figures 5.18 and 5.19). However, XRD examination of the 0.75 w/c mortars with limestone showed thaumasite, ettringite, and gypsum being the principal reaction products wheras for the Portland cements without limestone, only ettringite and gypsum were found. As well, compressive strengths of the limestone cements after the exposure were reduced more so than the Portland cements. It is interesting to note that no damage to the SRPC mortar was noted over the 1-year period of exposure.

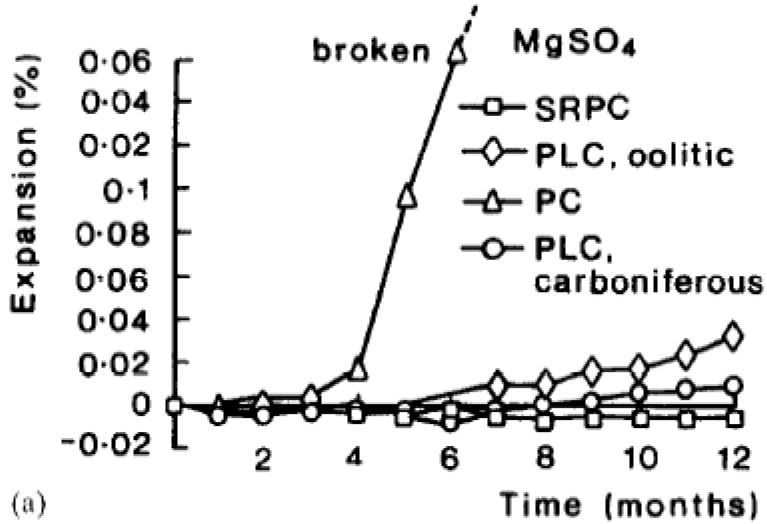


Figure 5.18. Expansion of 0.75 w/c mortars in 4,200mg/L SO_4 ($MgSO_4$) at 5°C. PLC is PC with 15% limestone (Barker and Hobbs, 1999)

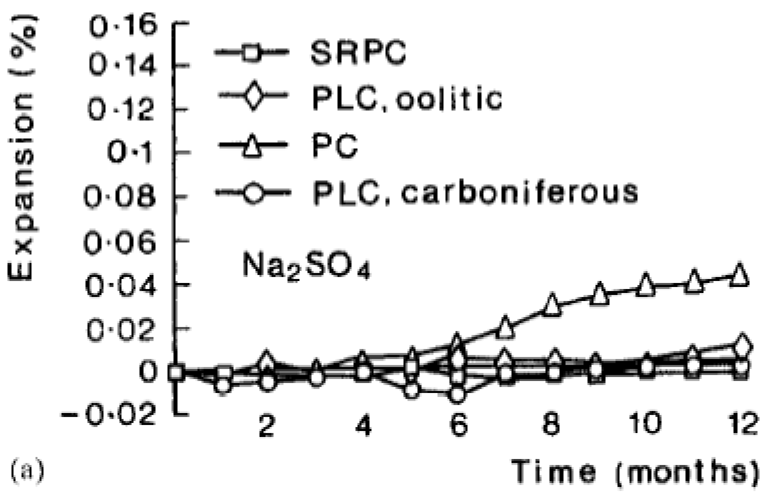


Figure 5.19. Expansion of 0.75 w/c mortars in 4,200mg/L SO_4 (Na_2SO_4) at 5°C. PLC is PC with 15% limestone (Barker and Hobbs, 1999)

Other researchers have demonstrated that the presence of amounts of limestone in the range from 10% to 20% can change the dominant reaction product from ettringite to thaumasite (Borsoi et al, 2000; Justnes, 2002), but the impact of the limestone on physical deterioration in these studies is not clear.

More recent work at the Building Research Establishment indicates that limestone-filled cements (typically containing much greater than 5% limestone) are the "least TSA-resistant binder types investigated" (Crammond, 2002b).

On contract to the British Cement Association, the Building Research Establishment (Holton, 2003) evaluated the resistance of concretes to TSA over a 3 year period at 5°C in Class 2 sulphate exposures 1400 mg/L sulphate as calcium sulphate and Class 3 Exposures 3000 mg/L sulphate (mixed calcium and magnesium). Evidence of thaumasite damage was found after 3 years in both types of sulphate exposures. Concretes had w/c from 0.40 to 0.50 and cement contents ranging from 330 to 460 kg/m^3were seal cured at 20^oC for 28 days prior to exposure. Concretes were evaluated by visual and depth of wear ratings. The resistance to TSA of Portland-limestone cement concretes (CEM II/A-L class 42.5 with 12% limestone and a clinker C_3A = 12%) with w/c ratios in the range 0.4 to 0.45 (Figure 5.20a) and minimum cement contents of 380 kg/m^3, was comparable to that of high C_3A PC concretes of 0.5 w/c ratio and 330 kg/m^3 minimum cement content (Figure 5.20b), with a range of high and low carbonate content aggregates. However, TSA was not prevented in these concretes. The C_3A content of the Portland-limestone cement had minimal effect on sulphate resistance. To quote Holton et al (2007), "In terms of UK practice the results lend support to extending the use of CEM II/A-L cements to concrete in class DS-2 conditions (0.4 to 1.4 g/l SO_4) where magnesium sulfate is frequently absent." Holton et al (2007) also suggested, "that a reduced C_3A level in a Portland-limestone cement may not be advantageous in preventing TSA. This is in agreement with the results of thermodynamic studies carried out by Juel *et al* (2003), who have shown that, at a given level of sulfate, thaumasite formation is favoured in cement systems that contain less aluminate."

