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

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KEYWORDS

Blended cement, calcium carbonate, compressive strength, concrete, concrete properties durability, hydration, limestone, particle size distribution, permeability, portland-limestone cement (PLC), quality control, setting, standards, Type IL, workability

ABSTRACT

This document is to serve as background technical information for engineers, specifiers, and other concrete technologists on use of portland-limestone cements with limestone contents in amounts up to 15% (focusing on amounts between 5% and 15%) and the use of these cements in concrete. Standard requirements for portland-limestone cements in the U.S. are found in ASTM C595 and AASHTO M 240, *Standard Specification for Blended Hydraulic Cements*. Environmental benefits are discussed as well as a history of use of cements with limestone, including a selection of case studies of projects in the U.S. and Canada. The chemical and physical effects of limestone on fresh and hardened properties of concrete are emphasized.

REFERENCE

Tennis, P. D.; Thomas, M. D. A.; Weiss, W. J.; Farny, J. A.; and Giannini, E. R., *State-of-the-Art Report on Use of Limestone in Cements at Levels of up to 15%*, SN3148.03, Portland Cement Association, Skokie, Illinois, USA, 2024, 101 pages.

EXECUTIVE SUMMARY

Portland-limestone cement (PLC), or Type IL cement, is a cement formulation based on portland cement clinker, with additional limestone used as an ingredient, in amounts up to 15% by mass. The environmental benefits of cements with limestone are appreciable: because less limestone is calcined to produce the clinker for a given amount of PLC, both calcination and fuel combustion CO_2 emissions are reduced. Although more grinding energy can be required compared to portland cements, the energy saved by reducing clinker in the finished cement outweighs the extra grinding energy. The 2021 industry-wide environmental product declarations (Portland Cement Association and ASTM International 2023a, 2023b), show that on average, a portland-limestone cement (averaging 10.8% limestone content) has an 8.2% lower carbon footprint than a portland cement (averaging 2.7% limestone content) in the U.S.

This report updates an earlier report (Tennis, Thomas, and Weiss, 2011). There is a wealth of published literature related to the use of limestone as an ingredient in PLCs. This literature includes both laboratory research studies and real-world installations.

Use of Limestone in Cement

Uncalcined (unfired) ground limestone has a long history of use in cement. Cements containing limestone have been used throughout Europe and in other countries since the 1960s. Following the adoption of EN 197-1 in 2000, use of PLC in Europe grew steadily. Canadian specifications in the CSA A3000 compendium have permitted limestone as an ingredient in portland cements since 1983 and contained provisions for PLCs since 2008.

In the U.S., limestone has been permitted as an ingredient in amounts of up to 5% in ASTM C150 portland cements since about 2004 (AASHTO approved a similar change to M 85 in 2007). PLCs meeting ASTM C1157 (a performance specification for hydraulic cement) with around 10% limestone were introduced in 2007 and used successfully in many projects (Innis 2018). In 2012, requirements for PLC (Type IL) with up to 15% limestone were defined in blended cement specifications ASTM C595 and AASHTO M 240, and these cements have seen increasing availability and acceptance in recent years. Experience with blended cements containing limestone has demonstrated that they can be used to produce strong, durable concretes and mortars.

Manufacture of PLC

Portland-limestone cements are typically developed by cement manufacturers to perform comparably to portland cement in concrete and other cement-based materials (i.e., PLC is designed to replace portland cement at the same cement content to result in similar 28-day compressive strength). The production of a well-designed PLC typically includes controlling cement fineness, particle size distribution, and sulfate content to provide similar performance when compared to portland cement made from the same clinker. When optimizing, limestone characteristics, limestone content, properties of other cement ingredients, and various options in manufacturing processes are often considered.

Performance of PLC

Research studies and real-world concrete placements have demonstrated that by following well-documented mixture design and quality control practices, concretes made using PLC can perform similarly to concretes made with portland cement. Although relatively inert compared to clinker or supplementary cementitious materials (SCMs), the limestone contributes directly to properties through three mechanisms:

- Particle packing effects: limestone particles typically broaden the particle size distribution of cement, which can lead to denser pastes;
- Nucleation effects: products of cement hydration reactions are accelerated slightly and better distributed; and
- Chemical reactions: while minor, carboaluminate phases are produced, reducing porosity.

Limestone is easier to grind than clinker and the fineness of a PLC is generally higher than that of portland cement from the same source. The fine limestone particles contribute to the mechanisms above, but an overall higher cement fineness may also increase water demand, depending on other factors in the concrete mixture design.

As durability of concrete is a primary concern in many applications, it is important to note that the same techniques used to provide properties such as freeze-thaw or sulfate resistance for portland cement mixes are also used with PLC mixtures. Just like concrete made with portland cements, concrete mixtures made with PLC should be tested to confirm fresh and hardened properties such as air void content, strength, freeze-thaw durability, sulfate resistance, etc., as needed for the project. For sulfate resistance, laboratory and simulated field exposure research results confirm that use of supplementary cementitious materials (SCMs) in combination with PLCs can produce highly sulfate-resistant concrete suitable for severe sulfate exposures. Performance testing of PLCs and PLC-SCM combinations is required to qualify the sulfate resistance characteristics of the cementitious system. In addition, some cement manufacturers also produce ASTM C595/AASHTO M 240 Type IL(MS) or Type IL(HS) cements, which have been tested (in accordance with ASTM C1012) to demonstrate moderate or high sulfate resistance, respectively, and can be used in similar applications to an ASTM C150/AASHTO M 85 Type II or Type V cements.

