

The Use of Limestone in Portland Cement: A State-of-the-Art Review

by Peter Hawkins, Paul Tennis, and Rachel Detwiler



Portland Cement Association

EB227



KEYWORDS: limestone, portland cement, admixtures, calcium carbonates, comminution, compressive strength, concrete, durability, flexural strength, hydration, particle size distribution, permeability, quality control, setting, standards, workability, volume change

ABSTRACT: Data from published literature and laboratory tests regarding use of limestone in portland cement are reviewed. Emphasis is placed on amounts of 5% or less. The effects of interground and blended limestone on the particle size distribution of cement and workability of mortar and concrete are reported. Hydration behavior is examined with regard to chemistry, heat evolution, microstructure, and setting time. The properties of hardened mortar and concrete made with limestone portland cement are examined and compared to those made with non-limestone portland cements—including compressive and flexural strength, volume stability, durability (permeability, carbonation, freeze/thaw resistance, sulfate and chloride resistance, and alkali-silica reaction), and interactions with mineral and chemical admixtures. Quality control of the limestone, limestone portland cement, and concrete is also discussed. In general, the use of up to 5% limestone does not affect the performance of portland cement. Strengths of cements with limestone can be optimized by grinding to an appropriate particle size distribution. An optimized portland cement containing up to 5% limestone can exhibit improvements in workability as compared to the same cement without limestone. Energy requirements for both pyroprocessing and comminution are reduced by the use of limestone.

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Table of Contents

KEYWORDS	i	4.0 HARDENED MORTAR AND CONCRETE	13
ABSTRACT	i	4.1 MECHANICAL PROPERTIES	13
REFERENCE	i	4.1.1 Strength and Strength Development	13
1.0 INTRODUCTION	1	4.1.2 Volume Stability	16
1.1 OBJECTIVES.....	1	4.2 DURABILITY	18
1.2 LIMESTONE IN INTERNATIONAL CEMENT STANDARDS	1	4.2.1 Permeability	18
1.3 SCOPE.....	1	4.2.2 Carbonation	19
2.0 PARTICLE SIZE DISTRIBUTION	3	4.2.3 Freeze/Thaw and Deicer Scaling.....	20
2.1 COMMUNUTION.....	3	4.2.4 Sulfate Resistance.....	21
2.2 WORKABILITY OF PASTE, MORTAR, AND CONCRETE	4	4.2.5 Chlorides.....	24
3.0 HYDRATION AND SETTING	7	4.2.6 Alkali-Silica Reactivity.....	25
3.1 CHEMISTRY.....	7	4.3 INTERACTIONS WITH MINERAL AND CHEMICAL ADMIXTURES.....	26
3.2 ANALYSIS OF COMPOSITION.....	8	5.0 SPECIFYING AND MONITORING QUALITY	27
3.3 HEAT EVOLUTION	10	5.1 LIMESTONE.....	27
3.4 MICROSTRUCTURE.....	10	5.2 CEMENT WITH LIMESTONE.....	28
3.5 SETTING TIME	11	5.3 CONCRETE	29
		6.0 SUMMARY AND CONCLUSIONS	31
		7.0 REFERENCES	33

CHAPTER 1

Introduction

1.1 OBJECTIVES

The purpose of this report is to review and summarize technical information on the use of limestone in portland cement. This review was prepared to substantiate a proposed change to ASTM C 150, "Standard Specification for Portland Cement," to allow up to 5% ground limestone in portland cement. Limestone is currently being used in cements produced throughout the world. For this report, research conducted in the U.S., Canada, and Europe over the past 20 years has been reviewed and summarized. While the primary focus is on cement with up to 5% limestone, in some cases the report contains data based on cements containing higher limestone levels to illustrate specific points.

1.2 LIMESTONE IN INTERNATIONAL CEMENT STANDARDS

The use of up to 5% ground limestone in portland cement has been permitted by the Canadian cement standard since the early 1980s. The CSA standard (CSA 1998) for portland cement, CAN/CSA-A5, defines portland cement as:

"The product obtained by pulverizing clinker consisting essentially of hydraulic calcium silicates to which calcium sulphate, limestone, water, and processing additions may be added at the option of the manufacturer."

Limestone is also provided for in the European standard EN 197-1 (CEN 2000) which allows cements to contain limestone in three different dosage levels. CEM I, "Portland cement," may contain up to 5% minor additional constituents, of which limestone is one possible

material. CEM II/A-L and CEM II/B-L, both called "Portland limestone cement," contain 6% to 20% and 21% to 35% ground limestone, respectively. Roughly 19% of all cement sold in Europe contains between 6% and 35% limestone (CEMBUREAU 2001). The requirements specified for limestone use pertain to effects on performance only and will be discussed in Section 5.1.

A review of *Cement Standards of the World* (CEMBUREAU 1991) shows that more than 25 countries allow the use of between 1% and 5% limestone in their P ("Portland") cements. Many countries also allow up to 35% replacement in PB ("Portland composite") cements. Since 1991, the latest edition of *Cement Standards of the World*, several countries have modified their standards to permit limestone in some amount, including Australia, Italy, New Zealand, and the United Kingdom.

1.3 SCOPE

This report contains a summary of research into portland cement interground or blended with limestone. Major topics covered include the effects of limestone use on the particle size distribution of the cement, including the effects on grinding and workability; the hydration and setting of the cement, including effects on reaction chemistry and kinetics, the Bogue calculation, heat evolution, microstructure, and setting time; the properties of mortars and concrete, including physical properties, durability, effects of mineral and chemical admixtures; and quality control aspects of the limestone, cement, and concrete. Emphasis has been placed on providing data from well-documented sources from published literature and test reports from laboratory studies.

CHAPTER 2

Particle Size Distribution

2.1 COMMINUTION

According to Schiller and Ellerbrock (1992), the characteristics of cements comprising several components are influenced by both the particle size distributions and the chemical-mineralogical compositions of the component materials. Since interground limestone often participates to a lesser extent or not at all in the hydration reactions, cements of the same fineness that contain significant quantities of interground additives will have lower strengths than corresponding cements without these additives, due partly to dilution and partly to a concentration of the clinker in the coarser particle fractions. The loss in strength may be compensated for either by a strength increase resulting from the narrower particle size distribution of the clinker fraction (the result of intergrinding with a more easily ground material such as limestone), or by overall finer grinding of the cement. Schmidt (1992a) reports that for levels of limestone between 5% and 10%, cement and concrete strengths are not normally reduced; thus finer grinding may not be necessary. However, Hawkins' (1986) data illustrate that in some cases finer grinding may be needed at low limestone contents (see Section 4.1.1). For cement near the AASHTO M 85 fineness limit ($400 \text{ m}^2/\text{kg}$), finer grinding may not be an option.

Sprung and Siebel (1991) point out that in portland limestone cements (CEM II), the saving of fuel energy that comes about by substituting limestone for some of the clinker is partially offset by the additional electrical energy required for the finer grinding to produce a cement with the same strength as the same cement without limestone. However, CEM II cements contain up to 30% limestone. The data of Schiller and Ellerbrock (1992) indicate that at the 5% level, the amount of additional finish grinding energy is less than 2 kWh/t . This increase would be more than offset by other savings in energy (Nisbet 1996), estimated to be on the order of 75 kWh/t .

In their study of the comminution of cements comprising several constituents of varying grindability, Schiller and Ellerbrock (1992) found that the particle size

distributions of any one constituent is greatly influenced by the grindabilities of the others. Material which is harder to grind becomes concentrated in the coarser fractions, while material which is easier to grind becomes concentrated in the finer fractions. Fig. 1 shows the particle size distributions of a portland limestone cement and its two individual constituents after intergrinding in an industrial ball mill. The particle size distribution of the clinker, which is harder to grind, is narrower, with a slope (n) equal to 1.1 on a Rosin-Rammler-Sperling-Bennett (RRSB) diagram. That of the more easily ground limestone, on the other hand, is wider, with a slope of 0.7. In addition, the position parameter (x') of the limestone fraction is $5 \mu\text{m}$, while that of the clinker fraction is $25 \mu\text{m}$. The position parameter is defined as the equivalent spherical diameter which 38.6% by mass of the material is coarser than, a measure of the fineness of the material. For the purposes of quality control of cement production, a

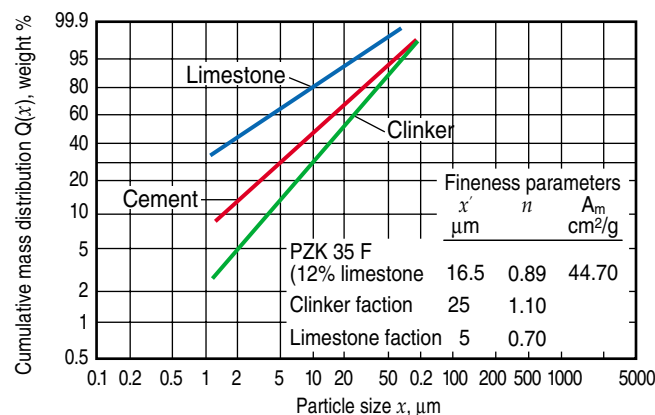


Figure 1. Cumulative mass distributions of a portland limestone cement with a limestone content of 12% by mass, as well as of the two individual constituent materials after intergrinding in an industrial ball mill (after Schiller and Ellerbrock, 1992).

similar relation would be determined for the specific materials in the specific proportions to be used, ground in the particular mill where they were to be produced, since the relative grindabilities and proportions of the materials and the specific grinding process all influence the outcome. According to Schiller and Ellerbrock (1992), to produce cements having a 28-day strength of 50 MPa, the position parameter would be reduced from 30 μm for a plain portland cement to 26 μm for a 10% limestone cement and to 14 μm for a 20% limestone cement.

Moir (1995) points out that in modern milling systems equipped with high efficiency separators, the particle size distributions are steeper than with conventional separators. This narrow particle size grading may result in increased bleeding and delays in initial setting time. The inclusion of up to 5% limestone broadens the particle size grading, offsetting these disadvantages. He cites the example of a cement plant which converted from an open circuit mill to a closed circuit mill with high efficiency separator in 1992. In this case interground limestone in the amount of 4.1% was required to control the strength while optimizing the rheological and setting behavior. The limestone in the cement is concentrated in the 5 to 20 μm size fraction.

Limestone need not be interground with the clinker, although dry blending produces a somewhat different particle size distribution. In a 1993 Building Research Establishment (BRE) study, the average specific surface of the cements increased from 300 to 350 m^2/kg and the 45 μm residue from 13.8% to 15.8% when 5% limestone was interground with the clinker (Jackson 1993). When cements were dry blended with 5% limestone, the specific surface increased from 395 to 486 m^2/kg and the 45 μm residue decreased from 12.0% to 10.8%. The authors caution that if the limestone is to be incorporated by blending rather than by intergrinding, it must be ground to an appropriate level of fineness to achieve a minimum water demand. Sprung and Siebel (1991) found that separate grinding of the limestone samples they studied in a batch-operated ball mill generally led to very wide particle size distributions with RRSB diagram gradients (n) of less than 0.9, and sometimes even less than 0.8. They observed that the wide particle size distribution with a high proportion of fines resembles the particle size distributions normally found in the limestone fraction of interground portland limestone cement. Ménétrier-Sorrentino (1988), however, implied that separate grinding of the constituents of portland limestone cements offers greater opportunity for optimization of the particle size distribution of the individual materials. She points out that the concentration of the clinker in the larger particle fractions may not allow the best use of the material, particularly for the development of early strength.

2.2 WORKABILITY OF PASTE, MORTAR, AND CONCRETE

Sprung and Siebel (1991) point out that particle size distribution has a considerable influence on the water demand of a cement. Narrow particle size distributions with RRSB gradients (n) greater than 1 generally result in high water demand, while wide particle size distributions lead to reduced water demand (Detwiler 1995). The easily ground limestone usually has a wide particle size distribution which allows the limestone particles to fill the gaps between the clinker particles, reducing the water demand and densifying the structure of the hardened cement paste. These physical effects apparently more than compensate for any surface effects that would tend to increase the water demand associated with the finer material. According to Sprung and Siebel (1991), this densifying effect can lead to increased strengths when the limestone content is less than 10%. They also found that water demand was related to the clay content of the limestone: If the methylene blue value (CEN 1998—discussed in Section 5.1 of this report) of a limestone was high, the water demand would be higher than would be expected from the particle size distribution alone.

The relationship among particle size distribution, strength, and water demand is well established. Schiller and Ellerbrock (1992) observed that portland cements having the same specific surface harden faster, but have higher water demands the narrower their particle size distributions. They studied portland limestone cements made by both intergrinding and blending the component materials. In one experiment they mixed ground clinker with a position parameter (x') equal to 20 μm and slope (n) equal to 0.88 with two different limestone meals having the same Blaine fineness of 580 m^2/kg , but different particle size distributions. The portland limestone cements having limestone contents of 10%, 20%, and 30% all had Blaine finenesses of about 390 m^2/kg . In quantities of up to 10%, the use of limestones, with either narrow or wide particle size distributions, decreased the water demand of the cement. Since both limestones had different particle size ranges than the clinker, mixing either of them with the clinker broadened the total particle size distribution. In greater quantities, the limestone with the wider particle size distribution continued to reduce the water demand of the cement, while that with the narrower particle size distribution increased the water demand. They also found that even when portland limestone cement had to be ground finer in order to achieve the same strength as portland cement made from the same clinker, the water demand was lower because of the improved particle size distribution.

Tezuka et al. (1992) found that the workability of mortars of different cement contents improved with the use of limestone even at 5% levels. This translated to a reduction in water:cement ratio from 0.49 to 0.48 to

achieve a constant consistency. Ground quartz added in the same proportions increased the water demand. They attribute the beneficial effect of limestone to a more favorable particle size distribution which better complements that of the clinker. Similarly, Brookbanks, reporting results from the Building Research Establishment study (1993), stated that replacing 5% of the cement with limestone dust or dried silt from a gravel aggregate increased the required water:cement ratio of concrete by an average of 0.01 and 0.02, respectively, over that required when a factory-made limestone-filled cement was used. This illustrates the advantage of optimizing the particle size grading of the limestone.