Cement	Aggregate	Free w/c ratio	Mix number
High C_3A PLC	Dolomitic limestone	0.45	A00/246
Year	1	2	3
Wear rating	2	4	7
Photograph			
Comment	Very minor exposure of aggregate on struck face and sides	Aggregate becoming exposed around top of side faces, layer of soft white paste on base	Aggregate exposed around top of cube with blisters developing elsewhere

Figure 5.20a. Photos of Concrete Cubes: 12% limestone cement at 0.45 w/c (Holton 2003)

Cement	Aggregate	Free w/c ratio	Mix number
High C_3A PC	Dolomitic limestone	0.5	A00/229
Year	1	2	3
Wear rating	1	2	4
Photograph			
Comment	Some exposed aggregate on sides	Thinly exposed aggregate on side faces	Aggregate thinly exposed on side faces but top and base still intact

Figure 5.20b. Photos of Concrete Cubes: High C_3A Portland cement at 0.50 w/c (Holton 2003)

A number of laboratory studies were conducted at Sheffield University in the UK (Hartshorn et al, 1999; 2001; 2002; Kakali et al, 2002; Torres et al, 2002; Torres et al, 2006) which indicates that increasing levels of limestone increase the rate of TSA. Hartshorn et al (2002) found severe deterioration due to thaumasite in mortar with 35% separately added limestone filler (>98% calcium carbonate) after 126 days at 5^oC and impending deterioration with 15% after one year. Hartshorn et al (1999) had previously found similar effects in cement pastes.

Torres et al (2006) extended this work, looking at thaumasite damage in mortars with 0, 5, 15, and 35% limestone exposed to 1.44% sulphate, as magnesium sulphate, for 5 years at 5°C. They conclude that TSA occurred in all mortars, but was worse with increasing levels of limestone filler above 5%. While increasing levels of limestone filler were implicated in the damage, it was stated that the source of carbonate causing TSA in the OPC mortar must have occurred due to atmospheric carbonation. While it is not mentioned in this paper, it is known (Torres et al, 2002) that, after 4 years, the storage solutions the bars were stored in were allowed to evaporate gradually at 5°C, leaving the bars in air, such that the likely primary source of reactive carbonate in all mortars was from atmospheric carbonation. The damage on re-examination at 5 years was much more severe than prior to drying.

Lipus and Puntke (2003) tested 14 day cured, 0.60 w/c mortar bars (10x40x160mm) exposed to 1500 and 29,800 mg/L SO_3 (sodium sulphate) for 2 years and 180 days respectively at both 8 and 20^oC. SRPC was used with or without 15% limestone as was a CEM III/B-HS slag cement (containing at least 66% slag). No deleterious expansions were measured with the SRPC (CEM I-HS) or CEM III/B plus limestone mixtures and the only thaumasite noted was confined to a surface layer, but was not associated with any damage. As well when 20 or 40% fly ash was used, with or without the 15% limestone, no deleterious expansions occurred at 8 or 20°C as shown in Figure 5.21.

In the same study, when 15% limestone was added to a high-C_3A CEM I cement to create a CEM II/A-LL cement, neither was sulphate resistant. Thaumasite was noted in cracks, but it was only noticed after primary ettringite and gypsum formation and cracking had already occurred. They conclude that if the primary ettringite cracking damage had not occurred, that TSA would not have occurred later.

Trägårdh and Kalinowski (2003) investigated self-compacting concrete (SCC) specimens stored at 5°C for approximately 2 years in three different $MgSO_4$-solutions with concentrations (100 mg/l, 500 mg/l and 1400 mg/l, as SO_4). A sulfate resistant Portland cement (CEM I) with low C_3A content and two blended Portland limestone cements (CEM II) with different C_3A contents were tested (Figure 5.22). The mix proportions used correspond to normal Swedish SCC and included 0, 50, 100 and 180 kg/m^3 added limestone filler. The results indicate that SCC with blended Portland limestone cements (CEM II/A-LL), with and without added limestone filler, showed evidence of TSA when exposed to the moderate 0.14 % SO_4 magnesium sulfate solution, but the most severe deterioration was for concretes with 50 kg/m^3 added limestone filler (see Figure 5.22). At weak sulfate concentrations (0.01 and 0.05 % SO_4), the SCC with blended Portland cements had not shown any sign of TSA. SCC containing cement with sulfate resistant

Portland cement with a low C_3A content (SRPC, CEM I) was intact in all solutions after 22 months exposure. Ettringite and ettringite-solid solution compounds formed prior to thaumasite formation. The important findings of this study are (a) that the low C_3A SRPC cement in combination with large volumes of separately added limestone filler (up to 180 kg/m3) was performing well, and (b) that the CEM II/A-LL cements were undamaged in what would be CSA Moderate exposure.