PLC Acceptance

Both the availability and acceptance of PLCs have increased over the past decade. Surveys conducted by PCA of its members in 2017 (covering 2012 through 2016) and 2019 (covering 2017 and 2018) show slowly increasing production of PLC in this time period, with a total of over 4.1 million metric tons produced in the U.S. by survey respondents over those seven years (Tennis 2019).

Beginning in 2021, U.S. Geological Survey (USGS) cement consumption data (McCarthy and Storck, 2023) show that the share of blended cements relative to total cement consumption increased sharply in the U.S. (see Figure A). While the blended cement category includes Type IP (portland-pozzolan), Type IS (portland blast-furnace slag), Type IL (portland-limestone), and

Type IT (ternary blended) cements, the strong uptick in blended cement production is the result of increased consumption of PLC (Type IL) more than the other cement types, with the USGS estimating that more than 95% of U.S. blended cement is PLC (Hatfield and Pisut, 2024). Over the past decade, technical research and communication efforts resulted in acceptance of PLC by major customer and specifier groups like the state Departments of Transportation as shown in Figure B (50 accepted its use by February 2024), users of AIA MasterSpec, Unified Facilities Guide Specifications (UFGS), the Federal Aviation Administration, and others. USGS data indicate that approximately 24.8 MMT of PLC was consumed in 2022 (McCarthy and Storck, 2023).

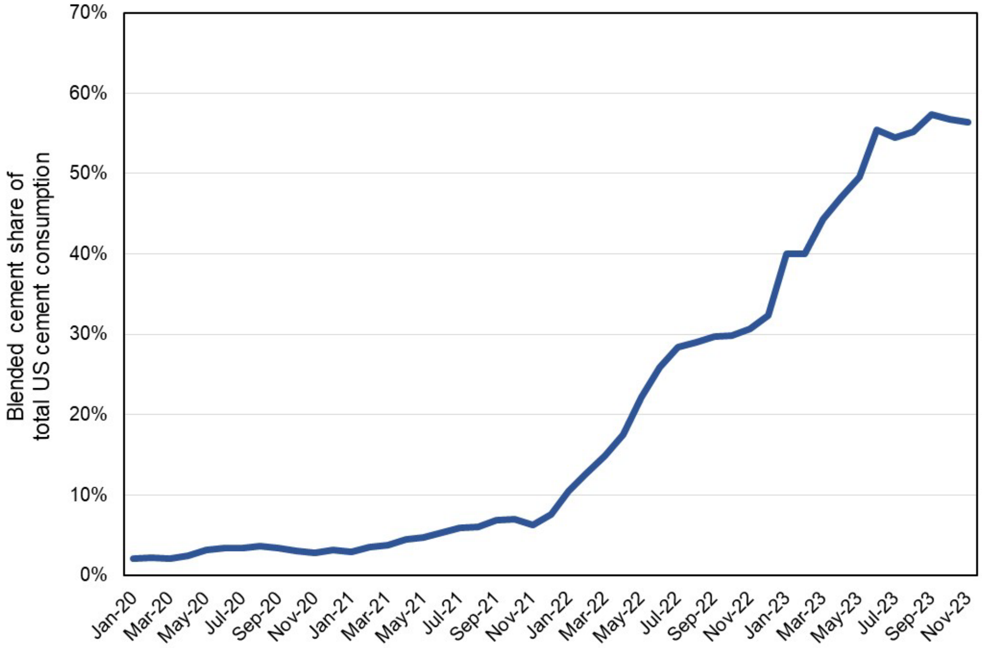
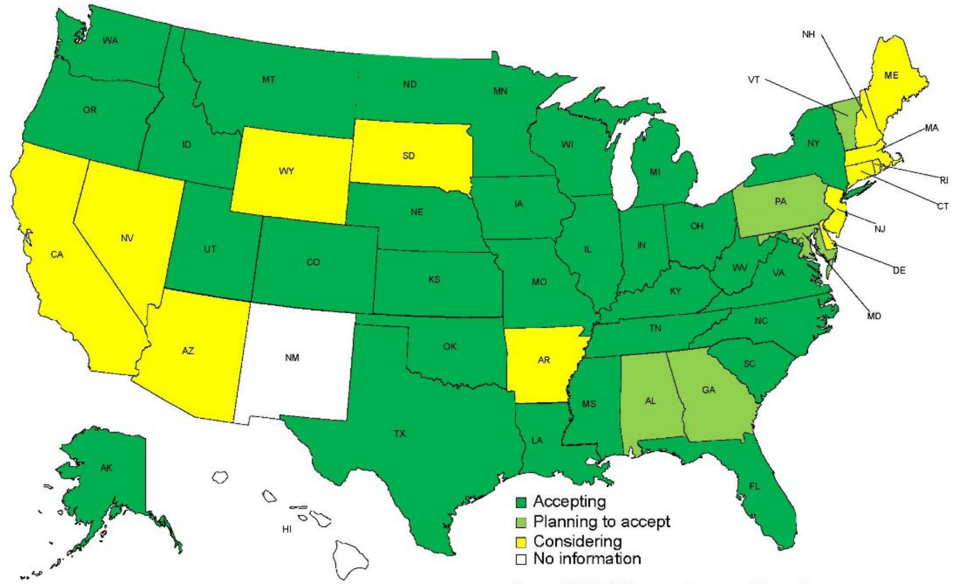


Figure A. U.S. Geological Survey data on consumption of blended cement from January 2020 to July 2023 (Figure from PCA Market Intelligence, based on data in Hatfield and Pisut, 2024).