In a study of cements containing up to 15% of a limestone having a relatively high CaCO_3 content, Neto and Campiteli (1990) found that in two-point measurements of the consistency, the yield point values were decreased and the plastic viscosity slightly increased by the presence of limestone, especially for the finer cements. In practical terms, this means that the mortar is somewhat stiffer and more inclined to stay in place, but less viscous and more easily consolidated by vibration.

Sprung and Siebel (1991) found that for concretes made according to the same mix design, those made with portland limestone cement were less stiff than those made from portland cements. In concrete, once surface forces are neutralized by a water-reducing admixture or superplasticizer, the water requirement is not a function of surface that must be wetted, but of interparticle space that must be filled. Schmidt (1992a) explains the beneficial effect of limestone on concrete rheology in terms of improvements in the particle size distribution: The fine particles displace some of the water from the voids between the coarser particles, making it available as an additional "internal lubricant." Thus the concrete is less stiff and water retention is improved. The effect is further reinforced if the hydration reactions are retarded so that less water is chemically combined due to the inertness of the limestone fraction. The latter effect will depend on the fineness and proportion of limestone in the concrete. Since less water is needed to make a workable mix, the water content can be reduced so that the strength is increased. Schmidt et al. (1993) cite the example of concretes having the same consistency. Those made with portland limestone cements (13% to 17% limestone) required about 10 l/m^3 less water, so that the water:cement ratio was reduced from 0.60 to 0.57 and the strength increased by as much as 8 MPa. Moir (1995) found that water demand in concretes made from portland cements with and without 5% limestone was not affected by the presence of limestone in normal and rich mixes, but was reduced in lean mixes. Brookbanks, reporting work done in the Building Research Establishment study (1993), found similar results. His data are shown in Table 1.

Finely ground limestone has long been used in masonry cements to improve the retention of water in the

Table 1. Water:Cement Ratio to Achieve 60-mm Slump (Brookbanks 1993)

Cement content, kg/m^3	0% Limestone	5% Limestone
225	0.92	0.89
300	0.60	0.60
350	0.52	0.52

mortar. Schmidt (1992a) studied the bleeding in mortars made with portland cement and portland limestone cement. After two hours standing time, the amount of bleed water from the portland limestone cement mortar was less than half that from the portland cement mortar.

Albeck and Sutej (1991) report the development of a portland limestone cement for strength class 35. Because of the high quality of the clinker used, the portland cement PZ 35 F had to be ground coarsely in order not to exceed the strength limit. By intergrinding 18% limestone (CaCO_3 content of 90.8%) with the clinker they were able to produce a portland limestone cement (PKZ 35 F) meeting the strength requirements. They measured the bleeding for a series of concretes and found that those made with PKZ 35 F always exhibited less bleeding and stopped bleeding sooner than those made with PZ 35 F. The coarser the sand used, the more significant the difference between the two cements. Their data are shown in Table 2.

In mass concrete, Kanazawa et al. (1992) found that finely ground limestone improved the workability, reduced bleeding, and aided in the development of early strength. This concrete mix also contained finely ground blast furnace slag. Because of the need to minimize heat generation, setting times were delayed, with the result that any tendency to bleed is exacerbated. The fine aggregate used was sea sand. In preparing this type of aggregate, the washing that is necessary to remove the salt also removes the finest sand fraction. The finely ground limestone replaced these fines, effectively controlling bleeding.

In studies of 5% limestone portland cements, Moir (1995) found that bleeding in concrete is related only to the cement surface area independent of the presence of limestone. That is, the effect of limestone at low concentrations is purely a physical one related to particle packing and surface forces. Brookbanks, reporting results from the Building Research Establishment study (1993), showed improvements in the bleeding characteristics of concretes made with cements containing 5% limestone over those made with cements of the same strength class without limestone. His data are summarized in Table 3. It should be noted that these two researchers are not reporting conflicting results. Moir is keeping surface area constant, while Brookbanks is not.

Table 2. Bleeding of Fresh Concrete, kg bleed water/m³ concrete (Albeck and Sutej, 1991).

Sand	Cement	0.5 h	1.0 h	1.5 h	2.0 h	2.5 h	3.0 h
Oberrhein	PZ 35 F	6.2	9.7	11.3	12.3	13.2	13.8
	PKZ 35 F	3.0	5.9	8.3	9.8	11.0	11.8
Pleinfeld	PZ 35 F	5.8	11.5	13.7	14.4	15.1	15.8
	PKZ 35 F	2.9	5.5	7.4	8.3	8.8	—
München B	PZ 35 F	4.8	7.4	9.0	9.9	8.6	10.1
	PKZ 35 F	4.0	5.5	6.4	6.8	6.9	—
Donau	PZ 35 F	6.0	8.3	9.1	9.9	10.2	11.0
	PKZ 35 F	2.6	4.3	5.3	5.5	—	—
München R	PZ 35 F	3.2	5.3	6.6	7.7	8.2	8.4
	PKZ 35 F	3.4	4.2	5.4	6.1	6.4	6.6
Standard	PZ 35 F	3.9	6.4	7.5	8.2	8.4	8.9
	PKZ 35 F	2.6	4.2	5.3	5.8	6.4	7.0
Allgäu	PZ 35 F	2.3	4.5	6.5	8.0	9.2	10.0
	PKZ 35 F	2.1	3.7	5.2	6.2	6.9	—

“—” indicates data not reported.

Table 3. Average Bleeding Characteristics for Concretes With and Without 5% Limestone in Cement (Brookbanks 1993)

	0% Limestone	5% Limestone
Bleeding rate, cm/min. x 10 ⁴	43	22
Bleeding capacity, ml/cm ²	0.27	0.18
Total bleed water, % by mass	10.0	6.5

Vuk et al. (2001) also noted a slight reduction (0.5%) in water demand with the use of 5% limestone and noted that the more important parameter influencing water demand was cement fineness.

CHAPTER 3

Hydration and Setting

3.1 CHEMISTRY

Ingram et al. (1990) studied cement pastes made from various proportions of Type I clinker, limestone, and gypsum and hydrated in sealed vials for 1, 3, 7, 14, and 28 days. X-ray diffraction showed that for a combination of 2% gypsum, 6% limestone, and 92% clinker, the CaCO_3 reacts with the C_3A in the clinker. (Care was taken to avoid exposing the pastes to atmospheric CO_2 .) They believe that the reaction begins with a $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 12\text{H}_2\text{O}$ product which with continued hydration forms compounds containing a molar ratio of C_3A to CaCO_3 between 0.5 and 0.25. At later stages, the product appears to stabilize as $\text{C}_3\text{A} \cdot X \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$, where X ranges from 0.5 to 0.25. During the course of this reaction ettringite formation proceeds normally.

Klemm and Adams (1990) studied the reaction of 5% or 15% calcium carbonate (either as reagent grade CaCO_3 or as ground limestone) and Type II cement with hydration times up to one year. They found that crystalline monocarboaluminate hydrate is slower to form than ettringite, and after 129 days of hydration, 80% to 90% of the limestone or calcium carbonate remains unreacted. They concluded that with Type II cements limestone acts primarily as an inert diluent. Based on the solubility products of the possible reaction phases, they predicted that the most stable reaction phase would be ettringite, followed by monocarboaluminate and then monosulfaluminate. Barker and Cory (1991) found monocarbonate forming in preference to monosulfate. They also found that for cement with higher C_3A contents the amount of monocarbonate increases at all ages with increasing levels of limestone as compared with cements having lower C_3A contents.

Feldman et al. (1965) found that the hydration of 90% pure C_3A is suppressed by CaCO_3 due to the formation of the low form of calcium carboaluminate ($\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$) on the surface of the C_3A grains. They concluded that C_3A reacts with CaCO_3 by a direct mechanism. Bensted (1980) found that in the absence

of gypsum, C_3A reacts with CaCO_3 in limestone to form both “hexagonal prism” phase tricarboaluminate $\text{C}_3\text{A} \cdot 3\text{CaCO}_3 \cdot 30\text{H}_2\text{O}$ and the “hexagonal plate” phase monocarbonate $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot 11\text{H}_2\text{O}$. In portland cement, ettringite is formed during early hydration, with monosulfate becoming significant only after the first 16 hours of hydration, when the concentration of sulfate ions is not sufficient for the formation of ettringite. Tricarboaluminate is much less stable than ettringite at ambient temperatures; thus tricarboaluminate does not form in cement hydration. Bensted examined the possibility of substituting limestone for some or all of the gypsum used to control the early hydration of C_3A and concluded that because of differences in their stereochemistry, sulfate ions enter more readily than carbonate ions into solid solution. Thus sulfate ions are more effective in controlling setting than carbonate ions. However, he concluded that in a given system it is possible to substitute limestone for 25% or even 50% of the gypsum without deleterious effect. The exact amount of substitution depends on the cement. Kantro (1978) found that limestone at 500 m^2/kg Blaine has some effect on the setting of cement, but is less effective than gypsum in controlling flash set. For high-sulfate clinker, however, times of set were not markedly different from those for cements in which the gypsum content was optimized.

Campitelli and Florindo (1990) examined the effects of limestone content and cement fineness on the optimum sulfate content of cement according to ASTM C 563. They found that optimum SO_3 increases with increasing fineness and decreases with increasing limestone content, but neither relationship is linear. They explain the results by noting that when part of the clinker is replaced by limestone, the coarser fractions of the interground cement will consist primarily of clinker, while limestone will be concentrated in the finer fractions. Thus when comparing cements with the same specific surface, replacing clinker with limestone implies coarser – and thus slower reacting – clinker particles.

Sprung and Siebel (1991) consider that the calcite from limestone participates only to a small extent, if at all, in the hydration reactions, primarily on the surface of the limestone particles. Thus in practice the limestone should be considered an inert material.

It is important to note that even a chemically inert material can have significant physical effects. The effects of improved particle packing on water demand and of increased surface area on bleeding have been noted in Chapter 2. An important physical effect on hydration is the provision of nucleation sites for the hydration products. Sellevold et al. (1982) found that the presence of nucleation sites accelerates the hydration of the cement. Livesey (1991b) also found that the use of 5% limestone resulted in an acceleration of the early hydraulic activity of the clinker. In their study of cements containing 0% to 35% limestone, Tezuka et al. (1992) found that the hydration of the cement during the first seven days was accelerated by the presence of blended limestone except at the 35% level. Their control cement had a C₃A content of 6% and a specific surface area of 339 m²/kg. Limestone finenesses were 350, 450, and 550 m²/kg. Soroka and Setter (1977) also found evidence of an acceleration effect due to the presence of limestone. Ramachandran and Zhang (1988) obtained a similar result even for 5% CaCO₃. Soroka and Stern (1976) also found evidence of an acceleration effect due to the increased number of nucleation sites.

Barker and Cory (1991) observed that the formation of calcium hydroxide and ettringite is enhanced at early ages in cements containing 5 and 25% limestone. They studied specimens hydrated for 1, 2, 4, 7, 28, 90, and 180 days using X-ray diffraction and TGA. They normalized their measured values to the clinker content in order to eliminate the dilution effect. They found that for 5% limestone, the amount of calcium hydroxide at 1 day was greater than for the parent cement, but after 2 days the calcium hydroxide contents were similar for the two cements. For the 25% limestone cements the amount of calcium hydroxide was generally similar, most likely because the finenesses of the cements were similar.

In contrast to the results of Sprung and Siebel (1991) who considered limestone to be inert, Stark, Freyburg, and Löhmer (1999) found that monocarboaluminate forms when C₃A or C₄AF reacts in the presence of 6% sulfate and 3% or 6% limestone. The difference may be attributed to the fineness of the limestones used; Stark, Freyburg, and Löhmer used a range of limestone finenesses from 680 to 1,370 m²/kg (Blaine) and noticed an increase in reactivity with finer limestones. Accelerated hydration of C₃S, C₃A, and C₄AF was also noted. Péra, Husson, and Guillhot (1999) also observed an acceleration of C₃S hydration using between 10% and 50% limestone at 680 m²/kg.

3.2 ANALYSIS OF COMPOSITION

The Bogue calculation is a means of estimating the amount of the dominant minerals available in a cement, based on its oxide composition. It assumes that equilibrium is achieved in the cement kiln and the compounds (C₃S, C₂S, C₃A, and C₄AF) have an ideal stoichiometry – assumptions that are often inaccurate (e.g. Taylor 1997). The effects of free lime, magnesia, and alkalis can also significantly affect the compositions.

However, knowing the potential phase compositions is important to assessing the properties of the cement. ASTM C 150 specifies an upper limit on the amount of C₃A for all but Type I and IA cements. For Type IV cements, there is also an upper limit on the amount of C₃S and a lower limit on the amount of C₂S. The Bogue equations used in ASTM C 150 are:

$$C_3S = 4.071 \text{ CaO} - 7.600 \text{ SiO}_2 - 6.718 \text{ Al}_2\text{O}_3 - 1.430 \text{ Fe}_2\text{O}_3 - 2.852 \text{ SO}_3$$

$$C_2S = 2.867 \text{ SiO}_2 - 0.7544 \text{ C}_3\text{S}$$

$$C_3A = 2.650 \text{ Al}_2\text{O}_3 - 1.692 \text{ Fe}_2\text{O}_3$$

$$C_4AF = 3.043 \text{ Fe}_2\text{O}_3$$

The 2.852 SO₃ term in the C₃S equation is used to correct the calculation for the amount of gypsum and thus does not apply to calculations for clinker. These equations apply for A/F ≥ 0.64. The rare case for which A/F < 0.64 will be ignored here; Gebhardt (1995) reports only 3 cases out of 387 cements meeting this criterion.