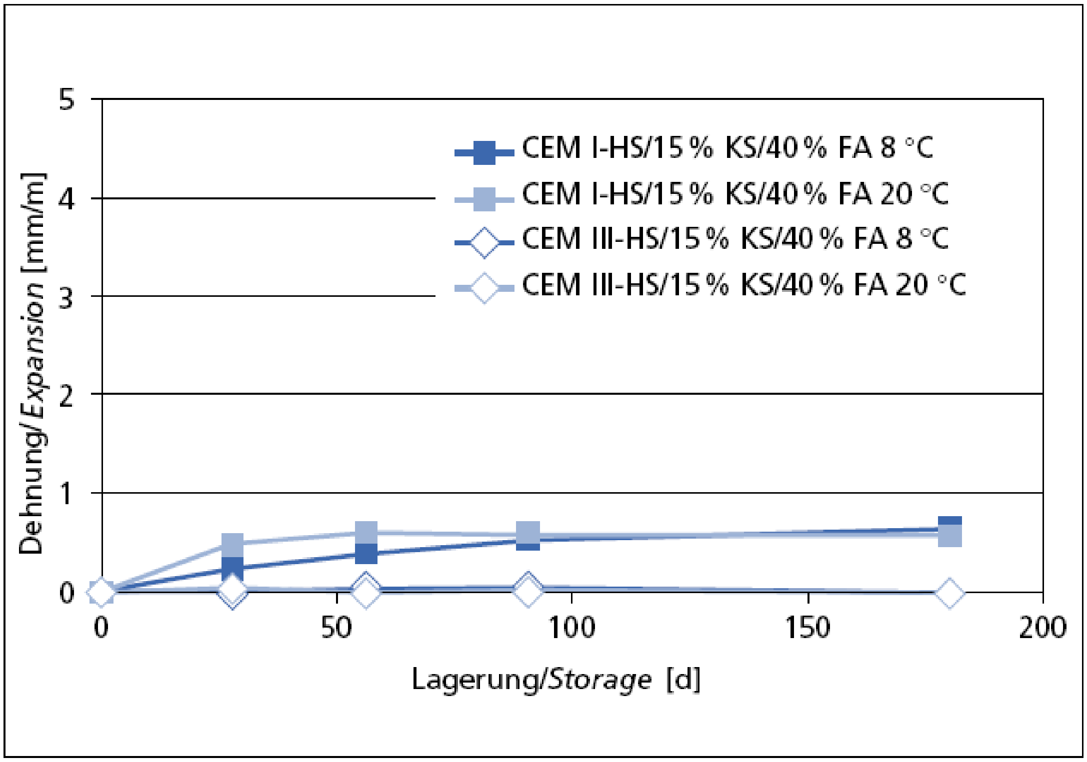


Bild 9: Dehnungsverhalten von Mörtelflachprismen aus HS-Zement/ Kalksteinmehl/Steinkohlenflugasche-Gemischen. Die Lagerung erfolgte in Natriumsulfatlösung (29 800 mg Sulfat/l). Die Prüfkörper wurden mit einem Wasserzementwert von 0,60 hergestellt und die Flugasche auf den Wasserzementwert mit k = 1,0 angerechnet.

Figure 9: Expansion behaviour of flat mortar prisms made from SR cement/limestone meal/pulverized fly ash mixes. The storage liquid was sodium sulfate solution (29 800 mg sulfate/l). The test pieces were made with a water/cement ratio of 0.60 which was calculated using the fly ash factor k = 1.0.

Figure 5.21: 15% limestone and 40% fly ash expansions (Lipus and Puntke, 2003)

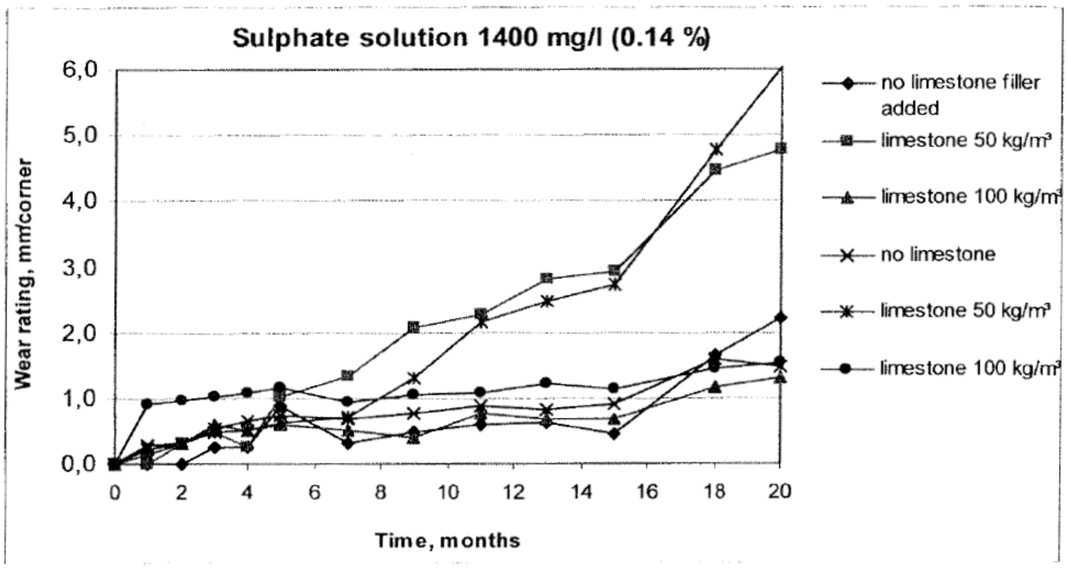


Figure 5.22. Wear Ratings of SCC Concrete Cubes made with CEM II/A, limestone cement plus 0, 50, and 100 kg/m^3 added limestone filler and Exposed to $MgSO_4$ at 5^oC (Trägårdh and Kalinowski, 2003)

Heat treated Concrete and Delayed Ettringite Formation

Kurdowski and Duszak (2003) looked at 0, 15, and 30 limestone replacement of a cement with 8.3% C3A. Mortar bars (40x40x160mm) were subjected to a heat curing cycle with a maximum temperature of 90^oC. While the Portland cement expanded to almost 0.6% after 18m in water, 15% limestone reduced expansion to about 0.2%, while 30% limestone mixtures did not expand at all after one year.

Heinz and Urbonas (2003) exposed pastes and EN 196 mortar prisms (10x40x160mm) to either a heat cycle of 95°C for 4h or to 20°C, followed by water immersion at both 5 and 20°C. The cement was CEM I 42.5 replaced with 0, 15, and 30% powdered Jurrasic limestone (94% - 63um). Without the heat curing, no deleterious expansion was observed after 2 years water storage. For the heat-cured mortars and pastes, expansions reduced with increasing levels of limestone. Paste expansions were lower than mortar expansions and are shown in Figure 5.23.