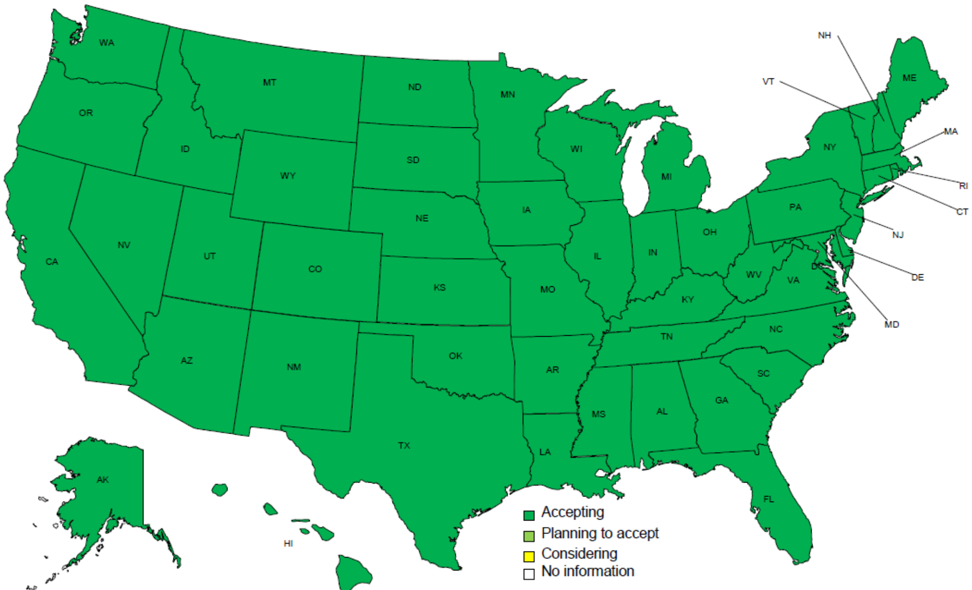
(1)



Note: FAA P-501 permits use of Type IL

January 2019

(2)



Note: FAA P-501, AIA MasterSpec, UFGS 03 30 00, and ACI and ICC building codes permit use of PLC

February 2024

Figure B. Acceptance of PLCs by U.S. State Departments of Transportation as of January of 2019 (1) and February 2024 (2).

References

Hatfield, A. K., and Pisut, C. K., "Cement in November 2023," *Mineral Industry Surveys*, National Minerals Information Center, U.S. Geological Survey, Reston, Virginia, USA, 2024, 34 pages.

Innis, F. A., "Portland-Limestone Cement after 10 Years in the Field," MAP Brief, October 2018, 7 pages, https://intrans.iastate.edu/app/uploads/2019/10/MAPbriefOctober2018.pdf.

McCarthy, E., and Storck, T., *Increased Adoption of Portland-Limestone Cement*, PCA Market Intelligence Report, Portland Cement Association, Skokie, Illinois, USA, June 2023, 3 pages.

Portland Cement Association and ASTM International, *Environmental Product Declaration for Portland Cement*, Portland Cement Association, 2023a, 13 pages, https://www.cement.org/docs/default-source/default-document-library/pca_epd_portland_athena_final_revised_nov2023.pdf?sfvrsn=f8a9febf_2.

Portland Cement Association and ASTM International, *Environmental Product Declaration for Portland-Limestone Cement,*" Portland Cement Association, 2023b, 13 pages. https://www.cement.org/docs/default-source/default-document-library/pca_epd_plc_athena_final_revised_nov2023.pdf?sfvrsn=aafebf_2.

Tennis, P. D., *U.S. Production of Portland-Limestone Cements—2012 through 2018*, SN3313b, Portland Cement Association, Skokie, Illinois, USA, 2019, 10 pages.

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

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

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CHAPTER 1 INTRODUCTION

The cement industry continues to introduce more sustainable practices and products for constructing and maintaining concrete infrastructure and buildings. A focus on sustainable development, the implementation of more restrictive environmental regulations on cement manufacturing, and a potential for global climate change legislation contributed to the addition of provisions for portland-limestone cements (PLCs) within specifications ASTM C595 and AASHTO M 240 in 2012. Such provisions are similar to those adopted by CSA A3000, with limestone contents greater than 5% and up to 15%. For many applications, PLCs can provide similar and potentially improved performance with reduced environmental impact. The purpose of this report is to document the development, use, and performance of these cements.