The effect that limestone will have on the calculated Bogue compositions depends on the oxide composition of the limestone itself. Table 4 shows analyses for several limestones and the apparent Bogue compound calculation for each. Note that the apparent Bogue compounds for limestone are fictional as the material is not pyroprocessed. It can be seen that the effect of incorporating limestone is to increase the apparent C₃S content and decrease the C₂S content. There is a very slight increase in apparent C₃A content. Thus, the effect of using 5% limestone on a typical portland cement is to raise the apparent (Bogue-calculated) amounts of C₃S and C₃A, while reducing the apparent C₂S content. As ASTM C 150 specifies maxima for C₃S and C₃A and minima for C₂S, the use of limestone, in effect, “forces” the cement to be further within the limits if no correction is made to the Bogue calculation for the cement with limestone. Table 5 gives examples of this effect for 2.5% or 5% limestone on average Type II and Type IV cements, those with the strictest limits on composition. Note that the corrected (including only pyroprocessed material) amount of C₃S accounts for the limestone content and thus is lower than the apparent value. Likewise, the corrected C₂S content is higher than the apparent value. The effect on the C₃A contents is negligible. If the apparent values, as estimated by the Bogue equations (without correction for limestone content), are within the values specified by ASTM C 150,

Table 4. Typical Limestone Compositions and Apparent Bogue Compositions

Limestone	A	B	C	D	E
SiO ₂	4.00	13.60	2.00	12.05	2.96
Al ₂ O ₃	0.77	2.50	0.80	3.19	0.79
Fe ₂ O ₃	0.30	0.90	0.20	1.22	0.30
CaO	51.4	43.4	52.9	43.5	52.3
MgO	1.30	3.20	0.90	1.68	1.30
SO ₃	0.10	0.10	0.20	0.56	0.03
LOI	42.0	35.6	42.5	36.21	42.18
Na ₂ O	0.01			0.12	0.04
K ₂ O	0.02	0.60	0.20	0.72	0.23
Total	99.9	99.6	99.7	99.25	100.13
Apparent values					
C ₃ S	173.0	55.0	155.9	60.7	184.6
C ₂ S	-119.0	-2.5	-111.9	-11.3	-130.8
C ₃ A	1.5	5.1	1.5	6.4	1.6
C ₄ AF	0.9	2.7	0.6	3.7	0.9
Source	Moore 1996	Bayles 1985	Bayles 1985	Klieger 1985	Klieger 1985

Table 5. Effect of Limestone¹ on Average² Type II and Type IV Cements' Bogue Calculation³

Bogue phase	Average cement: apparent	With 2.5% limestone: uncorrected ⁴	With 2.5% limestone: corrected ⁵	With 5% limestone: uncorrected ⁴	With 5% limestone: corrected ⁵
Type II, Limestone "R"					
C ₃ S	53	53	52	54	50
C ₂ S	21	20	20	19	20
C ₃ A	6	6	6	6	6
C ₄ AF	11	10	11	10	10
Type IV, Limestone "R"					
C ₃ S	41	42	40	43	39
C ₂ S	33	31	32	30	31
C ₃ A	4	4	4	4	4
C ₄ AF	15	15	15	15	14
Type II, Limestone "Q"					
C ₃ S	53	57	52	60	50
C ₂ S	21	16	20	13	20
C ₃ A	6	6	6	6	6
C ₄ AF	11	10	11	10	10
Type IV, Limestone "Q"					
C ₃ S	41	45	40	49	39
C ₂ S	33	28	32	24	31
C ₃ A	4	4	4	4	4
C ₄ AF	15	15	15	15	14

¹ Limestone data taken from Klieger 1985.² Gebhardt 1995.³ Per ASTM C 150.⁴ Based on weighted average of oxide compositions.⁵ Apparent Bogue composition corrected for limestone content.

then the corrected values will also be within the limits. Any error introduced by not correcting for the presence of limestone will be on the conservative side.

Other relevant ASTM C 150 limits are the maximum loss on ignition (LOI) of 3.0% (2.5% for Type IV) and the maximum insoluble residue (IR) of 0.75%. Pure calcite, CaCO_3 , the major component of limestone, has an LOI value of 44.0% (and an IR of 0.0%). Table 4 shows that the LOI of some limestones is as low as 35%. A 5% limestone content would increase the LOI by between about 1.7% and 2.2%. Since the average cement of any type has an LOI of more than 1.0% (see Table 6), the 3.0% limit could be

Table 6. Average Characteristics of Portland Cements (Gebhardt 1995)

	Loss on ignition	Insoluble residue
Type I	1.39	0.26
Type II	1.15	0.27
Type III	1.31	0.25
Type IV	1.18	0.21
Type V	1.02	0.25

exceeded if 5% is used. For many cements, this effectively places an upper limit on the maximum amount of limestone that can be used in ASTM C 150 cements.

Natural limestone is not pure calcite and can contain appreciable quantities of clays and other minerals, with insoluble residues of up to 30%. If a typical cement has an insoluble residue of 0.25% (Gebhardt 1995), then at a 5% limestone content, the insoluble residue of the limestone would be limited to about 10% in order not to exceed the insoluble residue limit in ASTM C 150. Thus the insoluble residue limit in ASTM C 150 also limits the maximum limestone usage.

3.3 HEAT EVOLUTION

Hooton (1990) obtained commercial cements from plants producing ASTM and CSA cements from the same clinker. He determined the 7-day values for heat of hydration according to ASTM C 186 and found that there was no consistent effect of limestone on heat of hydration: In one case the heat of hydration was unchanged, in one case higher, and in one case lower.

Albeck and Sutej (1991) found that the heat of hydration of the portland and portland limestone cements of the same strength grade were 290 and 280 J/g, respectively, since the finer grinding of the portland limestone cement compensated for the reduced clinker content.

Barker and Matthews, reporting results from the Building Research Establishment study (1993), discuss

isothermal conduction calorimetry and simulated large pour data for cements containing 5% limestone. They found that in general the use of 5% limestone tends to reduce the peak rate of heat evolution. However, its effect on the timing of the peak depends on the method of preparation of the limestone cements. Those prepared by blending show either no effect or some retardation, while those prepared by intergrinding (usually also having higher finenesses than the parent cements) show an acceleration of peak heat evolution. The cement prepared with a limestone having a high clay content retarded the peak heat evolution. In general, the total heat evolved is reduced by the presence of limestone. However, Ramachandran and Zhang (1988), using a 12.8% C_3A cement and reagent grade CaCO_3 with a nitrogen surface area of $6.5 \text{ m}^2/\text{g}$, found that the CaCO_3 increases the total heat evolved. Ramachandran (1988) also found that the total heat evolved in a C_3S paste in the first 24 hours increased with increasing CaCO_3 contents.

Livesey (1991a) determined the heat release characteristics of concretes made from cements having various limestone contents by isothermal conduction calorimetry. Increasing limestone content reduced both the rate and total amount of heat released. Where cements were of a similar fineness to that of the parent cement without limestone, the introduction of limestone retarded the maximum heat evolution, but where the limestone cements had greater fineness they accelerated heat evolution. He found a good correlation between concrete strength grade (28 days) and the temperature rise, regardless of cement type.

Vuk et al. (2001) found heat of hydration to be similar in cements with and without 5% limestone after 3 days, but for higher fineness cements (on the order of 400 to $440 \text{ m}^2/\text{kg}$ compared to cements on the order of 300 to $370 \text{ m}^2/\text{kg}$), a slight drop in heat of hydration of cements with 5% limestone relative to the control was noted.

3.4 MICROSTRUCTURE

In a study of the effects of silica fume on the hydration and pore structure of cement paste, Sellevold et al. (1982) used CaCO_3 having the main body of the particles smaller than $0.1 \mu\text{m}$ as one of the controls. They compared mercury intrusion data for mature pastes with and without 12% CaCO_3 . The specimens containing CaCO_3 had finer pore structures and somewhat reduced total pore volume. They attribute this observation to the nucleation effect: The introduction of a large number of nucleation sites could result in a more homogeneous distribution of calcium silicate hydrate and thus a less open pore structure. The effect appears to be in the capillary pore structure rather than in the gel pores.

Barker and Cory (1991) observed that use of 25% limestone influences both the size and distribution of calcium hydroxide deposits in cement paste. They found

that in ordinary portland cement paste small regions of calcium hydroxide are evenly distributed throughout the paste, while in the limestone-filled pastes larger regions of calcium hydroxide were unevenly distributed throughout the paste. Use of 5% limestone had little effect on the size or distribution of calcium hydroxide deposits. They also found that limestone added in amounts of 5% or 25% enhance the formation of hydration rims of calcium silicate hydrate surrounding C_3S particles because they increase the rate of hydration of C_3S . Increasing levels of limestone increased the formation of ettringite at early ages. The amount of ettringite then decreased slowly as hydration proceeded. They did not observe any monosulfate.

3.5 SETTING TIME

Hooton (1990) obtained commercial cements from plants producing ASTM and CSA cements from the same clinker

Table 7. Vicat Setting Times for ASTM and CSA Cements (Hooton 1990)

Cement	CaCO ₃ , % (TGA)	Initial set, minutes	Final set, minutes
1 (10.3% C ₃ A) 1c	0.3 4.1	175 167	355 323
2 (9.1% C ₃ A) 2c	0.8 4.7	134 119	283 224
3 (8.3% C ₃ A) 3c	0.3 2.6	153 170	294 340

and analyzed the CaCO₃ content by TGA. His data for ASTM C 191 setting times are shown in Table 7. There is no clear trend for the effect of limestone on setting times.

Hawkins (1986) conducted two test series. In the first, clinker and gypsum were ground in a laboratory ball mill with 0%, 3%, 5.5%, and 8% limestone to a more or less constant Blaine fineness. The use of limestone appears to have little effect on the setting time. In the second series, the procedure was repeated with 0%, 2%, 5%, and 8% limestone, except that the <325 mesh value was kept more or less constant. This series indicates a reduction in setting time with the use of limestone. In all tests a Type II low-alkali clinker with a C₃A content of 5.1% and a limestone having 85% CaCO₃ were used. The SO₃ content was maintained at 2.5%. His data are given in Tables 8 and 9 below.

A decrease in Vicat setting time was noted by Vuk et al. (2001) with use of 5% limestone in cements made from two different clinkers: Initial setting was reduced by 50 minutes with a clinker C₃S content of 35% and by 25 minutes with a clinker C₃S content of 46%. The authors note that the effects of clinker composition were less significant when the cement fineness was higher.

Bobrowski et al. (1977) indicate that false set is reduced considerably when limestone is used as a partial substitution for gypsum, and that the setting time was not markedly affected. Samples with and without limestone were heated to 280°C for 16 hours to force the base system to false set. The sample with limestone reacted much better, as indicated in Table 10. The system with limestone had less gypsum available to dehydrate upon heating (as might occur in finish grinding); therefore the tendency to false set might be expected to be less. However, appropriate control of C₃A reaction was observed in this study.

Table 8. Vicat Setting Times for Interground Cements at Constant Blaine (Hawkins 1986)

% Limestone by mass of total cement	0.0	3.0	5.5	8.0
< 325 mesh, % by mass	90.0	85.5	81.0	82.4
Blaine, m ² /kg	371	351	346	364
Initial setting time	2:40	2:50	2:50	2:45
Final setting time	5:00	5:00	4:55	4:50

Table 9. Vicat Setting Times for Interground Cements at Constant <325 Mesh (Hawkins 1986)

% Limestone by mass of total cement	0.0	2.0	5.0	8.0
< 325 mesh, % by mass	94.7	91.9	91.2	91.6
Blaine, m ² /kg	390	387	433	470
Initial setting time	3:20	2:25	2:30	2:20
Final setting time	5:10	4:05	4:00	3:50

Table 10. Use of Limestone Substitution to Reduce False Set (Gilmore) (Bobrowski et al. 1977)

	Base sample 4.5% gypsum	Test sample 1.75% gypsum + 2.25% limestone
Blaine surface area (m ² /kg)	479	481
SO ₃ (%)	1.96	0.95
Setting time: (min.)		
Full needle	0	58
Initial set	4	147
Final set	217	320
C 359: False set, mortar method		
Initial penetration	50+	50+
5 Minutes	17	50+
8 Minutes	1	47
11 Minutes	0	15
Remix	26	50+

CHAPTER 4

Hardened Mortar and Concrete

4.1 MECHANICAL PROPERTIES

4.1.1 Strength and Strength Development

Hooton (1990) tested three pairs of cements made from the same clinker with and without interground limestone conforming to the CSA limits. His data for the compressive strengths of mortar cubes are given in Table 11.

Albeck and Sutej (1991) showed that the strength development of their commercial portland cement (PZ 35 F) and portland limestone cement (PKZ 35 F) made from the same clinker to the same strength class (Blaine fineness of about 400 m²/kg) over the period January 1989 to May 1990 were quite similar, with the variability similar or somewhat lower for the portland limestone cement. Their data are shown in Table 12.

Hawkins (1986) conducted two test series. In the first, clinker and gypsum were ground in a laboratory ball mill with 0%, 3%, 5.5%, and 8% limestone to a more or less constant Blaine fineness. In the second series, the procedure was repeated with 0%, 2%, 5%, and 8% limestone, except that in this series the <325 mesh value was kept more or less constant. In all tests a Type II low-alkali

clinker with a C₃A content of 5.1% and a limestone having 85% CaCO₃ were used. The SO₃ content was maintained at 2.5%. His data are given in Tables 13 and 14. They show that with the fineness increase, limestone cements give comparable strengths.

Bédard and Bergeron (1990) studied the effect of carbonate use on the strength of heat-cured concrete. Two CSA Type 30 cements and companion cements with interground limestones from two different sources were used to make the concretes. The dosages of limestone were chosen to suit the chemistry of the cements. The first cement had a C₃A content of 10.4% and was tested with and without 4.1% Limestone A. The second had a C₃A content of 11.6% and was tested with and without 2.3% Limestone B. The particle size distributions of control and test cements were similar in both cases. Fig. 2 shows the strength developments for the concretes in the first 24 hours. The strengths are quite similar. Their data for normal curing are shown in Table 15. In all cases, except the cement with and without Limestone B at 1 day, the differences between the concrete strengths are negligible.