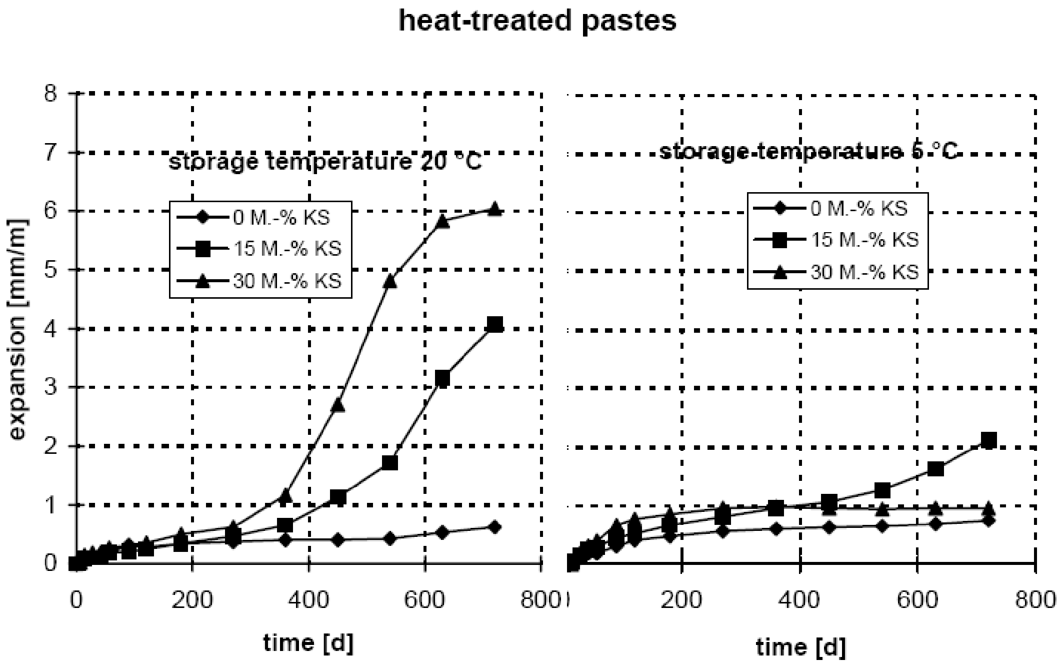


Figure 5.23: Paste expansions at 20 and 5°C after a 95°C heat treatment, showing reduction in DEF expansion with increasing limestone (KS) replacement of cement (Heinz and Urbonas, 2003)

By XRD, immediately after heat treatment, monocarboaluminate hydrates were not found, however, after water exposure, increasing limestone resulted increasing levels of monocarboaluminate hydrates as well as ettringite, whereas pastes without limestone exhibited presence of both monosulphate and ettringite. While in theory, they suggest that thaumasite could occur, they were not able to identify thaumasite in the 5°C stored specimens.

Effects of Supplementary Cementing Materials on Sulphate Resistance of Limestone Cement

Higgins (2002) studied the effect of slag on the sulphate resistance of portland, 60% slag, and 60% slag plus 4% limestone concretes (100mm cubes) immersed in 1.5% SO_3 using either sodium or magnesium sulphate at 20°C. Gypsum (2 and 3%) was also added in some mixtures. Concretes were evaluated for strength and wear ratings for up to 6 years. Mortar prisms (10x40x160mm) were sieved from concrete mixtures and moist cured for 14 days prior to immersion in the same solutions as well as 2.4% SO_3 using sodium sulphate for 6 years. He found that the 4% limestone resulted in a large improvement in sulphate resistance of the 60% slag mixtures.

It has been shown that 70% ground granulated blast-furnace slag had a positive effect on preventing the formation of TSA in concretes without limestone fillers (Higgins and Crammond, 2002). The concretes were 0.5 w/c, 350 kg/m^3, 100mm cubes exposed to four different sodium or magnesium sulphate solutions at both 5 and 20°C.

It is possible then that use of slag may improve the performance of limestone cements, if there was a concern with the potential for TSA for concrete applications in certain cool, wet environments, and this was confirmed by Tsivilis et al (2003). As well, pozzolans such as metakaolin (Smallwood et al, 2003; Tsivilis et al, 2003) appear to significantly reduce TSA expansions and damage. Slower reacting pozzolans such as fly ash and natural pozzolans appear to retard the damage but not prevent it (Tsivilis et al, 2003).

Summary on Sulphate Resistance and Gaps in Knowledge

- There are inconsistencies in the trends found by different researchers as to whether limestone improved or worsened sulphate resistance either for ettringite or for thaumasite related deterioration. This likely needs more work in the Canadian context (eg. at CSA exposure levels and sulphate types).
- For thaumasite damage to occur at low temperatures, from the data in the literature, magnesium sulphate exposure appears to be more of a concern than with either sodium or calcium sulphate exposures.
- There is little data for 10% limestone levels, but there is more for 15%.
- The purity and the fineness of the limestone appear to be important performance variables.
- As well, whether the limestone is added separately or interground may affect the performance as limestone is easier to grind than clinker, so equal Blaine fineness will reduce activity of the cement. In addition, the optimum sulphate levels for a limestone cement will reduce with the percentage of added limestone (at least up to 7.5% limestone), and this may impact on later performance in sulphate exposure (Campiteli and Florinda, 1990).
- It must also be noted that most of the cited studies evaluated the performance of high C_3A cement with limestone additions in sulphate exposure, and one has to consider whether this is relevant information, as these cements would not be allowed to be used in CSA sulphate exposures with out use of sufficient SCMs.
- More work is needed on the performance at both ~5^{o}C and 23^{o}C of limestone cements in combination with levels of SCMs currently known to provide good sulphate resistance as well as on CSA MS and HS cements.

6.0 General Summary

Limestone cements have been used in many countries since the 1960's and the EU CEM II/A 6 to 20% limestone cements are the largest single type of cement currently produced in the European countries.