The first edition of this report was published in 2011, just prior to the addition of provisions to define Type IL cement in the ASTM C595 and AASHTO M 240 standards. This 2023 update to the report has been developed to add information based on another decade of research and experience with PLCs in practice. Portland-limestone cements have been in common use around the world for several decades, and the limestone content can exceed the 15% maximum limit adopted in the ASTM C595/AASHTO M 240 blended cement standards. For reasons described in this report, the performance of PLCs with limestone contents up to 15% typically have comparable performance to the historically dominant cement used in the U.S., ASTM C150/AASHTO M 85 portland cement. Limiting the limestone content to 15% maximum in the U.S. specifications offered the fastest route to adoption and acceptance by user groups, allowing the sustainability benefits to be realized. For this reason, the bulk of information/research/results reported here is focused on cements with 5% to 15% limestone content. Some research reported here includes results for PLCs with limestone contents exceeding 15%.

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Given that many countries have classes of cement with limestone content above 15% that are regularly used for certain applications, there is enough data available to present results for some of those cement or concrete properties. In those cases, it is clearly denoted.

Prior to the 2012 inclusion of the Type IL designation in ASTM C595/AASHTO M 240, similar cements were produced in the U.S. under ASTM C1157, *Standard Performance Specification for Hydraulic Cements,* the performance standard for hydraulic cements. ASTM C1157 remains an active standard; however, it is not widely specified. The availability of PLCs in the U.S. via ASTM C1157 since about 2006 offers a unique opportunity to assess real-world projects in the U.S. that have been in use for more than 15 years, demonstrating performance of PLC-based concrete, at times in direct comparison to portland-cement concrete, as part of the early research efforts. Many of the earliest uses of PLC in the U.S. were for pavement applications. In each known case, satisfactory performance in field applications was achieved.

1.1 SCOPE OF REVIEW

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

Achieving comparable performance in concrete using PLC to that obtained using conventional portland cement is possible because finely ground limestone can contribute to development of microstructure, particularly when fineness and chemistry of the finished cement are carefully controlled by the manufacturer. Mechanisms affecting performance include particle packing, establishment of nucleation sites for cement hydration, and reaction with calcium aluminate phases in the portland cement clinker or supplementary cementitious materials to form calcium carboaluminates. These are discussed in more detail in Chapter 2. Chapter 3 covers fresh concrete properties, including workability, bleeding, heat of hydration, and setting time. Chapter 4 reviews effects on hardened concrete properties: strength development, modulus, creep, and volume stability. Durability topics are included in Chapter 4 as well: permeability, chloride resistance, carbonation, freeze-thaw, sulfate attack (including thaumasite sulfate attack), alkali-silica reactivity (ASR), and abrasion resistance. Requirements for specifying and monitoring the quality of cements and limestone used in cements are discussed in Chapter 5. Chapter 6 presents selected U.S. and Canadian case studies on PLC usage in the field, including the construction and follow-up monitoring of trial paving projects. Chapter 7 summarizes key points throughout this report. Sources of information that informed this report include experience and published literature spanning decades of PLC use in Europe, more recent data developed to determine requirements in U.S. and Canadian standards, findings from U.S. state DOT-funded research studies, and lessons learned from projects using PLC in the field.

1.2 WORLDWIDE USE OF LIMESTONE IN CEMENT

1.2.1 North America

1.2.1.1 United States. In 2012, ASTM and AASHTO adopted provisions for PLCs as Type IL blended cements in ASTM C595/C595M and AASHTO M 240M/M 240. Blends containing both limestone and a pozzolan or slag cement are designated as Type IT, ternary blended cements, in these specifications. Type IL and Type IT cements can contain a maximum of 15% limestone by mass, and the target limestone content is declared in the product designation. For example, Type IL(12) denotes a PLC with 12% target limestone content. Blended cements under these specifications may also have special property designations to denote their suitability for use in certain applications, if requested by the purchaser. Table 1.1 compares these designations to ASTM C150/C150M and AASHTO M 85M/M 85 portland cement types. To be noted is that for decades portland cements in the U.S. have used C_3A contents to define sulfate-resistant cement types, with limits of 8% for moderately sulfate resistant and 5% for highly sulfate resistant. Although clinkers with the same C_3A contents are used to produce Type IL cements, sulfate resistance for blended cements is defined by ASTM C1012, which is a more conservative approach.

The naming convention for ternary blends containing limestone follows the Type IT(AX)(BY), with “A” and “B” denoting the other components of the cement (P = pozzolan, S = slag cement, L = limestone), and X and Y indicating the targeted amounts of those ingredients. Pozzolans may comprise up to 40% by mass of a Type IT cement, and slag cements up to 70% by mass. If the cement contains an air-entraining addition, the suffix (A) is also added; this designation comes with additional requirements for mortar air content and reduced minimum mortar compressive strengths.

Table 1.1 ASTM C150 / AASHTO M 85 portland cement types compared to ASTM C595/ AASHTO M 240 portland-limestone cements with special property designations.

Application	ASTM C150 / AASHTO M 85 cement type	ASTM C595 / AASHTO M 240 cement type*
General use	I	IL(X)
Moderate sulfate resistance	II, II(MH)**	IL(X)(MS)
Moderate heat of hydration	II(MH)**	IL(X)(MH)**
High early strength	III	IL(X)(HE)
Low heat of hydration	IV**	IL(X)(LH)**
High sulfate resistance	V	IL(X)(HS)

*X refers to the targeted percentage of limestone (by mass) in the cement.

**ASTM and AASHTO have approved changes to these standards that will remove MH and LH designations, and Type IV cement. These changes are anticipated to be published in 2024.