Table 11. ASTM C 109 Mortar Cube Strengths, MPa (Hooton 1990)

Cement	1	1c	2	2c	3	3c
% C ₃ A	10.4	10.0	9.1	9.8	8.3	7.3
% CaCO ₃ (by TGA)	0.3	4.1	0.8	4.7	0.3	2.6
Age						
2 days	27.0	21.4	22.7	21.2	18.5	21.0
3 days	29.3	24.1	26.4	24.2	22.4	24.7
7 days	33.4	28.7	31.5	29.3	27.8	29.0
28 days	40.8	36.4	41.3	36.4	35.0	35.3
16 months	51.1	49.6	45.6	42.1	43.6	45.4

Table 12. Average Strengths and Standard Deviations for Cements Produced at Mergelstetten Plant January 1989 – May 1990, MPa (Albeck and Sutej, 1991)

	Mean	Standard deviation		Mean	Standard deviation
PZ 35 F 2-day strength	24.1	1.59	PKZ 35 F 2-day strength	24.4	1.59
28-day strength	52.0	1.87	28-day strength	50.2	1.61

Table 13. Strengths of Cements at “Constant” Blaine, psi (Hawkins 1986)

% Limestone	0.0	3.0	5.5	8.0
< 325 mesh, %	90.0	85.5	81.0	82.4
Blaine, m ² /kg	371	351	346	364
1 day	930	740	700	680
3 days	2700	2340	2120	2040
7 days	3760	3280	2890	2870
28 days	5150	4590	4070	3940
3 months	5860	5530	5040	4930
6 months	6210	5930	5800	5630
12 months	6430	6270	6050	6000

Table 14. Strengths of Cements for “Constant” < 325 Mesh, psi (Hawkins 1986)

% Limestone	0.0	2.0	5.0	8.0
< 325 mesh, %	94.7	91.9	91.2	91.6
Blaine, m ² /kg	390	387	433	470
3 days	2930	3020	3070	3180
7 days	4010	4020	4160	4100
28 days	5790	5670	5660	5650
3 months	6560	6680	6580	6560
6 months	6320	6620	6580	6430
12 months	6490	6680	6670	6510

Table 15. Compressive Strengths for Concretes Made With Cements With and Without Limestone, MPa (Bédard and Bergeron, 1990)

	Control A	Test A (4.1% limestone)	Control B	Test B (2.3% limestone)
1 day	34.0	34.4	38.4	33.4
7 days	49.3	48.1	52.1	51.7
28 days	56.5	56.0	59.2	57.2
56 days	59.1	62.0	61.4	60.4

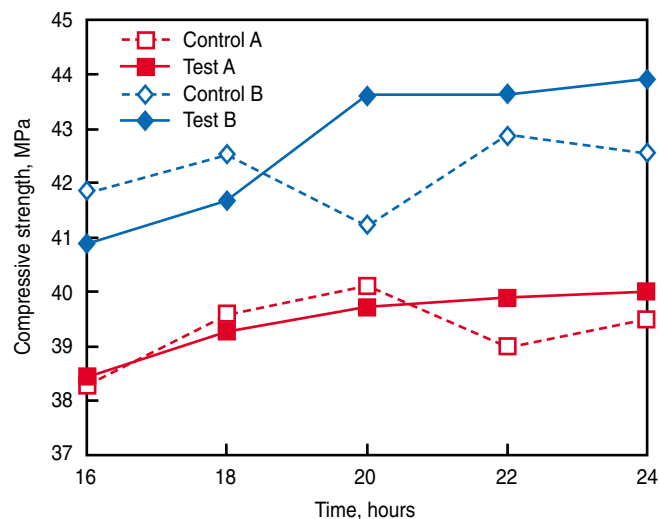


Figure 2. Effect of heat curing on the compressive strength of concretes made with and without limestone. “Test A” contains 4.1% limestone and “Test B” contains 2.3% limestone (after Bédard and Bergeron, 1990).

Sprung and Siebel (1991) found that the use of inert material as a very fine filler can lead to an increase in strength due to improved packing of the particles (i.e., filling of voids between the cement grains). This effect is seen at early ages, but unlike the case with fly ash or other pozzolanic materials, does not produce additional increases in strength with continued curing. When limestone is included in large quantities (15% to 25%) it acts as a diluent, so that strengths are lower than for comparable portland cements. To an extent, the loss of strength due to dilution can be offset by finer grinding. Schmidt (1992a) observed that cement and concrete strengths normally are not reduced by using 5% to 10% limestone. The dilution effect is seen at higher dosages unless the cement is ground finer to compensate. Reductions in the water:cement ratio are often possible because of the improved particle packing; these will further compensate for the dilution effect.

Livesey (1991b) reports an investigation of concretes of constant workability made from cements containing up to 25% limestone. He found that the use of 5% limestone had little effect on performance, although at higher levels the properties of the limestone can be significant. Cement containing 5% limestone showed a somewhat accelerated strength gain at early ages, particularly when the cement was more finely ground. The same author in the Building Research Establishment study (1993) reports that the presence of 5% limestone has no significant effect on strength, as some strengths are slightly higher and some slightly lower.

Vuk et al. (2001) used a statistically designed experiment to examine the effects of 5% limestone, cement fineness, and clinker chemistry on strength. Early strengths of EN 196 mortars increased with use of limestone; however, later strengths either remained the same or decreased relative to the control depending on the fineness and the clinker chemistry. The clinkers were low in C_3A content (1.3% or 1.4%) and relatively low in C_3S content (35% or 46%).

Figs. 3 and 4 show a large assortment of data from different sources that summarize the available data. The ratio of compressive strength for samples of concrete or mortar made with and without limestone in portland cement is plotted as a function of the age of the sample at testing. Limestone in amounts up to 6% are included. It is interesting to note that the mean value of this ratio for these data is between 97% and 105% at every age where more than two data points are available. This result is surprising, as many of the cements were not optimized for strength,

but had arbitrary amounts of limestone added. A test program such as that used to optimize the gypsum/sulfate content of cements (ASTM C 563) might be used to determine an optimum value of the limestone content for a given cement. At the least, these figures confirm that portland cements with up to 5% limestone can provide strengths equivalent to portland cements without limestone. Table 16 gives the summary statistics for the data.

Figs. 5 and 6 show a subset of the data in Figs. 3 and 4 for samples made with Type II cements (those with C_3A contents below 8%). Although limited, these data also indicate that equivalent compressive strengths can be achieved.

Figs. 7 and 8 summarize the data for flexural strength ratio. Although less data are available, the trends are the same: The average of the ratios is between 0.99 and 1.08 for all ages, and the overall average is 1.0.

4.1.2 Volume Stability

Adams and Race (1990) studied the effect of blended limestone on the drying shrinkage of Type I and Type II cements using ASTM C 596. They found slight increases in drying shrinkage. Some of their data are shown in Tables 17 and 18. They also found that optimization of the sulfate content and/or the use of functional additions could offset the increased shrinkage.

Hooton (1990) compared pairs of cements ground from the same clinker with and without limestone in quantities conforming to the CSA limits. His data on autoclave expansions are given in Table 19. The use of carbonate had no adverse effect.

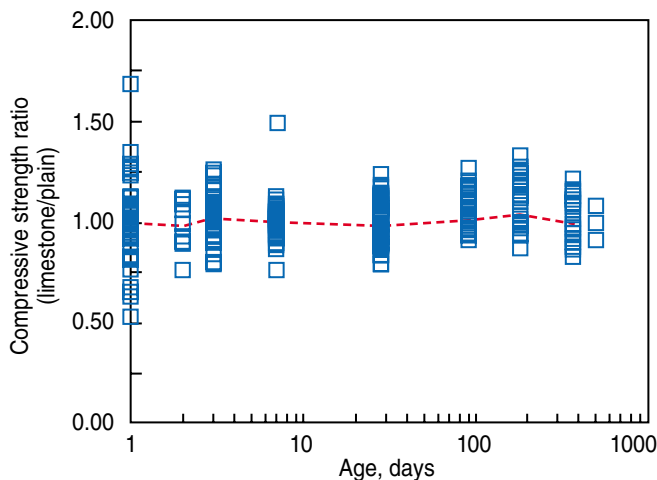


Figure 3. The ratio of compressive strengths for mortars made with portland cements with up to 6% limestone to that of companion samples made with portland cement without added limestone. The dashed line connects the mean values at each age. The data represent 374 sets of samples from 11 sources (Bobrowski et al. 1977; Bayles 1985; Crawford 1980; Combe and Beaudoin, 1979; Hawkins 1986; Hooton 1990; Klieger 1985; Livesey 1993; Lane 1985; Matkovic et al. 1981; and Tsivilis et al. 1999).

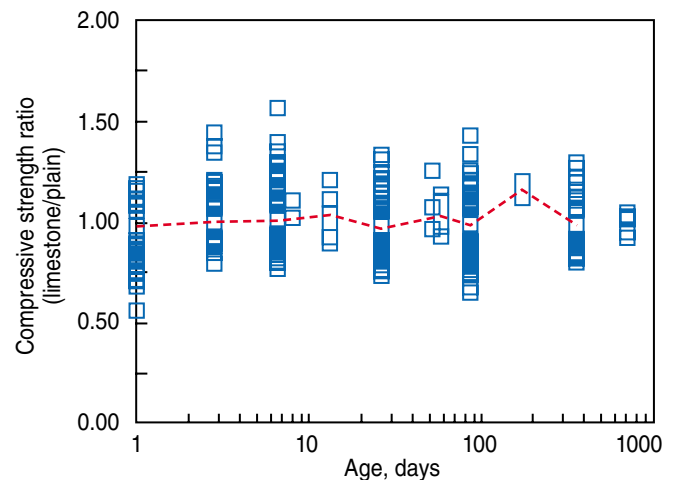


Figure 4. The ratio of compressive strengths for concrete made with portland cement with limestone to that of companion samples made with portland cement without limestone. The dashed line connects the mean values at each age. The data represent 491 sets of samples from 10 sources (Bayles 1985; Bedard and Bergeron, 1990; Bobrowski et al. 1977; Detwiler 1996; Hawkins 1986; Klieger 1985; Livesey 1993; Matkovic et al. 1981; Nehdi et al. 1996; and Suderman 1985).

Table 16. Summary Statistics for the Compressive Strength Ratio Data in Figures 3 and 4.

Age	Mortar data, Fig. 3			Concrete data, Fig. 4		
	Mean	Standard deviation	Number of data points	Mean	Standard deviation	Number of data points
1 day	0.98	0.15	71	0.97	0.12	49
2 days	1.00	0.11	8	—	—	—
3 days	1.02	0.17	60	1.00	0.11	49
7 days	1.01	0.09	83	1.01	0.10	115
14 days	—	—	—	1.03	0.08	10
28 days	0.99	0.06	83	0.97	0.09	127
56-60 days	—	—	—	1.02	0.08	16
90-91 days	1.01	0.07	25	0.98	0.11	74
180 days	1.04	0.09	21	1.15	0.04	2
365 days+	0.99	0.07	23	0.99	0.09	49
Overall	1.00	0.111	374	1.00	0.18	491

* — indicates no data.

Table 20 shows the shrinkage data Detwiler (1996) observed for concretes incorporating either a Type I portland cement or a Type 10 portland cement ground from the same clinker with 2.5% interground limestone. The table shows that the drying shrinkage is not affected by the use of limestone for the control concretes with or without Class C fly ash.

Shrinkage has been measured on concrete specimens made with cements from two different plants with and without 20% limestone by Alunno-Rossetti and Curcio (1997). Their data are presented in Table 21. Although, as expected, an increase in shrinkage with increased cement content is noted, no differences between the cements from the same plant were observed, in either evolution of shrinkage or final values.

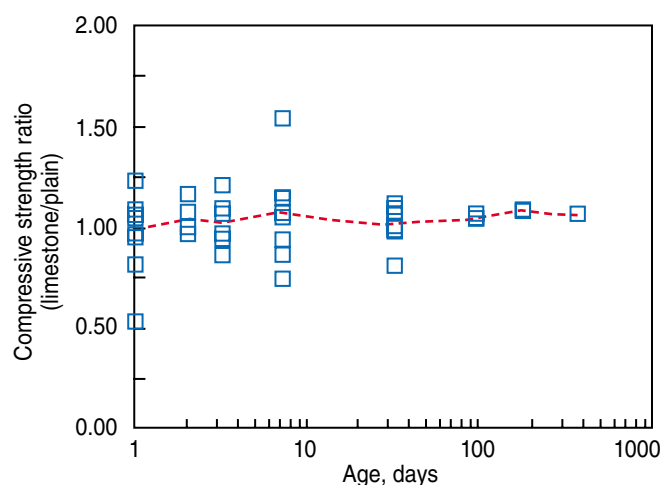


Figure 5. The ratio of compressive strengths for mortars made with portland cement with limestone to that of companion samples made with portland cement without limestone. The dashed line connects the mean values at each age. The data represent 44 sets of samples from 4 sources with cement C_3A contents less than 8% (Bobrowski et al. 1977, Hawkins 1986, Livesey 1993, and Tsivilis et al. 1999).

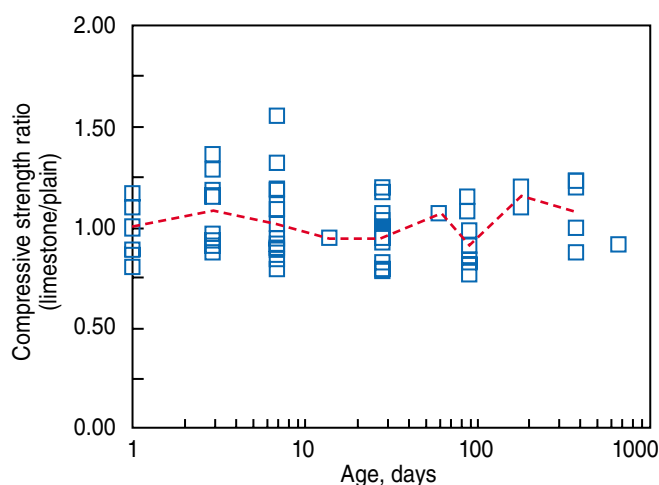


Figure 6. The ratio of compressive strengths for concretes made with portland cement with limestone to that of companion samples made with portland cement without limestone. The dashed line connects the mean values at each age. The data represent 72 sets of samples from 5 sources with cement C_3A contents less than 8% (Bobrowski et al. 1977, Hawkins 1986, Livesey 1993, Nehdi et al. 1996, and Suderman 1985).