In general, the benefits of Portland limestone cements (PLC) are: (a) reduced greenhouse gas emissions due to reduced CO_2 resulting from reduced clinker factor in the cements, (b) improved workability and pumpability, (c) similar physical performance to current Portland cements when the cements are properly optimized, (d) similar durability to chloride ingress, and ASR. Potential weaknesses are: (a) increased susceptibility to the thaumasite form of sulphate attack, (b) increased potential to carbonation.

One area where there is very little data is on the influence of limestone cements when used in conjunction with SCMs. A question that needs to be answered is whether the use of limestone cements will reduce the replacement levels of SCMs that can effectively be used?As well, will durability issues be affected for typical replacement levels used now for issues such as AAR, sulphate resistance, and de-icer scaling?

Finally, it must be noted that some of the literature reviewed is difficult to evaluate, since performance of limestone cements is affected by (a) the quality of limestone used, (b) whether the limestone was interground or blended, and (c) changes in particle size distribution. In many studies the PLC was finer than the comparison Portland cement, as the system was optimized for equal physical properties, and this is likely the way that such limestone cements would be produced in Canada.

7.0 Recommendations

7.1 Recommendations for Current CSA Specifications

One option for the CSA committee is to consider making no changes at this time. However, with recent announcement of legislation to target reductions in green house gas emissions, this would not be helpful.

It is feasible to consider developing a new class of Portland-limestone cements within CSA A3001. These could allow up to 15% limestone replacement of clinker and be designated with a subscript L (eg. GU_L). Since there is insufficient information about how this would affect sulphate resistance, it is suggested that, if adopted, that limestone cements not be allowed in the MS and HS categories at this time. Therefore there could be 4 new types of cement under this class: GU_L, HE_L, MH_L, and LH_L. It is suggested that the EN requirements for the quality of limestone be adopted to control the limestone quality in such cements. It is also suggested that such cements be required to meet the same physical requirements as the existing Portland cements.

7.2 Recommendations for Further Study

1. Data on sulphate resistance, especially TSA, is conflicting and may relate to differences in limestone quality and particle size distribution. Further testing is suggested, especially at low temperature and in combination with sulfate resistant (blended) cements
2. There is a need to evaluate the performance of limestone cement-SCM combinations for durability issues such as alkali-aggregate resistance, sulphate resistance, de-icer scaling, and chloride resistance.
3. Determine whether there are any effects on carbonation if CSA A23.1 maximum w/cm, minimum strength limits and curing requirements are met. This also needs to be considered with limestone-SCM combinations.
4. Evaluate the durability of low-strength, high w/cm residential concrete mixtures.
5. Evaluate the effects on de-icer scaling resistance, especially with PLC-SCM combinations.
6. Determine if there is an influence on abrasion resistance.

8.0 References

Albeck, J. and Sutej, B. 1991. "Characteristics of concretes made of portland limestone cement," Beton, 41, 5, May, 240-244. (In German. English translation by Susan U. Lauer available from PCA Library.)

Barker, A. and Cory, H. 1991. "The early hydration of limestone-filled cements", in: N. Swamy (Ed.), Blended Cements in Construction, Elsevier, London, 107-124.

Barker, A.P. and Matthews, J.D. 1994. "Concrete durability specification by water/cement or compressive strength for European cement types". Proc. 3rd Int. Conf. on the Durability of Concrete, ACI SP-145, American Concrete Institute, Detroit, 1135-1160.

Barker, A.P. and Hobbs, D.W., 1999. "Performance of portland limestone cements in mortar prisms immersed in sulfate solutions at 5°C." Cement and Concrete Composites, 21, 129-137.

Bentz, D.P. and Conway, J.T. 2001. "Computer modeling of the replacement of "coarse" cement particles by inert fillers in low w/c ratio concretes: Hydration and strength", Cement and Concrete Research 31 (2001) 503-506

Bentz, D.P. 2006. "Modeling the influence of limestone filler on cement hydration using CEMHYD3D', Cement & Concrete Composites, 28, 124–129.

Bentz, D.P. 2005. "Replacement of "coarse" cement particles by inert fillers in low w/c ratio concretes II. Experimental validation", Cement and Concrete Research, 35, 185–188.

Bickley, J.A., Hemmings, R.T., Hooton, R.D. and Balinski, J. 1994. "Thaumasite related deterioration of concrete structures," ACI SP-144, 159-175.

Bonavetti, V., H. Donza, V. Rahhal, and E. F. Irassar. 1999. "High-strength concrete with limestone filler cements" Proc. 2nd CANMET/ACI Int. Conf on High-Performance Concrete and Performance and Quality of Concrete Structures, ACI SP-186, American Concrete Institute, Detroit, 567-580.

Bonavetti, V., Donza, H., Rahhal V. and Irassar, E. 2000. "Influence of initial curing on the properties of concrete containing limestone blended cement." Cement and Concrete Research, 30, 5, 703-708.

Bonavetti, V., Donza, H., Menéndez, G., Cabrera, O. and Irassar, E.F. 2003. "Limestone filler cement in low w/c concrete: A rational use of energy." Cement and Concrete Research, 33, 865–871.

Borsoi, A., Collepardi, S. Coppola, L., Troli, R and Collepardi, M. 2000. "Sulfate attack on blended portland cements," ACI SP-192, 1, 417-432. (www.encosrl.it/enco%20srl%20ITA/)

Brown, P.W. and Hooton, R.D. 2002. "Ettringite and Thaumasite formation in laboratory concretes prepared using sulphate-resisting cement", Cement and Concrete Composites, 24, 361-370.

Building Research Establishment, 1993.U.K. Seminar: Performance of Limestone-Filled Cements: Report of Joint BRE/BCA/Cement Industry Working Party, 28 November 1989, Building Research Establishment, Garston, Watford, England.