1.2.1.2 Canada. In 2008, Canada’s cementitious materials compendium, CSA A3000, adopted provisions for PLCs, and some of those provisions have been subsequently amended, most recently in 2022. Portland-limestone cements are defined by CSA as containing more than 5% and up to 15% limestone. The following provides a brief synopsis of Canadian PLC specifications, while Chapter 5 includes more detailed information on requirements for limestone and cements.

Although it is a prescriptive specification, CSA A3000 uses a naming convention similar to that used by ASTM C1157; however, it includes 4 primary classes of cements for concrete construction: portland cement, blended cement, PLC, and portland-limestone blended cement. As examples, Type GU and Type GUL refer to portland cement and PLC, respectively, and indicate that the cement is intended for general use in concrete construction. CSA lists four types of PLC as shown in Table 1.2. In addition, four types of portland-limestone blended cements are also defined. This is a significant difference between ASTM C595 (AASHTO M 240) and CSA A 3000: PLCs are considered a different class of cement, neither portland nor blended, although portland-limestone blended cements are also defined. These would be considered ternary blended cements in ASTM C595/AASHTO M 240.

While the European standard EN 197-1 includes provisions for PLCs containing limestone in amounts up to 35% for some concrete exposure conditions, the CSA A3001 limit is set at a maximum of 15% to help ensure comparable performance to conventional portland and blended cements. CSA PLCs must meet the same physical requirements as portland cements or blended cements of parallel type designation. See Section 5.2.2 for a summary of requirements.

Table 1.2 CSA A3001-18 (Amendment 2021) Naming Convention for Portland, Blended, and Portland-Limestone Cements

Application	Portland cement type	Blended cement type	Portland-limestone cement type	Portland-limestone blended cement type
General use	GU	GUb	GUL	GULb
Moderate sulfate resistance	MS	MSb	MSL	MSLb
High early strength	HE	HEb	HEL	HELb
High sulfate resistance	HS	HSb	HSL	HSLb

1.2.3 Europe

Although specification EN 197-1, *Cement – Part 1: Composition, Specifications and Conformity Criteria for Common Cements,* was formally adopted in 2000 by members of the European Committee for Standardization (CEN), limestone cements have a long history of use in Europe. Spanish standards permitted up to 10% limestone in 1960 (raised to 35% in 1975 for cements used in some concrete exposures), French standards adopted provisions for use of up to 35% limestone in 1979 (Moir 2003), and German standards for PLC were adopted in 1994 (Mans et al. 2000), although cements with up to 20% limestone were manufactured for specialty applications in Germany as far back as 1965. EN 197-1 has been updated since its original adoption, most recently in 2011.

All 27 cement types defined in EN 197-1 may contain up to 5% of a minor additional constituent (MAC), which is commonly limestone. Limestone is used at higher levels in CEM II cements with 6 different designations: CEM II/A-L and CEM II/A-LL cements contain between 6% and 20% limestone (by mass) while CEM II/B-L and CEM II/B-LL cements contain between 21% and 35% limestone. (The -L or -LL suffixes identify the total organic carbon (TOC) content of the limestone used: LL cements use limestone with a maximum TOC of 0.20% by mass, while L cements are made with limestones with a TOC of up to 0.50% TOC.) Limestone is also commonly used in "portland composite cements" CEM II/A-M and CEM II/B-M cements (the -M suffix stands for multiple ingredients) in which the total amount of non-clinker constituents is less than 20% by mass or less than 35% by mass, respectively. Table 1.3 summarizes the European nomenclature.

Table 1.3 Nomenclature of European Portland-Limestone Cements

Type	Name	Range of limestone content, mass %	Notes
CEM II/A-L	Portland-limestone cement	6 to 20	TOC*≤0.50%
CEM II/A-LL	Portland-limestone cement	6 to 20	TOC≤0.20%
CEM II/A-M	Portland composite cement	Less than 20**	
CEM II/B-L	Portland-limestone cement	21 to 35	TOC≤0.50%
CEM II/B-LL	Portland-limestone cement	21 to 35	TOC≤0.20%
CEM II/B-M	Portland composite cement	Less than 35**	

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

**Portland composite cements contain more than one main constituent (besides clinker) totaling 12 to 20% or 21 to 35% by mass respectively for CEM II/A-M and CEM II/B-M.

The EN 197-5 standard, released in 2021, includes definition of five additional blended cement types, three of which may contain between 6 and 20% limestone as an ingredient. CEM II/C-M cements are portland-composite cements containing 50-64% clinker and 36-50% of up to two additional ingredients, which may be SCMs or limestone. The proportion of limestone (if used) in CEM II/C-M cement must be 6-20% of the mass of the cement. CEM VI cements are composite cements that are ternary blends containing 35-49% clinker, 31-59% blast-furnace slag, and 6-20% of either a natural pozzolan, siliceous fly ash, or limestone. Types CEM VI(S-L) and CEM VI(S-LL) contain limestone as the third ingredient. Limestone used in CEM II/C-M and CEM VI cements is subject to the same total organic carbon limits (with “L” and “LL” suffix designations) as cements under EN 197-1.

1.2.4 Other Regions

The 2017 edition of *Cement Standards of the World* (Cembureau 2017) documents multiple countries that reference cements that permit limestone as an ingredient in their cements.