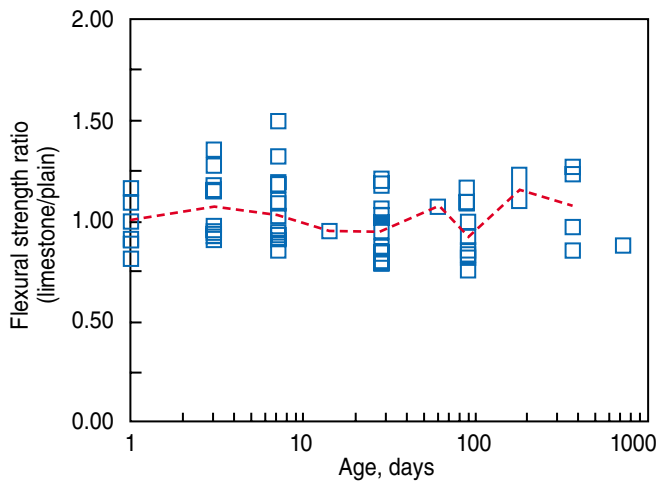


Figure 7. The ratio of flexural strengths for mortars made with portland cement with limestone to that of companion samples made with portland cement without limestone. The dashed line connects the mean values at each age. The data represent 59 sets of samples from 3 sources (Combe and Baudouin, 1979; Livesey 1993; and Matkovic et al.1981).

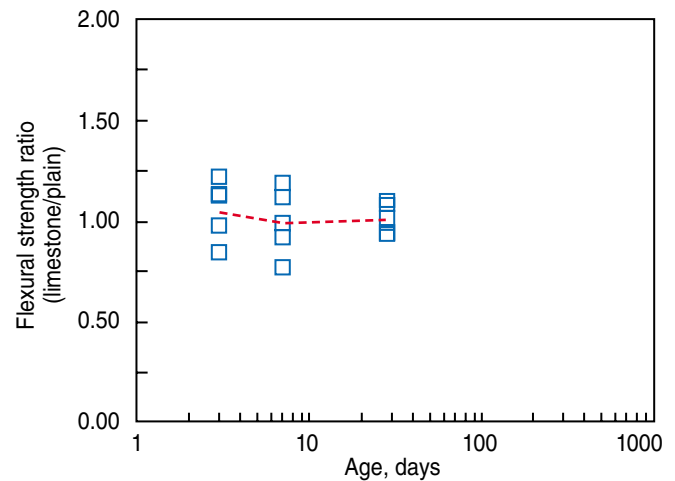


Figure 8. The ratio of flexural strengths for concrete made with portland cement with limestone to that of companion samples made with portland cement without limestone. The dashed line connects the mean values at each age. The data represent 15 sets of samples from 1 source (Matkovic et al. 1981).

Table 17. Effect of Blended Limestone on Type II Cement, 6.4% C_3A , 400 m^2/kg (Adams and Race, 1990)

	Control	3% Limestone	5% Limestone
Limestone source	—	CA	CA
Limestone fineness, m^2/kg	—	966	966
Flow for constant water, %	110	108	103
ASTM C 596 drying shrinkage			
4 days, %	0.046	0.049	0.050
11 days, %	0.064	0.067	0.068
18 days, %	0.075	0.077	0.079
25 days, %	0.081	0.085	0.085

Table 18. Effect of Blended Limestone on Type I Cement, 11.4% C_3A , 339 m^2/kg (Adams and Race, 1990)

	Control	5% Limestone
Limestone source	—	TX
Limestone fineness, m^2/kg	—	1035
Flow for constant water, %	99	100
ASTM C 596 drying shrinkage		
4 days, %	0.044	0.050
11 days, %	0.063	0.071
18 days, %	0.070	0.079
25 days, %	0.072	0.082

Table 19. ASTM C 151 Autoclave Expansions, % (Hooton 1990)

Cement	$CaCO_3$	Autoclave expansion	MgO	Free CaO
1	0.3	0.038	2.38	0.34
1c	4.1	0.034	2.38	0.18
2	0.8	-0.010	1.88	0.71
2c	4.7	0.029	1.91	1.12
3	0.3	0.093	2.91	0.38
3c	2.6	0.026	2.84	0.34

Table 20. Drying Shrinkage of Concretes (Detwiler 1996)

Cement	Cement content (kg/m ³)	Fly ash: content and type	4 days	7 days	14 days	28 days	56 days	112 days
Type I	362	none	0.002	0.009	0.015	0.025	0.039	0.044
Type 10			0.003	0.008	0.017	0.025	0.038	0.046
Type I	308	25% Class C	0.004	0.019	0.019	0.020	0.023	0.046
Type 10			0.003	0.011	0.022	0.026	0.029	0.046

Table 21. One-Year Drying Shrinkage (UNI Standard 6555*) of Concretes Made With Cements With or Without 20% Limestone (Alunno-Rossetti and Curcio, 1997)

	Plant B				Plant G			
Cement content, kg/m ³	270		330		270		330	
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Shrinkage, $\mu\text{m/m}$	635	640	680	690	540	560	615	595

* Italian national standard. Specimens stored at 50% relative humidity.

4.2 DURABILITY

4.2.1 Permeability

Permeability is the key to the durability of a porous material in all but the most protected environments. With the exceptions of abrasion and erosion, deterioration mechanisms involve the ingress of water and/or other harmful species (oxygen, carbon dioxide, chlorine ions, sulfate ions, acids, etc.). Frost damage does not occur in concrete unless it has reached a critical level of saturation. Corrosion requires water and oxygen, and is catalyzed by chlorine ions. Alkali-silica reaction requires water. While in some cases the water present in the original concrete mix—particularly if the concrete does not dry adequately after curing—is sufficient to allow deterioration to proceed, in general more water from the environment is needed. For deterioration of concrete in a hostile environment, low permeability reduces the rate of deterioration, allowing the concrete a longer service life. Unfortunately there are no simple, widely accepted test methods for the measurement of permeability. Thus, the data reported in this section are from a wide variety of test methods that are not directly comparable. Also, the permeability or diffusivity of concrete varies depending on what is moving through it—either because of interactions with the concrete components (for example, water will hydrate previously unhydrated cement, and chlorides can be bound by the hydration products of C_3A) or because the size of ion, atom, or molecule affects its mobility.

Permeability is, of course, related to pore structure. Pore size is less important than the connectivity of the pore system. Referring to the data reported by Sellevold et al. (1982) in Section 3.3 above, the improvement of pore structure attributed to the nucleation effect of the fine particles

of CaCO_3 was not due to the (slight) reduction in total pore volume, but to the refinement of the pore structure, which reduced its connectivity.

Moir and Kelham, reporting results from the Building Research Establishment study (1993), found that the permeability to oxygen for a series of concretes made with cements with or without 5% or 25% limestone was slightly reduced by the presence of limestone. Not surprisingly, extended curing reduced the permeability significantly. Porosity was very similar for the control and 5% limestone cements. Water sorptivity was much the same for the control and 5% limestone cements.

Schmidt (1992b) tested the permeability of air-entrained concretes made with portland cement and portland limestone cement by DIN 1048. In general the performance of the two types of cement was similar and well within specified limits (DIN 1045). He also determined the permeability coefficients for a series of concretes made from the two types of cement. In all cases the permeability coefficients for the portland limestone concretes were slightly lower than for the comparable concretes made with portland cement, as shown in Fig. 9. Due to the limited number of tests, Schmidt was not sure whether the data indicated a trend of superior performance due to finer grinding and/or more efficient particle packing. However, it is clear that these cements perform at least as well as portland cements in concrete having the same cement content and curing, even without taking advantage of the lower water demand to reduce the water:cement ratio.

Alunno-Rosetti and Curcio (1997) presented data (Table 22) on water absorption of concretes made with cements with and without 20% limestone. The authors note that there are larger differences between cements

Table 22. Water Absorption (UNI Standard 7699*) of Concretes Made With Cements With or Without 20% Limestone (Alunno-Rossetti and Curcio, 1997).

	Plant B				Plant G			
Cement content, kg/m ³	270		330		270		330	
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Water absorption, %	4.8	4.8	4.2	4.5	5.5	5.5	5.3	5.1

* Italian national standard.

from different plants than between cements from the same plant, irrespective of whether limestone is used.

4.2.2 Carbonation

Sprung and Siebel (1991) found that in general concretes made with portland limestone cement (6 to 20% limestone) showed increased rates of carbonation as compared with those made with portland cements, even when the

strengths were the same. Tezuka et al. (1992) found the depth of carbonation for mortars containing various quantities of limestone comparable to those for the control portland cement mortars for limestone contents up to 10%. Baron (1988) found that the depth of carbonation for standard mortars made with 15% limestone cements was the same as for the control mortars.

Barker and Matthews (1994) studied the durability of two series of concretes: Series A made with constant cement content and water:cement ratio, and series B made with constant slump and 28-day strength. Their carbonation depth data for the portland cement concretes and those made with various limestone contents are presented in Table 23. The concretes were stored at 20°C and 65% RH. They found that regardless of the composition of the cement, the depth of carbonation correlated well with the strength of the concrete.

Schmidt (1992b) observed carbonation depths for concretes made with portland limestone cement (13% to 17% limestone) that were higher than for comparable concretes made with portland cement, but lower than for concretes made with slag cement. However, he maintains that since the field performance for slag cements has been good, this result should not be interpreted as disadvantageous to the durability of concrete. In any case the increases in carbonation depths measured after three years of exposure were minimal. Fig. 10 from Schmidt et al. (1993) shows the depth of carbonation for concretes cured in water for 6 days and then exposed to a standard atmosphere of 65% R.H. at 20°C for three years. These concretes were designed for constant water:cement ratio, so that the workabilities were different.

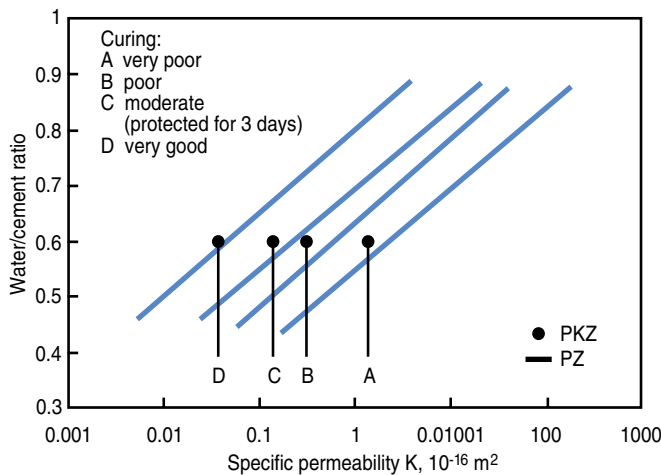


Figure 9. Permeability coefficient of concretes made with portland cement (PZ) and portland limestone cement (PKZ) containing 13 to 17% limestone and subjected to different curing regimes. In all cases the portland limestone cements have lower permeabilities, but it is not clear from the small number of tests whether this is generally true. After Schmidt et al. 1993.

Table 23. Carbonation Depths at 90 days and 1 year, mm (Barker and Matthews, 1994).

Cement	Moist curing	Series A 90 days	Series A 1 year	Series B 90 days	Series B 1 year
Portland	1 day	3.3	8.0	3.3	8.0
	3 days	2.4	6.6	2.4	6.6
9% Limestone	1 day	3.9	7.6	4.6	8.4
	3 days	3.1	6.2	3.3	6.6
15% Limestone	1 day	6.0	9.9	3.4	6.2
	3 days	5.3	9.0	2.7	5.0
24% Limestone	1 day	6.6	11.0	3.4	6.9
	3 days	6.9	9.7	2.6	6.3

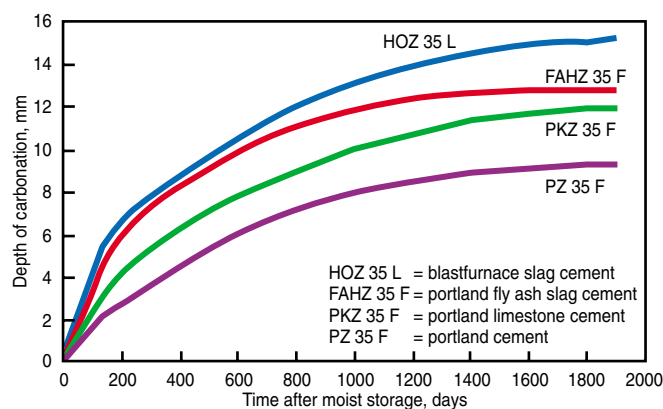


Figure 10. Carbonation of concretes made from different cements and exposed to 20°C, 65% R.H. for three years. Water:cement ratios were between 0.60 and 0.65 and the cement content was between 280 and 300 kg/m³. Limestone content of PKZ 35 was 13% to 17% (adapted from Schmidt et al. 1993).

Moir and Kelham (1993), reporting the results of the Building Research Establishment study, found that carbonation depth is inversely related to concrete strength. Tests of concretes containing 5% or 25% limestone, as well as fly ash or slag, showed that carbonation depths have the same relationship to concrete strength regardless of cement type. Increasing the wet curing time from 1 to 3 days reduced the carbonation depths by approximately 40% for all cement types.

Alunno-Rosetti and Curcio (1997) presented data (Table 24) on carbonation depth in concretes made with cements with and without 20% limestone. Use of limestone in cement did not impact depth of carbonation.

4.2.3 Freeze/Thaw and Deicer Scaling

European research shows that even when the limestone content of the cement is much higher than that proposed for ASTM C 150 cements, it is possible to make concrete with good frost resistance. Sprung and Siebel (1991) found that, in general, concretes made with portland limestone cement showed reduced resistance to frost damage as compared with those made with portland cements, even when the strengths were the same. They tested portland limestone cements containing 15% limestone by the “cube” method. Concretes having a cement content of

300 kg/m³ and a water:cement ratio of 0.60 were wet cured for 6 days and then moist cured for an additional 28 or 56 days. The cubes were subjected to 100 freeze/thaw cycles. Any concrete that experiences a mass loss of less than 10% is considered frost resistant. They concluded that it is possible to make concretes from portland limestone cement that are as frost resistant as comparable concretes made with portland cement provided the limestone meets the criteria for composition limits specified by EN 197-1, the limestone content does not exceed 20% by mass of cement, and equal concrete strengths are reached. It should be noted that the most important criterion for limestone quality as related to frost resistance is the clay content, since clays can adsorb moisture which expands on freezing. They consider the methylene blue test to be an adequate measure of this tendency.