Campiteli, V.C. and Florinda, M., 1990. "The influence of limestone additions on optimum sulfur trioxide content in portland cements," ASTM STP 1064, pp. 30-40.

CEN, 2003. "National specifications and recommendations for sulphate resisting cement," European Committee for Standardization, CEN TC51/WG 6 Draft Report, Dec., 13pp.

Chatterji, S. and Jeffery, J.W. 1963, "A new hypothesis of sulphate expansion," Magazine of Concrete Research, 15, 44, 83-86.

Collepardi, M., Monosi, S., Favoni, O., and Ogoumah-Olagot, J.J., 2003. "Resistance to sulfate attack of mixtures with limestone-portland blended cements," Proceedings, 6th International Conference on Durability of Concrete, ACI SP-212, 941-949.

Collepardi, M, Collepardi, S., Ogoumah Olagot, J.J. and Simonelli, F. 2004. "The influence of slag and fly ash on the carbonation of concrete." Proc. 8th CANMET/ACI Int. Conf. on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, ACI SP-221, American Concrete Institute, Detroit, 483-493.

Crammond, N.J. 2002a. "The occurrence of thaumasite in modern construction," Cement and Concrete Composites, 24, 393-402.

Crammond, N.J. 2002b. "The thaumasite form of sulfate attack in the U.K." Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 809-818)

Dhir, R.K., Limbachiya, M.C., McCarthy, M.J. and Chaipanich, A. 2007. "Evaluation of portland limestone cements for use in concrete construction." Materials and Structures, 40, 459-473.

El-Didamony, H., Salem, T., Gabr, N. and Mohamed, T. 1995. "Limestone as a retarder and filler in limestone blended cement", Ceramics – Silikaty, 39, 1, 15-19.

Ghezal, A. and K. H. Khayat, K.H. 2002. "Optimizing self-consolidating concrete with limestone filler by using statistical factorial design methods", ACI Mater J., 99, 3, 264-272.

González, M.A. and Irassar, E.F. 1998. "Effect of limestone filler on the sulfate resistance of low C_3A portland cement," Cement and Concrete Research, 28, 11, 1655-1667.

Guemmadi, Z., Escadeillas, G., Houari, H., Clastres, P. and Toumi, B. 2005. "Iinfluence of limestone fillers on the mechanical performances of cement pastes", Proc Intl Conf on Cement Combinations for Durable Concrete, 339-350.

Hagelia, P., Sibbick, T., Crammond N.J., Gronhaug, A. and Larsen, C.K., 2001. "Thaumasite and subsequent secondary calcite deposition in sprayed concrete in contact with sulfate alum-bearing shale, Oslo, Norway", Proceedings of the Euroseminar on Microscopy Applied to Building Materials, Athens, Sept.4-7, pp. 131-138.

Halliwell, M.A., Crammond, N.J. and Barker, A.P. 1996. "The thaumasite form of sulfate attack in limestone-filled cement mortars." BRE Laboratory Report - BR307, Construction Research Communications Ltd (CRC), UK.

Hartshorn, S. and Sims, I. 1998. "Thaumasite – a brief guide for engineers." Concrete, 32, 24-27.

Hartshorn, S.A., Sharp, J.H. and Swamy, R.N. 1999. "Thaumasite formation in portland limestone cement pastes." Cement and Concrete Research, 29, 1331-1340.

Hartshorn, S.A., Sharp, J.H. and Swamy, R.N. 2001. "Engineering properties and structural implications of portland limestone cement mortar exposed to magnesium sulfate attack." Advances in Cement Research, 13, 31-46.

Hartshorn, S.A., Sharp, J.H. and Swamy, R.N. 2002. "The thaumasite form of sulfate attack in portland-limestone cement mortars stored in magnesium sulfate solution." Cement & Concrete Composites, 24, pp.351-359.

Hawkins, P, Tennis, P.D. and Detwiler, R.J. 2003. "The use of limestone in portland cement: A state-of-the-art review", Report EB227, Portland Cement Association, Skokie, Illinois, USA, 44.

Hawthorn, F. 1989. "Ten years' experience with composite cements in France." In Performance of Limestone-Filled Cements – Proceedings of a Seminar held at BRE in 1989, BR 245, Building Research Establishment, Garston, U.K. (published 1993).

Heikal, M., El-Didamony, H. and Morsy, M.S. 2000. "Limestone-filled pozzolanic cement, Cement and Concrete Research, 30, 1827-1834.

Heikal, M., Helmy, I., El-Didamony, H. and Abd El-Raoof, F. 2004. "Electrical properties, phsysio-chemcial and mechanical characteristics of fly ash-limestone-filled pozzolanic cement", Ceramics − Silikáty 48, 2, 49-58.

Heinz, D. and Urbonas, L. 2003. "Durability of heat-cured mortars and pastes made with portland limestone cements," Proceedings of 11th International Congress on the Chemistry of Cement, South Africa, 1627-1639.

Hekal, E.E., Kishar, E. and Moatafa, H. 2002. "Magnesium sulfate attack on hardened blended cement pastes under different circumstances," Cement and Concrete Research, 32, 1421-1427.

Higgins, D.D. 2002. "Increased sulfate resistance of ggbfs concrete in the presence of carbonate." Proceedings of the 1st International Conference on Thaumasite in Cementitious

Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 913-919)

Higgins, D.D. and Crammond, N.J. 2002. "Resistance of concrete containing ggbfs to the thaumasite form of sulfate attack", Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 921-929)

Hobbs, D.W. 1983. "Possible influence of small additions of pfa, gbfs and limestone flour upon expansion caused by the alkali-silica reaction," Magazine of Concrete Research, 35, 122, 55-58.

Holton, I., 2003. "Final report on 3-year investigation to establish sulfate resistance of Portland limestone cement concretes," BRE Report 209-164 for the British Cement Association.