Many non-EU countries around the world also refer to EN 197-1 for cement specifications, and thus also have experience with PLCs. These include Algeria, Israel, Malaysia, Kazakhstan, Singapore, South Africa, Turkey, and the UK, although some of these countries may not have adopted the most recent version of EN 197-1 or may use it in conjunction with national standards (Cembureau 2017). Likewise, international use of ASTM cement specifications is common, leading to options for use of limestone as a cement ingredient in those countries. Examples include countries like the Philippines, Kuwait, Oman, Qatar, Saudi Arabia, and the United Arab Emirates (Cembureau 2017).

In Mexico, NMX-C-414 defines cement Type CPC, termed a blended portland cement, that may contain between 6% and 35% limestone, and may include other ingredients such as granulated blast-furnace slag, pozzolan, or silica fume in amounts such that the clinker and gypsum fraction is not less than 50% by mass. Brazil and other South American countries also commonly include limestone in several cement types (Cembureau 2017). It should be noted that some cement types do not have compositional requirements, so limestone may not be expressly permitted or forbidden by their specifications.

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

The 2010 version of Australian standard AS 3972 permits up to 7.5% limestone in general purpose (GP) cements, while limestone portland cements (GL) may contain up to 20% limestone. Limits on methylene blue index (MBI) and total organic carbon (TOC) apply to limestone containing between 75 and 80% calcium carbonate (Mohammadi and South 2016). For more information on MBI and TOC, see Sections 2.2 and 5.1.

1.3 IMPACT ON SUSTAINABILITY

Concrete is the most widely used material in the world after water. In the U.S. alone, annual production is estimated at about 390 million cubic yards (Lobo 2022). Although cement is only a small portion of concrete, it is the most energy- and carbon-intensive ingredient. Slag cements and portland cement together account for as much as 95% of the environmental impacts of concrete mixtures (NRMCA 2022). Given the high global warming potential (GWP) and other impacts of cements, industry is invested in finding more sustainable solutions to producing concrete.

After thoroughly evaluating potential improvements to manufacturing, members of the U.S. construction industry published a *Roadmap to Carbon Neutrality* (PCA 2021a). It identifies potential technological improvements for clinker and cement production that will help to reduce energy use and CO_2 generation. The *Roadmap* also addresses targeted improvements in the full cement and concrete value chain, including the production of concrete in construction, the service life of concrete structures, and end-of-life recycling and reuse.

Portland-limestone cements, or PLCs, are a key aspect of the *Roadmap*. The specifications for PLC were established to allow users to replace an ASTM C150/AASHTO M 85 portland cement without significantly modifying concrete production or installation procedures. When ASTM Committee C01 on Cement instituted changes to allow for the use of finely ground limestone in ASTM C595 blended cements in 2012, these changes were coordinated with the American Association for State Highway Transportation Officials for the parallel standard on blended cements, AASHTO M 240, so that producers can simultaneously meet either the ASTM C595 or AASHTO M 240 specification with the same product.

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

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

In general, portland-limestone blended cements are ground more finely than portland cements and thus they may require higher grinding energy. However, this is a relatively smaller energy usage than clinker production, and the net change is for lower CO_2 emissions and energy use to produce blended cements. Figure 1.1 provides specific examples for CO_2 emission reductions for three German cement plants (Schmidt 1992). The calculations include the total energy demand of all steps in the production process taking into account the specific demand of fuel energy. Similar results can be calculated for the emissions of nitrous oxides (NO_x) and sulfur dioxide (SO_2).

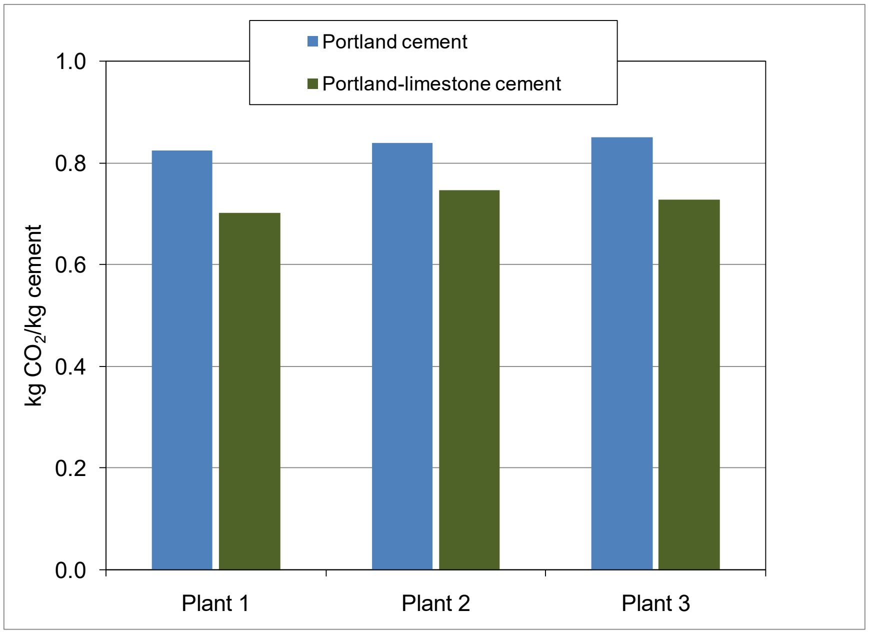


Figure 1.1 Specific CO_2 emissions from the production of portland cement or portland-limestone cement for 3 German cement plants (adapted from Schmidt 1992).