Siebel and Sprung (1991) report that the results of a European round robin on the frost resistance of concretes made with portland limestone cements showed that one such cement did not provide adequate frost resistance. Thus not all limestones are suitable for portland limestone cement. They studied three commercial portland limestone cements having 11%, 26%, and 12% limestone. They tested concretes having different water:cement ratios for frost resistance and found that concretes having a water:cement ratio greater than 0.60 were not frost resistant, while those with water:cement ratios less than or equal to 0.60 were adequately frost resistant except for the cement having 11% limestone. (They believe the limestone used in this cement was unsuitable.) The German standard DIN 1045 specifies a maximum water:cement ratio of 0.60 for frost-resistant concrete.

Schmidt (1992b) tested concretes for frost resistance by the “cube” method. The specimens made from portland limestone cement (13% to 17% limestone) performed as well as or slightly better than those made from portland cement. He also tested concrete specimens for deicer scaling according to Austrian Standard 3303, in which concrete slabs are ponded with a salt solution and subjected to 70 freeze/thaw cycles. The specimens had air contents of 4% to 5% by volume. The performance of the specimens made with the portland limestone cement was similar or even slightly better than those made with portland cement.

Albeck and Sutej (1991) report that experiments performed by the study group on interground materials at

Table 24. Carbonation Depths (UNI Standard 9944*) at 900 days in Concretes Made With Cements With or Without 20% Limestone (Alunno-Rosetti and Curcio, 1997)

	Plant B				Plant G			
Cement content, kg/m ³	270		330		270		330	
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Carbonation depth, mm	20	10	18	13	19	21	15	16

* Italian national standard.

the VDZ (German Cement Works' Association) showed that the frost resistance of concretes made from portland limestone cements is the same as for portland cement provided that the organic material content of the limestone is less than 0.20% by mass as measured by total organic carbons.

Fig. 11 from Schmidt et al. (1993) shows how the quality of limestone can affect the frost resistance of concretes made with portland limestone cements with limestone contents of 13% to 17%. Portland limestone cements were made using different limestones to the same strength class (32.5 MPa). In all cases but one, the portland limestone cement concretes performed as well as the portland cement concrete. The one exception, F1, did not conform to the requirements of EN 197. Fig. 12 shows the results of cube tests for concretes made with portland limestone cement were better than for companion specimens made with portland cement, but all concretes had mass losses significantly lower than the 10% maximum limit. In these tests the water:cement ratio was 0.60, which is higher than recommended by ACI for concretes exposed to a hostile environment.

Baron (1988) found that tests of frost resistance performed at different laboratories yielded conflicting results. A new approach which was just then being tested in the laboratory involved determining the required air void spacing factor for mortars made with different cements individually, rather than prescribing the same spacing factor for all cements. Preliminary data suggested that 15% limestone cements require smaller spacing factors than portland cements in order to provide good frost resistance.

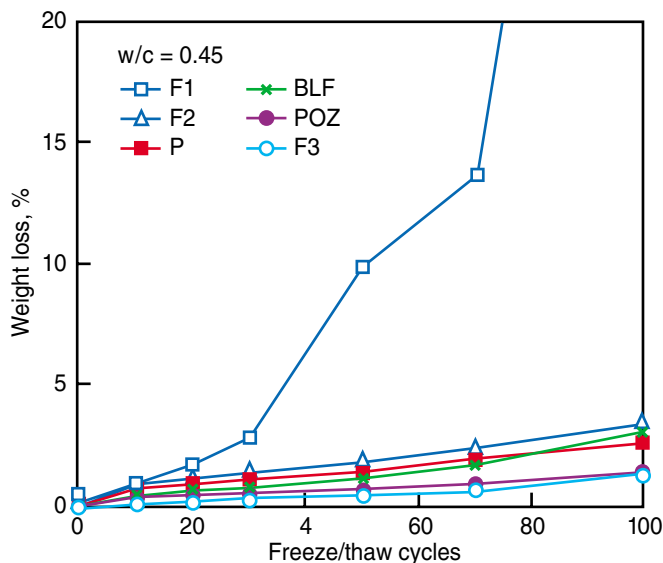


Figure 11. Effect of type of limestone on frost resistance of concrete. Portland limestone cements of class 32.5 were produced from the same clinker, but with different types of limestone in amounts of 13% to 17%. In most cases the frost resistance is comparable to that of the portland cement (after Schmidt et al. 1993).

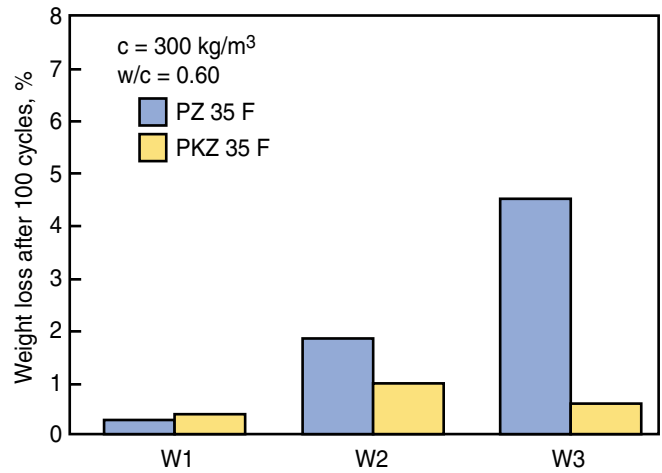


Figure 12. Results of “cube” tests for the frost resistance of concrete. Mass loss of less than 10% is considered acceptable. Here the portland limestone cements, PKZ 35 F (with limestone contents of 13% to 17%), performed better than the companion portland cements, PZ 35 F (adapted from Schmidt et al. 1993).

Klieger (1985) reports the results of deicer scaling tests (ASTM C 672) after 300 cycles for air-entrained concretes made with six cements: Two with no limestone, two with 3% interground limestone, and two with 3% blended limestone. The cements with interground limestone performed equal to or better than the cements with no limestone, while for the blended limestone cements, one performed slightly better and one slightly worse.

4.2.4 Sulfate Resistance

Soroka and Stern (1976) studied the effect of reagent-grade CaCO_3 and CaF_2 (used as an inert filler) on the sulfate resistance of portland cement mortars having a water:cement ratio of 0.75. Specimens $25.4 \times 25.4 \times 158.7$ mm in size were immersed in a 5% Na_2SO_4 solution. Their time to cracking data are shown in Table 25. It can be seen that the CaCO_3 has a beneficial effect beyond the reduction of the C_3A content of the cement.

Table 25. Time to Cracking for Mortar Prisms Exposed to 5% Na_2SO_4 (Soroka and Stern, 1976)

Mortar	Time to cracking, weeks	28-day compressive strength, MPa
Reference	6	25.3
10% CaCO_3	10	27.0
20% CaCO_3	12	27.3
30% CaCO_3	14	29.7
40% CaCO_3	16	30.9
10% CaF_2	6	23.7
20% CaF_2	6	28.2
30% CaF_2	6	32.6
40% CaF_2	6	28.9

Soroka and Setter (1980) followed up this preliminary study by examining the expansion and deterioration of mortars containing various amounts of ground limestone, dolomite, or basalt and immersed in 5% Na_2SO_4 solution for up to 11 months. The additive contents were 10%, 20%, 30%, and 40% by mass. They found that the limestone imparted some improvement in sulfate resistance as compared with the control. The fineness of the additive was also significant, as can be seen in Table 26. However, they found that after long periods of exposure the intensity of cracking of the limestone-filled mortars was essentially the same as for the others. Thus they conclude that the use of limestone improves the sulfate resistance of mortars, but not to such an extent as to produce sulfate-resistant mortars.

Hooton (1990) tested pairs of commercially produced cements made from the same clinker with and without limestone. Both ASTM C 452 and C 1012 were used. In ASTM C 452, the SO_3 content is raised to 7.0% using gypsum and the mortar bars are stored in water while

expansions due to the internal sulfate attack are measured. In ASTM C 150 the 14-day expansion limit for sulfate resistant cement is 0.040%, while in CSA/CAN-A5 the limit is 0.035% for sulfate resisting cement and 0.050% for moderate sulfate resisting cement. Hooton's data are shown in Table 27. There is no clear trend with regard to the effect of carbonate on sulfate resistance. Cements 2, 2c, 3, and 3c meet the CSA criterion for moderately sulfate resisting cement.

In ASTM C 1012, which was developed for the evaluation of blended cements, mortar bars are exposed to 5% Na_2SO_4 solution once companion cubes have reached a compressive strength of 21 ± 1 MPa. Tentative expansion limits for this method are 0.10% at 6 months for moderate sulfate resisting cement and 0.05% at 6 months or 0.10% at 12 months for highly sulfate resisting cements. Hooton reported expansion data up to 365 days for the six cements. The time to reach 0.10% expansion is given in Table 28. Again, there is no clear trend as to the effect of carbonate use on sulfate resistance. Hooton concluded that sulfate resistance is not affected by carbonate and is primarily determined by C_3A content.

González and Irassar (1998) also evaluated effects on sulfate resistance (ASTM C 1012) of mortars made with Type II and Type V cements with 0%, 10%, and 20% limestone. Their results indicate no significant difference in sulfate resistance of low- C_3A cements with or without 10% limestone; however, for 20% replacement levels, the sulfate resistance was lowered. Their results are summarized in Table 29.

Table 26. Time to Cracking for Mortar Prisms Exposed to 5% Na_2SO_4 with 30% Filler, Weeks (Soroka and Setter, 1980)

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	

Table 27. ASTM C 452 Expansions, % (Hooton 1990)

Cement	1	1c	2	2c	3	3c
% C_3A	10.4	10.0	9.1	9.8	8.3	7.3
% CaCO_3 (by TGA)	0.3	4.1	0.8	4.7	0.3	2.6
Age, days						
14	0.054	0.058	0.036	0.041	0.039	0.036
28	0.071	0.092	0.053	0.054	0.051	0.043
56	0.084	0.126	0.066	0.058	0.058	0.050
91	0.086	0.142	0.075	0.058	0.061	0.054
105	0.088	0.144	0.077	0.059	0.062	0.055
119	0.088	0.145	0.079	0.059	0.062	0.056
170	0.087	0.146	0.079	0.059	0.064	0.056
261	0.088	0.148	0.079	0.059	0.065	0.057
365	0.090	0.150	0.080	0.060	0.068	0.060

Table 28. ASTM C 1012: Time to 0.10% Expansion (Hooton 1990)

Cement	1	1c	2	2c	3	3c
% C_3A	10.4	10.0	9.1	9.8	8.3	7.3
% CaCO_3 (by TGA)	0.3	4.1	0.8	4.7	0.3	2.6
Time to 0.10% expansion, days	117	142	167	161	196	236

Table 29. Sulfate Resistance in ASTM C 1012 Mortars (González and Irassar, 1998)

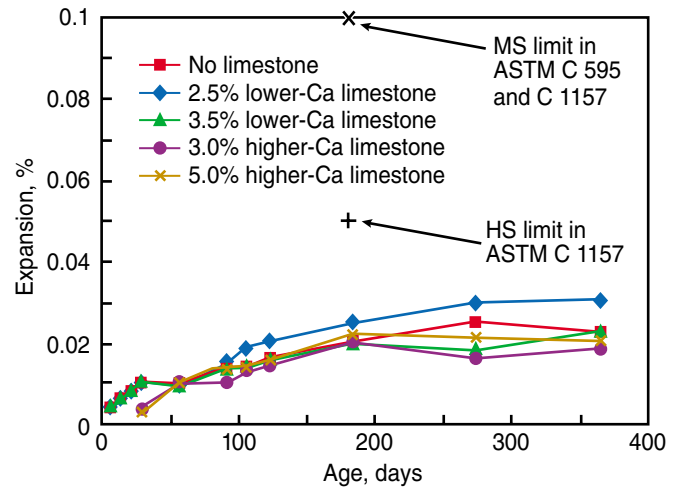
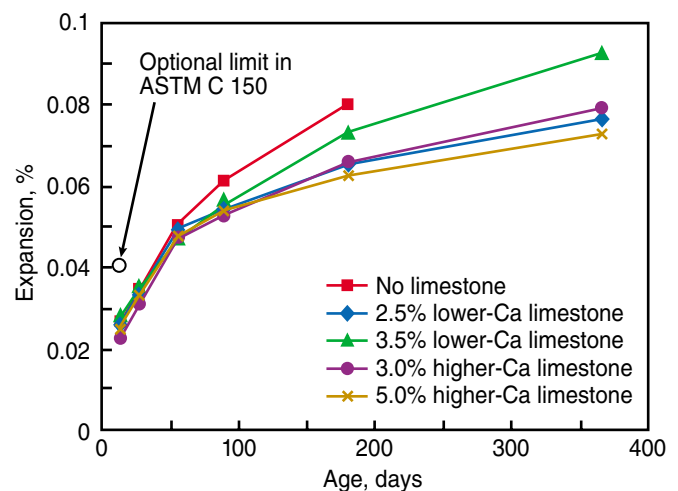
Cement	Type V			Type V			Type II		
C ₃ A content, % by mass	0			1			6		
C ₃ S content, % by mass	40			74			51		
Limestone replacement	0	10	20	0	10	20	0	10	20
Time to 0.10% Expansion, days	1260	857	208	148	164	92	165	209	108
Reduction in compressive strength (1 year in sulfate solution), %	3	4	5	29	17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

Marsh and Joshi (1986) studied the effects of large quantities (30% and 50%) of limestone on the sulfate resistance of concrete. In their work limestone was added to cement paste rather than to the cement, since the Canadian standard limits the limestone content of cement to 5%, but allows additional amounts to be used in concrete. Specimens were cast and sealed in plastic molds $25 \times 25 \times 300$ mm and were rotated until set. After 24 hours they were demolded and cured in saturated limewater for 28 days at either 20°C or 50°C. The specimens were cut to size at age 7 days. The resistance to sulfate attack was determined by measuring the length change of 125 mm cement paste prisms immersed in 0.35 M Na₂SO₄ solution at 20°C. The pH of the solution was maintained at approximately 7 by the addition of 0.5 M H₂SO₄ as needed. At these dosages the use of limestone resulted in increased expansions due to sulfate attack. However, in the specimens cured at 50°C all of the pastes were resistant to sulfate attack for exposure periods in excess of one year.