Holton, I.R., Crammond, N.J. and Price, W.F., 2007. "Comparative performance of portland-limestone cement concretes and portland cement concretes in cold calcium sulfate solutions," (personal communication of unpublished draft paper).

Hooton, R.D. and Thomas, M.D.A. 2002. "The use of limestone in portland cements: effect on Thaumasite form of sulfate attack", PCA Report SN2658, 9pp.

Hooton, R.D. 1990. "Effects of carbonate additions on heat of hydration and sulfate resistance of portland cements", in Carbonate Additions to Cement, ASTM STP 1064, 73-81.

Ingram, K., Poslusny, M.m Daugherty, K. and Rowe, W. 1990. "Carboaluminate reactions as influenced by limestone additions", ASTM Special Technical Publication, STP-1064, 14-23.

Irassar, E.F., Bonavetti, V.L., Menhdez, G., Donza, H. and Cabrera, O. 2001. "Mechanical properties and durability of concrete made with portland limestone cement". Proc. 3rd CANMET/ACI Int. Symp. On Sustainable Development of Concrete, ACI SP-202, American Concrete Institute, Detroit, 431-450.

Irasser, E.F., Bonavetti, V.L., Trezza, M.A., and González, M.A., 2005. "Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20^{o}C," Cement and Concrete Composites, 27, 77-84.

Juel, I., Herfort, D., Gollop, R., Konnerup-Madsen, J., Jakobsen, H.J. and Skibsted, J. 2003. "A thermodynamic model for predicting the stability of thaumasite," Cement and Concrete Composites, 25, 8, 867-872.

Justnes, H. 2002. "Thaumasite formed by sulfate attack on mortar with limestone filler", Proceedings, Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 955-959)

Kakali, G., Tsivilis, S., Aggeli and E., Bati, M. 2000. "Hydration products of C_3A, C_3S and portland cement in the presence of $CaCO_3$", Cement and Concrete Research, 30, 7, 1073-1077

Kakali, G., Tsivilis, S., Skaropoulou, A., Sharp, J.H. and Swamy, R.N. 2002. "Parameters affecting thaumasite formation in limestone cement mortar." Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 977-981)

Klemm, W. A., and Adams, L. D. 1990. "An Investigation of the formation of carboaluminates," Carbonate Additions to Cement, ASTM STP 1064, P. Klieger and R. D. Hooton, Eds., American Society for Testing and Materials, Philadelphia, 60-72.

Kurdowski, W. and Duszak, S. 2003. "Influence of limestone and fly ash additions to cement that caused expansion of heat-treated mortar due to DEF," Proceedings of 11th International Congress on the Chemistry of Cement, South Africa 1610-1615.

Lipus, K. and Puntke, S. 2003. "Sulphate resistance of concretes with different compositions," Beton Jg., 53, 2, 169-180.

Livesey, P. 1991. "Performance of limestone-filled cements," Blended Cements in Construction, R. N. Swamy, Ed. Elsevier, 1-15.

Matschei, T., Lothenbach, B. and Glasser, F.P. 2007. "The role of calcium carbonate in cement hydration", Cement and Concrete Research, 37, 118–130.

Matthews, J.D. 1989. "Background to the joint working party and scope of programme." In Performance of Limestone-Filled Cements – Proceedings of a Seminar held at BRE in 1989, BR 245, Building Research Establishment, Garston, U.K. (published 1993).

Matthews, J.D. 1994. "Performance of limestone filler cement concrete." In Euro-Cements – Impact of ENV 197 on Concrete Construction, (Ed. R. K. Dhir and M. R. Jones), E&FN Spon, London, pp. 113-147.

Moir, G.K., and Kelham, S., 1997. "Developments in the manufacture and use of Portland limestone cement," ACI Special Publication SP 172-42, pp. 797-819.

Nehdi, M., Mindess, S. and Aïtcin, P-C. 1998. "Rheology of high-performance concrete: Effect of ultrafine particles", Cement and Concrete Research, 28, 5, 687–697.

Nehdi, M. 2000. "Why some carbonate fillers cause rapid increases of viscosity in dispersed cement-based materials", Cement and Concrete Research, 30,10, 1663-1669.

Opoczky, L., 1992. "Progress of particle size distribution during the intergrinding of a clinker-limestone mixture", Zement Kalk Gips, Vol45, 12, 648.

Ramachandran, V.S. and Zhang, C-M. 1988. "Cement with calcium carbonate additions," 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Brazil, VI, 178-182.

Ramachandran, V. S. 1988. "Thermal analysis of cement components hydrated in the presence of Calcium Carbonate," Thermochimica Acta, 127, 385-394.

Rogers, C., Thomas, M. and Lohse, H. 1997. "Thaumasite from Manitoba and Ontario, Canada." Proceedings of the 19th International Conference on Cement Microscopy, Cincinnati, U.S.A.

Sawicz, Z. and Heng, S.S. 1996. "Durability of concrete with addition of limestone powder," Magazine of Concrete Research, 48, 175, 131-137.

Schiller, B. and Ellerbrock, H-G. 1992. "Grinding and properties of cements with several principal constituents", ZKG International, Edition B. 45, 7, 325-34.

Schmidt, M. 1992a. "Cement with interground additives - Capabilities and environmental relief, Part 1." Zement-Kalk-Gips, 45, 2, 64-69 (English part in 45, 4, 87-92.).

Schmidt, M., 1992b. "Cement with interground additives–capabilities and environmental relief, Part 2," Zement-Kalk-Gips, 45, 6, 296-301.

Schmidt, M., Harr, K., and Boeing, R. 1993. "Blended cement according to ENV 197 and experiences in Germany," Cement, Concrete, and Aggregates, 15, 2, 56-164.

Siebel, E. and Sprung, S. 1991. "Influence of limestone in portland limestone cement on the durability of concrete," Beton, 41, 3, 113-117. (In German. English translation by Susan U. Lauer available from PCA Library.)