Data on greenhouse gas emissions contained in environmental product declarations (EPDs) further document the reduction in emissions in PLCs compared to portland cements. Industry-average EPDs for PCA members in the U.S that were published in 2021 (PCA 2021b and 2021c) state that portland cements have an average GWP of 922 kg CO_2-eq per metric ton of cement (a drop of 11.3% since 2016), while PLCs (averaging 10.8% limestone content in 2021) have a GWP of 846 kg CO_2-eq per metric ton of cement, or 8.2% less than portland cements. Both comparisons are useful to understand how cement production is improving. Over a 5-year period, the 11.3%

drop in portland cement's GWP shows that industry has made significant recent progress. That is due partly to changes that cement manufacturers have implemented at their plants, from upgrading to more efficient equipment and processing to modifying cement formulations. It's also due to an external factor, the greening of the power grid, because manufacturers purchase a significant amount of electricity to run grinding mills and other equipment.

The 2021 EPDs were developed in accordance with the 2020 Cement Product Category Rule (PCR) and account for all embodied energy and emissions associated with the production of a metric ton of cement, from extraction and processing of the raw feedstock materials to when the finished cement leaves the plant (cradle-to-gate boundary for the life cycle assessment).

Another benefit of PLCs is their lower raw material demand which reduces the consumption of natural resources. To produce 1 ton of portland cement, about 1.6 tons of raw materials are needed. PLCs need less primary raw materials (between about 4% to 16% less limestone in the raw material).

An analysis of the environmental impact of up to 5% limestone in the production of *portland* cement is found in Nisbet (1996). Based on the approach used in that analysis, an estimate is given in Table 1.4 assuming 10% or 15% limestone for *blended* cements. These provide conservative estimates of reductions in environmental and energy impacts that can be achieved through use of limestone, as compared to portland cement without limestone. It should be noted that portland cements in the U.S. have been permitted since 2004 to contain up to 5% limestone (with a level of about 3% on average, when used (Tennis 2016)), which will reduce the savings noted in Table 1.4. Even if the maximum amount of limestone (5%) is used in portland cements, use of PLCs with a total of 10% to 15% limestone will result in significant additional reductions in energy and emissions.

Table 1.4 Estimated Annual Reduction in Energy Usage and Emissions Resulting from the Use of 10% or 15% Limestone in Blended Cement*

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

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

1.4 REFERENCES

AASHTO M 85, *Standard Specification for Portland Cement*
AASHTO M 240, *Standard Specification for Blended Cement*
ASTM C150/C150M, *Standard Specification for Portland Cement*

ASTM C595/C595M, *Standard Specification for Blended Cements*

ASTM C1157, *Standard Performance Specification for Hydraulic Cement*

CSA A3000, *Cementitious Materials Compendium*

CSA A3001, *Cementitious Materials for Use in Concrete*

EN 197-1:2011, *Cement - Part 1: Composition, Specifications and Conformity Criteria for Common Cements*, European Committee for Standardization, Brussels, 2011.

Cement Association of Canada (CAC), *Portland Limestone Cement*, Ottawa, Ontario, Canada, August 2009, 3 pages.

Cembureau, *Cement Standards of the World*, Cimeurope, Villeneuve D'Ascq, France, 2017.

Environmental Product Declaration, Portland-Limestone Cement, ASTM International, EPD 196, March 2021.

Environmental Product Declaration, Portland Cement, ASTM International, EPD 195, March 2021.

Hooton, R. D., Nokken, M. A., and Thomas, M. D. A., *Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A3000*, SN3053, Cement Association of Canada, Ottawa, Ontario, Canada, 2007, 59 pages.

Lobo, C., *Industry Fact Sheet*, National Ready Mixed Concrete Association, Alexandria, Virginia, USA, personal communication, May 2022.

Manns, Wilhelm; Thielen, Gerd; and Laskowski, Christina, "Evaluation of the results of tests for building inspectorate approval of Portland limestone cements," *Concrete Technology Report 1998 to 2000*, Verein Deutscher Zementwerke, Dusseldorf, Germany, March 2001, pages 15 to 23.

Mohammadi, I., South, W., "General Purpose Cement with Increased Limestone Content in Australia," *ACI Materials Journal*, V. 113, No. 3, 2016, pages 335 to 347.

Moir, G.K., "Limestone Cements: Gaining Acceptance," *International Cement Review*, March 2003, pages 67 to 70.

Nisbet, M.A., *The Reduction of Resource Input and Emissions Achieved by Addition of Limestone to Portland Cement*, SN2086, Portland Cement Association, Skokie, Illinois, USA, 1996, 11 pages.

NRMCA, *Environmental Product Declaration: NRMCA Member Industry Average EPD for Ready Mixed Concrete*, National Ready Mixed Concrete Association, Silver Spring, MD, January 3, 2022, 33 pages. See also: https://www.nrmca.org/association-resources/sustainability/environmental-product-declarations/

NSF International, *Product Category Rule Environmental Product Declarations, PCR for Portland, Blended, Masonry, Mortar, and Plastic (Stucco) Cements*, v3.1, Sept. 2020.

PCA, *Roadmap to Carbon Neutrality*, 2021a, 73 pages. See: https://www.cement.org/docs/default-source/cement-concrete-applications/pca_roadmap-to-carbon-neutrality_jan-2022.pdf?sfvrsn=33d8fcbf_2.