Matthews reports that in the Building Research Establishment study (1993) no relation was found between limestone content and sulfate resistance of concretes. The C₃A content of the parent cement determined the sulfate resistance.

Taylor (2001a, b) studied effects of use of limestone in low-C₃A content portland cements on sulfate resistance. In one study (Taylor 2001a), a clinker with C₃A content of 8% was interground with one of two limestones: One limestone was interground at either 2.5 or 3.5%, while another was interground in amounts of 3.0% and 5.0%. Both ASTM C 1012 and C 452 data indicated acceptable performance (per ASTM C 150, C 595, or C 1157) performance for all cements. Data are summarized in Figs. 13 and 14.

In another study, Taylor (2001b) evaluated two cements with C₃A contents of 3% and 5% interground with limestone in amounts of 4.0% and 3.5%, respectively. Results of ASTM C 452 and C 1012 testing demonstrated acceptable performance according to cement specifications (ASTM C 150, C 595, or C 1157). Expansion data are plotted as a function of time in Figs. 15 and 16.

**Figure 13. Expansion in test method ASTM C 1012 (after Taylor 2001a) for Type II cements with two levels of two different limestones.****Figure 14. Expansion in test methods ASTM C 452 (after Taylor 2001a) for Type II cements with two levels of two different limestones.**

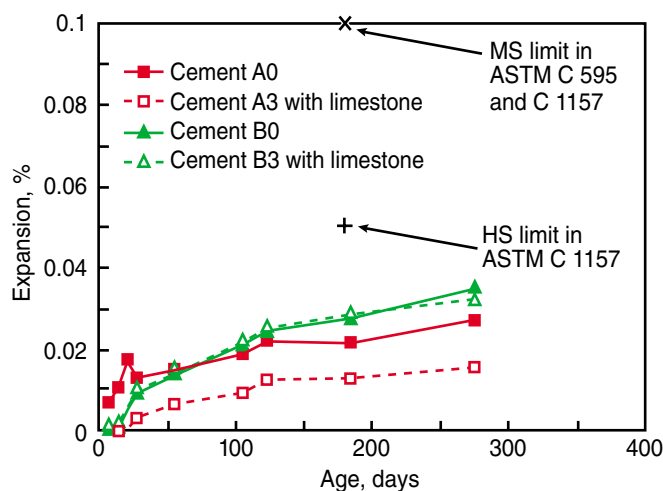


Figure 15. Expansion in test method ASTM C 1012 test for cements with C_3A contents of 5% or less. Cements A3 and B3 were interground with 3% limestone (after Taylor 2001b).

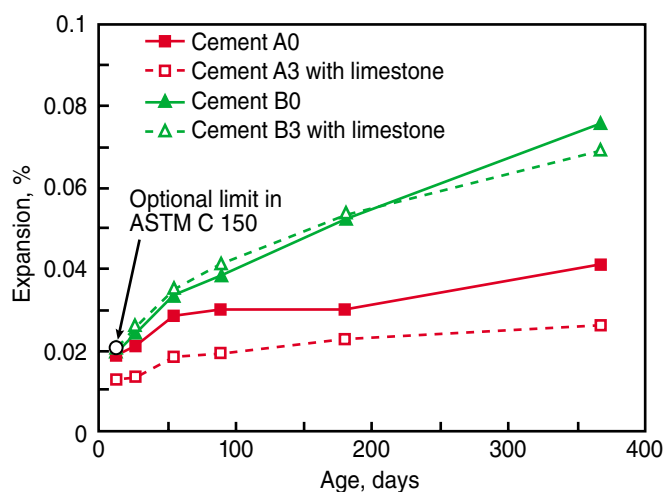


Figure 16. Expansion in test method ASTM C 452 for cements with C_3A contents of 5% or less. Cements A3 and B3 were interground with 3% limestone (after Taylor 2001b).

4.2.4.1 Thaumasite. Formation of thaumasite, a calcium-silicate-sulfate-carbonate mineral ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15 H_2O$), has relatively recently received attention as a potential deterioration mechanism. The mere presence of thaumasite in a concrete or a deteriorated concrete is not sufficient to implicate it as a cause of problems. In the relatively few cases of thaumasite sulfate attack, several factors have been common (Hooton and Thomas, 2002), including presence of sulfate and/or sulfides in the ground, mobile groundwater, carbonate sources (usually limestone aggregate), and low temperatures, generally below $15^\circ C$. (Some researchers use 0 to $5^\circ C$ as a more typical temperature range, for example, Bensted 1999.) However, Hooton and Thomas (2002) reviewed published literature on thaumasite sulfate attack and concluded:

Field experience with up to 5% limestone in portland cement in Canada and Europe for over 20 years has not

produced any known cases where this has contributed to thaumasite sulfate attack. Based on the literature reviewed, there does not appear to be any significantly increased susceptibility to sulfate attack with respect to use of up to 5% limestone in portland cements. Research does exist concerning much higher levels of limestone (15% to 35%, or where the carbonate fines originate from the aggregate), where used in cold temperatures combined with wet and aggressive sulfate environments, that indicates more susceptibility to the thaumasite form of sulfate attack. Overall, the data available support use of up to 5% limestone in portland cements.

4.2.5 Chlorides

Ramachandran et al. (1990) studied mortars containing 0%, 2.5%, 5%, and 15% precipitated $CaCO_3$ (particle size 1 to 5 μm) or ground limestone – (particle size 1 to 40 μm) at water:cement ratios of 0.42 and 0.60. The specimens were hydrated in limewater or in laboratory prepared “seawater” (2.7% NaCl, 0.32% $MgCl_2$, 0.22% $MgSO_4$, and 0.13% $CaSO_4$) for up to one year. They monitored length and modulus of elasticity periodically. They found that the strengths of the mortars were not affected by the ground limestone, but at 15% replacement, precipitated $CaCO_3$ reduced the strength by about 50%. When the compressive strengths were similar, specimens at a water:cement ratio 0.60 or containing precipitated $CaCO_3$ exhibited much higher expansions than the controls when exposed to seawater. Only those specimens with a water:cement ratio of 0.42 containing the ground limestone showed similar expansions to the controls. Moduli of expansion were similar to the control for the lower water: cement mortars, except at the 15% replacement level by precipitated $CaCO_3$, which was much lower. Exposure to seawater generally lowered the moduli, with more reduction in the higher water:cement ratio mortars. The same authors (Feldman et al. 1992) also looked at limestone portland cement mortars exposed to NaCl and $MgCl_2$ solutions, concluding that the moduli are reduced and expansions increased compared to controls exposed to $Ca(OH)_2$ solution. The magnitude of the changes depended on the water:cement ratio, and the amount and fineness of the limestone used.

Deja et al. (1991) subjected mortar specimens containing 5% ground limestone to a low pressure steam treatment (maximum temperature $80^\circ C$) followed by immersion for up to one year in a mixed salt solution loosely based on the composition of seawater. Three types of specimens were tested: 25 × 25 × 100 mm prisms for strength tests, cylinders with steel bars along the axis for steel passivation studies, and 40 × 40 × 160 mm prisms with embedded steel plates for mass loss studies. Their data on the effect of chloride exposure on the compressive and flexural strength (Table 30) show that chloride exposure is equally deleterious to the strength of mortars with or without limestone. The mass loss of the steel

Table 30. Strengths of Mortars Exposed to Mixed Salt Solution, MPa (Deja et al. 1991)

Age	Compressive		Flexural	
	Control	5% Limestone	Control	5% Limestone
Initial	41.2	42.1	8.8	8.6
56 days: in water in solution	47.8	47.1	11.5	11.1
	45.4	42.3	11.3	12.1
365 days: in water in solution	49.2	47.6	11.0	11.3
	36.6	36.9	10.2	8.8

plates for the control and 5% limestone specimens stored in water for one year were 6.82 and 8.68 g/m², respectively, while for the specimens stored in the salt solution they were 32.51 and 7.13 g/m², respectively. Thus the limestone was effective in protecting the steel from corrosion. The passivation data lead to a similar conclusion.

Tezuka et al. (1992) determined the diffusion coefficient for chloride ions for a series of mortar specimens containing different quantities of limestone ground to 450 m²/kg. They found that the diffusion coefficients for the control and the 10% limestone mortars were comparable (51.2×10^{-9} cm²/s and 53.1×10^{-9} cm²/s, respectively), and that for the 5% limestone was lower (14.3×10^{-9} cm²/s).

Moir, reporting the results of the Building Research Establishment study (1993), found no clear trend regarding the effect of 5% limestone on the resistance of concrete to chloride penetration. The best predictor of chloride ion penetration was compressive strength: The higher the strength, the more resistant the concrete to chloride ions. However, for concretes of the same strength class exposed to seawater for two years, chloride concentration 30 mm from the surface increases with cement C₃A content.

Baron and Douvre (1987) state that for marine exposure, the limestone content should be limited to 10%,

based on laboratory and field tests. They also recommend that the limestone and clinker be tested for compatibility with each other and the environment in which the limestone portland cement is to be used.

Alunno-Rosetti and Curcio (1997) presented data (Table 31) on chloride penetration of concretes made with cements with and without 20% limestone. The authors note that there are larger differences between cements from different plants than between cements from the same plant, irrespective of whether limestone is used.

4.2.6 Alkali-Silica Reactivity

Hobbs (1983) reported on the effects of 5% limestone on the expansion due to alkali-silica reactivity of 25 × 25 × 250 mm mortar bars made from Thames Valley sand and a Beltane opal rock having particles 150 to 300 μm in size. The proportion of Beltane opal was adjusted to give the critical alkali-reactive silica ratio. The expansion at 200 days averaged 0.009% for the portland cement specimens and 0.021% for the specimens with 5% limestone. Times to cracking were as shown in Table 32. Hobbs concluded that although there is some effect on the average expansion, the use of 5% limestone neither reduces the time to cracking below the minimum observed for portland cement mortars

Table 31. Chloride Penetration (UNI Standard 7928*) of Concretes Made With Cements With or Without 20% Limestone (Alunno-Rosseti and Curcio, 1997)

	Plant B				Plant G			
	270		330		270		330	
Cement content, kg/m ³								
Limestone content of cement, % by mass	0	20	0	20	0	20	0	20
Chloride penetration, mm								
at 28 days	43	102	38	48	212	197	115	146
at 60 days	63	113	49	79	281	264	183	182

* Italian national standard.

Table 32. Time to Cracking Due to ASR, Days (Hobbs 1983)

Water/solids	Cement alkalies	Portland cement	5% Limestone
0.41	1.00%	5, 6	8, 8
0.53	1.00%	28, 39	54, 54
0.53	0.79%	*	*

*The bars had not cracked at age 250 days.

nor increases the expansion at 200 days above the maximum observed for portland cement mortars. He therefore concludes that it does not increase the likelihood of deleterious expansions due to alkali-silica reaction.

4.3 INTERACTIONS WITH MINERAL AND CHEMICAL ADMIXTURES

Chemical admixtures (water-reducing, air entraining, accelerating, and retarding admixtures) are an important part of concrete manufacture and can directly affect both short and long term properties. Mineral admixtures (also known as supplementary cementing materials, or SCMs), including silica fume, blast furnace slag, fly ash, and other pozzolans, have likewise become important components of blended cements for the properties they enhance. The performance of some of these materials in portland cements with limestone has recently been investigated by Detwiler (1996) and Nehdi, Mindess, and Aïtcin (1996ab).

Detwiler (1996) has reported the results of concrete strength tests using two cements ground from the same clinker at the same plant: A Type I containing no limestone and a Type 10 that had 2.5% by mass limestone inter-ground. Both water-reducing and air-entraining admixtures were used. For the Type 10 cement concretes, slightly more air entraining admixtures were required. The compressive strengths of concretes tested with and without fly ash show similar results when the limestone cement was used. The compressive strength data are shown in Table 33. Freeze/thaw durability was above 93% for all samples with no significant differences between the concretes made with Type I or Type 10 cements. Deicer scaling was comparable in the Type 10 cement concretes and drying shrinkage was also similar in both concretes.

Nehdi, Mindess and Aïtcin (1996ab) studied high strength, superplasticized mortars and concretes containing portland cement blended with limestone and silica fume. The mortar strengths were not affected by replacement of cement with limestone of up to 10% to 15%. With 10% silica fume also included, higher strengths were attained after about 7 days. For their concrete system, the 12-hour strength was improved from less than 3 MPa to about 9 MPa by substituting 10% limestone (with no silica fume). At 7 days the strength was best at middle levels (about 5%) of both silica fume and limestone, while at 91 days the strength of the concretes made with 5% limestone was slightly lower than those made without limestone.

Brookbanks, describing results from the Building Research Establishment study (1993), reported that the amount of Vinsol resin air entraining agent required to achieve $6.0 \pm 0.5\%$ air in fresh concrete was the same, 1.1 ml/kg cement, for the cements with 0% and 5% limestone and only slightly higher, 1.3 ml/kg cement, for the cements with 16% to 28% limestone. Only in the case of a limestone not meeting the compositional standard of EN 197 was the required amount of admixture much higher (2.5 ml/kg cement).

Gartner (1996) reports that a proprietary additive improves the performance of portland cements and portland-limestone blended cements by complexing the iron in the C_4AF and allowing a carbonated AFm phase to form more readily. This leads to enhanced hydration for the other phases (as an iron bearing precipitate does not form on the surface of the hydrating grains, hindering their reaction) as well, leading to higher strengths. In portland cement containing limestone, the enhancement is generally better, as shown in the Table 34. Each "run" in the table represents a different clinker and compares the additive to an additive-free control sample.

Table 33. Compressive Strengths of Concretes, MPa (Detwiler 1996)

Cement	Cement content (kg/m ³)	Unit weight (kg/m ³)	7 days	28 days	56 days
Type I	362	2270	29.4	36.1	39.5
Type 10		2305	29.4	36.7	41.1
Type I	362	2250	22.7*	30.1	30.5
Type 10		2300	24.6*	31.7	36.5
Type I	308	2295	18.8*	25.0	27.2
Type 10		2245	19.1*	23.9	28.2
Type I	308	2290	23.6	30.9	30.4
Type 10		2310	23.1	30.3	29.0

* Averages of two 102 × 203-mm cylinders at 8 days. All other values are the average of three 102 × 203-mm cylinders.