Sims, I. and Huntley, S.A. 2002. "The thaumasite form of sulfate attack – breaking the rules." Proceedings 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 26, 2004, 837-844).

Smallwood, I., Wild, S. and Morgan, E. 2002. "The resistance of metakaolin-portland cement concrete to the thaumasite-type of sulfate attack-programme of research and preliminary results" Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 931-938)

Soroka, I. and Stern, N. 1976. "Effect of calcareous fillers on sulfate resistance of portland cement," Bulletin of the American Ceramic Society, 55, 6, 594-595.

Soroka, I., and Setter, N. 1977. "The effect of fillers on strength of cement mortars," Cement and Concrete Research, 7, 4, 449-456.

Soroka, I. and Setter, N. 1980. "Effect of mineral fillers on sulfate resistance of portland cement mortars," in Durability of Building Materials and Components, ASTM STP 691, 326-335.

Sprung, V.S, and E. Siebel, E. 1991 "Assessment of the suitability of limestone for producing portland limestone cement", ZKG International, 3, 43-48

Sprung, S., and Siebel, E. 1991. "Assessment of the suitability of limestone for producing portland limestone cement (PKZ)," Zement-Kalk-Gips, 44, 1, 1-11.

Tezuka, Y., D. Gomes, J. Martins and J.G. Djanikian. 1992. "Durability aspect of cement with high limestone filler content." Proc. 9th Int. Congr. On the Chemistry of Cement., New Delhi, India, V, pp. 53–59.

Thaumasite Expert Group 1999. "The Thaumasite form of sulfate attack: Risks, diagnosis, remedial works and guidance on new construction", Report of the Thaumasite Expert Working Group, DETR, London, 180p.

Thomas, M.D.A., Rogers, C.A. and Bleszynski, R.F. 2002. "Occurrences of thaumasite in laboratory and field concrete." Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 1045-1050)

Thomas, M.D.A., Hooton, R.D., Mukherjee, P.K. 1993. "Deleterious effects of fly ash and bottom ash fills on embedded concrete." Proceedings of the Tenth International Ash Use Symposium, Volume 1, EPRI TR-101774, Electric Power Research Institute, Palo Alto, Ca., pp 16.1-16.13.

Torres, S.M., Sharp, J.H., Swamy, R.N., Lynsdale, C.J. and Huntley, S.A. 2002. "Long-term durability of portland limestone cement exposed to magnesium sulfate attack." Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K. (Also, in Cement and Concrete Composites, 25, 8, 2003, 947-954)

Torres, S.M., Lynsdale, C.J., Swamy, R.N., and Sharp, J.H., 2006. "Microstructure of 5 year old mortars containing limestone filler damaged by Thaumasite," Cement and Concrete Research, 36, 384-394.

Trägårdh, J. and Kalinowski, M. 2003. "Investigation of the conditions for a thaumasite form of sulfate attack in SCC with limestone filler," Proceedings, International RILEM Symposium on Self-Compacting Concrete, PRO 33, 844-854.

Tsivilis, S., G. Kakali, E. Chaniotakis, A Souvaridou, 1998. "Study on the hydration of Portland limestone cement by means of TG, Journal of Thermal Analysis and Calorimetry 52 3 863-870

Tsivilis, S. Chaniotakis, E., Badogiannis, E., Pahoulas G. and Ilias, A. 1999a. "A study on the parameters affecting the properties of Portland limestone cements." Cement and Concrete Composites, 21, 2, 107-116

Tsivilis, S., Chaniotakis, E., Batis, G., Meletiou, C., Kasselouri, V., Kakali, G., Sakellariou, A., Pavlakis G. and Psimadas. C. 1999b. "The effect of clinker and limestone quality on the gas permeability, water absorption and pore structure of limestone cement concrete." Cement and Concrete Composites, 21, 2, 139-146

Tsivilis, S., G. Batis, E. Chaniotakis, Gr. Grigoriadis and D. Theodossis. 2000. "Properties and behavior of limestone cement concrete and mortar." Cement and Concrete Research, 30, 10, 1679-1683.

Tsivilis, S. Chaniotakis, E. Kakali, G. and Batis, G. 2002. "An analysis of the properties of Portland limestone cements and concrete" *Cement and Concrete Composites,* Vol. 24, pp. 371-378.

Tsivilis, S. Kakali, G. Skaropoulou, A. Sharp, J.H. and Swamy, R.N., 2003. "Use of mineral admixtures to prevent thaumasite formation in limestone cement mortar," Cement and Concrete Composites, 25, 8, 969-976.

Tsivilis, S., Tsantilas, J., Kakali, G., Chaniotakis, E. and Sakellariou. A. 2003. "The permeability of Portland limestone cement concrete." Cement and Concrete Research, 33, 1465–1471.

Turker, P. and. Erdoğdu, K. 1999. "Effects of limestone addition on microstructure and hydration of cements, Proceedings of the International Conference on Cement Microscopy Ed - Jany, L.; Nisperos, A., 22ND 265-283

Voglis, N., G. Kakali, E. Chaniotakis, S. Tsivilis. 2005 "Portland-limestone cements. Their properties and hydration compared to those of other composite cements." Cement & Concrete Composites, Vol. 27, pp. 191–196.

Vuk, T., V. Tinta, R. Gabrovšek and V. Kauĉiĉ. 2001. "The effects of limestone addition, clinker type and fineness on properties of Portland cement." Cement and Concrete Research, Vol. 31, No. 1, pp. 135-139.

Xiong, X. and K. van Breugel, Hydration Processes of Cements Blended with Limestone Powder: Experimental Study and Numerical Simulation, Cement's Contribution to the Development in the 21st Century Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC) 11 - 16 May 2003, Durban, South Africa, pp. 1983-1992