Table 34. Relative Strengths with Additive* (Gartner 1996)

Number of runs	Limestone content	Percentage of runs where strength increase exceeded 5%	
		at 1 day	at 28 days
36	0-5%	39	30
21	4-12%	65	59
3	20-25%	0	80

* Added in amounts of 400 g/t.

CHAPTER 5

Specifying and Monitoring Quality

5.1 LIMESTONE

Sprung and Siebel (1991) point out that since pure dense limestone consisting primarily of calcite is not normally available for industrial grinding in cement plants, certain minimum requirements must be stipulated for its composition, and maximum limits put on its quantity in cement. Natural limestones contain clay minerals, which above a certain proportion can increase water demand and significantly reduce the frost resistance of concrete.

The CSA standard (CSA 1998) for portland cement, CAN/CSA-A5, allows a maximum of 5% limestone in normal portland cement, Type 10, and high-early-strength portland cement, Type 30. Such limestone must be of a quality suitable for the manufacture of portland cement clinker, but no specific limits on composition are given.

The European standard, EN 197-1, allows CEM I portland cement to contain up to 5% minor additional constituents (MAC), of which limestone is one possible material. The requirements for minor additional constituents are only that they do not detract from performance:

Fillers are specially selected, natural or artificial inorganic mineral materials which, after appropriate preparation, on account of their particle size distribution, improve the physical properties of the cement (such as workability or water retention). They can be inert or have slightly hydraulic, latent hydraulic or pozzolanic properties. However, no requirements are set for them in this respect.

Fillers shall be correctly prepared, i.e. selected, homogenized, dried and comminuted depending on their state of production or delivery. They shall not increase the water demand of the cement appreciably, impair the resistance of the concrete or mortar to deterioration in any way or reduce the corrosion protection of the reinforcement.

European portland limestone cement can contain up to 35% ground limestone. In this case, with the limestone constituting a larger proportion of the cement, EN 197 specifies limits on the composition of the limestone:

CaCO ₃ content	≥ 75% by mass
Clay content (EN 933-9)	≤ 1.20 g/100 g
Total organic carbon (prEN 13639)	≤ 0.20% by mass for class L ≤ 0.50% by mass for class LL

Schmidt (1992a) adds that the MgO content should be limited to 5% by mass, although this restriction does not appear in the current version of EN 197-1. Baron and Douvre (1987) note that the MgO limit is intended to limit the amount of dolomite in the limestone.

The clay content is determined by prEN 933-9, "Test for geometrical properties of aggregates—Part 9: Assessment of fines—Methylene blue test" (CEN 1998). In this test a 10 g/l solution of methylene blue is injected in a series of 5 ml doses into the sample beaker. After each addition of methylene blue solution, the sample is mixed at least 1 minute and then a stain test is performed. The stain test consists of placing a drop of the sample onto filter paper. The test is considered positive when a halo of a persistent light blue ring of about 1 mm forms around the central deposit. The procedure is repeated until the end point is reached. The end point must be confirmed by repeating the stain test at 1-minute intervals for 5 minutes without adding more methylene blue solution, as the clay may adsorb more dye over time. The total volume of dye solution is used to calculate the methylene blue value to the nearest 0.1 g of dye per kilogram of sample.

Sprung and Siebel (1991) examined different limestones and their effects on the performance of cement. These limestones contained different proportions of clay minerals. They found that montmorillonite has about eight times the absorptive capacity of illite, while kaolinite has only about half that of illite. Thus the methylene blue test does not measure clay content per se, but the absorptive capacity of the clay component of the limestone. For the purposes of determining the suitability of a limestone for use in cement, this measure is actually more appropriate. In their studies of the frost resistance of concrete, they found that the EN 197 criteria for limestone composition are suitable for evaluating limestone for use in

portland limestone cement. However, they found a few borderline cases in which reliability would have been improved by raising the minimum CaCO_3 content from 75% to 80% by mass.

In the Building Research Establishment study (1993), some testing was done with a limestone that did not meet the EN 197-1 criteria: Its methylene blue sorption value was 2.7 g/100 g (as opposed to the specified limit of 1.20), its total organic carbon content was 0.38% (specified limit 0.20%), and its CaCO_3 concentration was lower than the minimum specified. Fig. 17 shows the water:cement ratio needed to achieve a given slump in concretes made with different cements, each made with or without its own limestone. Comparison of the water:cement ratios for 0% and 5% limestone contents shows that the poor quality limestone did not affect the water demand for the 5% limestone cement even though it had a deleterious effect on the water demand when the limestone content exceeded 16%.

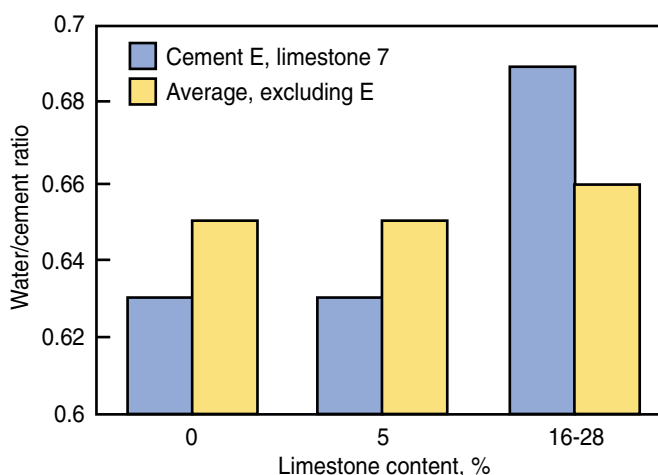


Figure 17. Required water:cement ratio to achieve a slump of 60 to 70 mm in concretes made with different cements. Cement E contained a limestone not conforming to the EN 197-1 criteria. Comparison of the water:cement ratios for 0% and 5% limestone contents shows that the poor quality limestone did not affect the water demand for the 5% limestone cement, but had a deleterious effect on the water demand when the limestone content exceeded 16% (after Brookbanks 1993).

5.2 CEMENT WITH LIMESTONE

Livesey (1991a) points out the need to consider the suitability of the limestone and the composition and fineness of the cement in order to achieve optimum performance.

Sprung and Siebel (1991) determined that it is possible to make concretes with portland limestone cement that have the same frost resistance as concrete made with portland cement, provided that the limestone meets the EN 197 criteria, that the limestone content of the portland limestone cement does not exceed 20% by mass of cement,

and that the portland limestone cement reaches the same strength as the portland cement.

Yellepeddi et al. (1993) describe a test method that can be used to determine the limestone content of cement for the purposes of quality control. They consider X-ray fluorescence to be less than adequate because it is not directly correlated to a phase such as CaCO_3 . Instead it gives only the total carbon concentration. In addition, X-ray fluorescence analysis of carbon is subject to several difficulties:

- The fluorescence yield of light elements such as carbon is poor, and the carbon fluorescence escapes from only a very thin layer at the sample surface, the rest being absorbed by the sample matrix. Thus the measured value represents only a small part of the sample.
- Surface contamination and materials used in the preparation of the sample can affect the results because of their own carbon content.
- When carbon is measured by X-ray fluorescence, all errors are multiplied by a factor of eight when converting to limestone concentrations.

However, quantitative X-ray diffraction can analyze the CaCO_3 content directly. X-ray diffraction has the additional advantages of representing a larger portion of the sample (due to the high energy of the X-rays) and being insensitive to surface contamination or the presence of materials used in sample preparation. They developed calibration curves based on the CaCO_3 peak intensities in sets of white and gray cement standards and found standard errors of estimate of 0.17% and 0.08%, respectively. They also found that repeated analyses of the same standard over time were quite stable. Should peak positions and backgrounds change due to sensitivity to such parameters as grain size and matrix effects, peak search and peak integration can be used to provide an accurate analysis.

Particle size distribution can be monitored by sieving a sample of cement and analyzing the separate fractions in order to determine how much limestone and how much clinker are in each fraction. Ménétrier-Sorrentino (1988) found such techniques to be useful in her studies. Since the compositions of the limestone and clinker are known, it is possible to do such a separation after the fact.

Hawthorn, reporting in the Building Research Establishment study (1993) on the experience with composite cements in France, addresses the concern that limestone-filled cements might be of less consistent quality than other cements. He maintains that the quality of limestone cements is actually quite uniform over time, particularly in comparison to that of cements containing fly ash or slag. Selection of the parts of a quarry that provide consistent material, and a large supply of material in the quarry, allow a uniformity of raw material that is much greater than for industrial byproducts such as slag or fly ash. Moir (1995) also points out that the limestone content can be adjusted to give more uniform strengths.

Table 35. Production Data for Cements With and Without Limestone (Helinski 1996)

Number of samples	Type I Cement 250+		Type 10 Cement with limestone 75	
	Mean	Standard deviation	Mean	Standard deviation
LOI	1.4	0.2	2.2	0.1
SiO ₂	20.03	0.23	19.98	0.22
Fe ₂ O ₃	2.00	0.08	1.96	0.08
Al ₂ O ₃	5.69	0.12	5.23	0.14
CaO	62.54	0.26	62.22	0.26
Free lime	1.17	0.30	1.05	0.29
MgO	2.62	0.08	2.62	0.08
SO ₃	4.10	0.15	4.13	0.17
K ₂ O	1.08	0.03	1.09	0.02
Na ₂ O	0.28	0.01	0.28	0.02
Blaine (m ² /kg)	377	10	384	10
% Passing 45 µm	95.6	13	93.8	1.4
Flow	121	6	120	5
Compressive strength (MPa)				
3 days	27.1	1.5	27.4	1.4
7 days	34.2	1.5	34.1	1.4
28 days	42.1	1.8	42.0	1.8

Although ASTM cement standards specify only minimum strength limits, cement companies could set their own targets for strengths and use limestone to maintain their cement strengths, producing a more uniform product than they can without the use of limestone. Indeed, data summarizing two years worth of grab samples shipped from a modern cement plant producing cements both with and without limestone from the same clinker (Table 35) shows that a similar level of quality control on both cements can be achieved, as evidenced by the similar spread in the chemical and physical data (Helinski 1996).

5.3 CONCRETE

Concrete strength is a major factor in the prediction of its performance. The type of cement is not significant with regard to strength gain except as it relates to the amount required to obtain the strength needed (Livesey 1991a).

Barker and Matthews (1994) examined the criteria specified in the European standard for concrete, EN 206, which provides maximum water:cement ratios and minimum cement contents for concrete that will be exposed to various environments. They believe that while water:cement ratio may be an appropriate criterion for use

with a given cement type, concrete strength should also be specified when the standard is to apply to many types of cement. They tested two series of concretes made with a range of cements including slag, fly ash, and limestone—one with equal cement contents and water:cement ratios, and the other with equal strength grade and workability. They measured permeability, carbonation, and frost resistance in order to assess the durability of these concretes. They found that carbonation depths at one year ranged from 1.0 to 15.7 mm for the equal water:cement ratio concretes and from 0.9 to 11.4 mm for the equal strength concretes. Similarly, the permeability to oxygen was quite variable among the concretes having the same water:cement ratio, but much the same—and lower—among those designed to have the same strength. Frost resistance also correlated much better with concrete strength than with water:cement ratio. They observe that one reason for the poor correlation between durability characteristics and water:cement ratio may be that with cement containing secondary components, there is a question as to what constitutes “cement.” EN 206 treats all cements equally, although if the separate components are added at the concrete mixer the standard takes a different view of the cementitious value of the secondary components. They recommended adding the strength criterion to the specification.

CHAPTER 6

Summary and Conclusions

1. As limestone is, in general, easier to grind than clinker, at the same Blaine fineness the clinker will tend to be concentrated in the coarser fractions and limestone in the finer. Strength levels of the cements with limestone can be controlled by utilizing these differences in grindability.
2. The easier grindability of limestone allows for a broader particle size distribution in closed circuit milling with high efficiency separators. This leads to improved workability and less bleeding in limestone portland cement concretes when compared to controls. The wider particle size distribution also reduces the water demand, increasing the density and the strength.
3. Limestone is not solely an inert additive; the CaCO_3 reacts to a small extent with C_3A to form monocarboaluminate. However, the practical effects of limestone in small amounts are physical—improving particle packing and providing nucleation sites for clinker hydration products.
4. The effect of limestone in amounts up to 5% on the Bogue calculation as given in ASTM C 150 is to provide conservative estimates of C_3S (higher) and C_2S (lower). The effect on calculated C_3A content is minimal. The current limits on loss on ignition and insoluble residue in C 150 provide further controls on the amount of limestone that can be used in portland cement.
5. The heat of hydration is reduced (compared to a control) for some cements containing limestone and increased for others. Setting time also varies. The tendency to false set has been shown to be reduced with partial substitution of limestone for gypsum.
6. A wide range of data show the average strengths of mortars and concretes with and without limestone are the same. However, there is wide range in the strength data, which indicates the optimum amount of limestone needs to be determined for each combination of limestone and clinker.
7. Drying shrinkage and carbonation depths show mixed results, in some cases being increased and in some decreased in limestone portland cements when compared to control portland cements. The differences are of limited practical significance in the context of overall concrete mix variations.
8. Permeability is somewhat reduced by use of limestone, probably due more to a reduction in the connectivity of the pores rather than to their volume.
9. Freeze/thaw resistance is equivalent in portland and limestone portland cements if the amount of entrained air, or more specifically, the air void system is controlled.
10. Some tests have shown improved sulfate resistance for cements containing limestone. This effect appears to be related to the rate of potential deterioration. If the test period is extended, the performance of limestone cements is equivalent to that of the controls. Sulfate resistance is primarily a function of C_3A content and water:cement ratio.
11. Available data suggest that use of up to 5% limestone in cement does not increase the susceptibility of mortars to ASR.
12. The performance of mineral admixtures is unaffected by limestone in cement.
13. Similar levels of quality control are achievable in cement production runs where the same clinker was ground with limestone or without.

CHAPTER 7

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Portland Cement Association

An organization of cement companies to improve and extend the uses of portland cement and concrete through market development, engineering, research, education, and public affairs work.

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