PCA, *Environmental Product Declaration for Portland Cements*, Portland Cement Association, Skokie, IL, and ASTM International, West Conshohocken, PA, March 12, 2021b, 13 pages. https://pcr-epd.s3.us-east-2.amazonaws.com/634.EPD_for_Portland_Athena_Final_revised_04082021.pdf.

PCA, *Environmental Product Declaration: Portland-Limestone Cements*, Portland Cement Association, Skokie, IL, and ASTM International, West Conshohocken, PA, March 12, 2021c, 13 pages. https://pcr-epd.s3.us-east-2.amazonaws.com/635.EPD_for_PLC_Athena_Final_revised_04082021.pdf.

Schmidt, M., "Cement with Interground Additives - Capability and Environmental Relief," *Zement-Kalk-Gips*, Vol. 45, No. 2, 1992 pages 64 to 69; and Vol. 45, No. 6, 1992 pages 296 to 301.

Tennis, P.D., *Chemical and Physical Characteristics of U.S. Cements: 2014*, R&D SN3284, Portland Cement Association, Skokie, Illinois, USA, 2016, 32 pages.

CHAPTER 2 EFFECTS OF LIMESTONE ON CEMENT

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

2.1 PARTICLE SIZE DISTRIBUTION

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

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

Material (mass %)	Fineness of grinding (m^2/kg)	Calculated packing density (% vol.)	Voids content (% vol.)	Water requirement (EN 196)
Limestone	578	66.6	33.4	
CEM 32.5	262	65.5	34.5	25.5
CEM 42.5	338	64.8	35.2	27.5
10% LS + 90% CEM 32.5	303	65.8	34.2	24.0
15% LS + 85% CEM 32.5	331	65.9	34.1	24.0
20% LS + 80% CEM 32.5	341	66.0	34.0	24.0
10% LS + 90% CEM 42.5	365	65.0	35.0	27.0
15% LS + 85% CEM 42.5	382	65.2	34.8	27.0
20% LS + 80% CEM 42.5	399	65.3	34.7	26.5

Limestone, when ground for optimum fineness, can lower the water demand, reduce bleeding, improve workability, and increase strength due to improved overall particle size distribution of a cement (Schmidt 1992). In general, the use of 15% to 20% limestone can result in optimal packing density; however, this may be less pronounced in cements that are finer

(Schmidt et al. 1994). When the clinker and limestone are interground, the limestone is normally easier to grind and tends to become the majority of the smaller particles (Figure 2.1), thus broadening the particle size distribution. It is generally necessary to grind PLCs 8 to 10 m^2/kg finer for each percentage of limestone than portland cement to achieve similar performance of the cement they replace (Barcelo et al. 2013). Kurtis et al. (2017) noted that Blaine values may not always provide a sufficient measure of fineness, and recommended characterizing portland-limestone cements (PLCs) using laser diffraction analysis to permit classification based on the 50th and 90th percentile particles sizes (D_{50} and D_{90}). They also stated that it was critical for PLCs to be ground finer than portland cements to achieve nucleation and filler effects on hydration and microstructure.

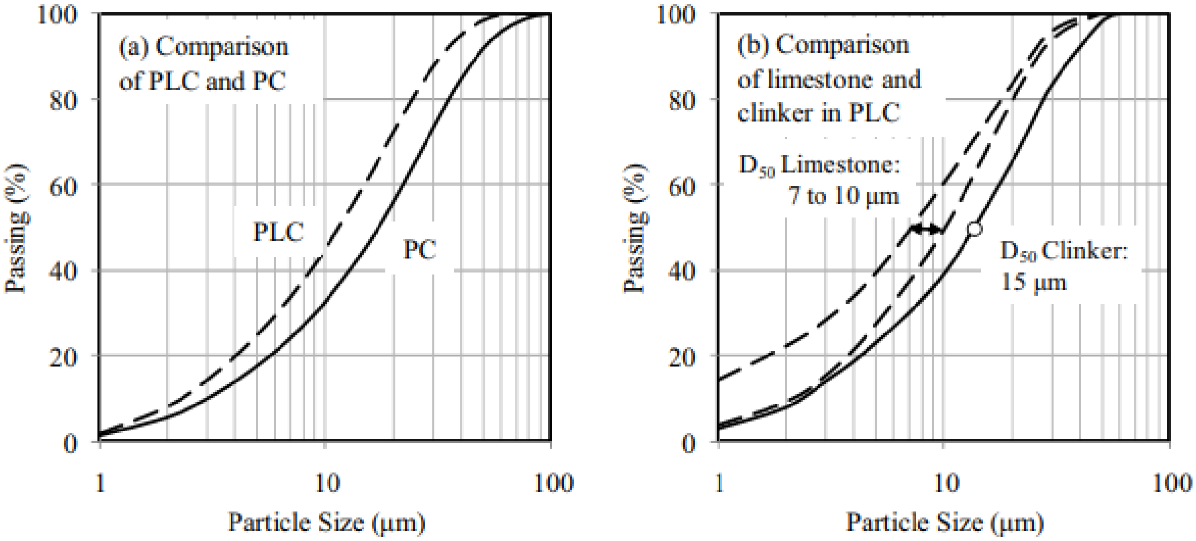
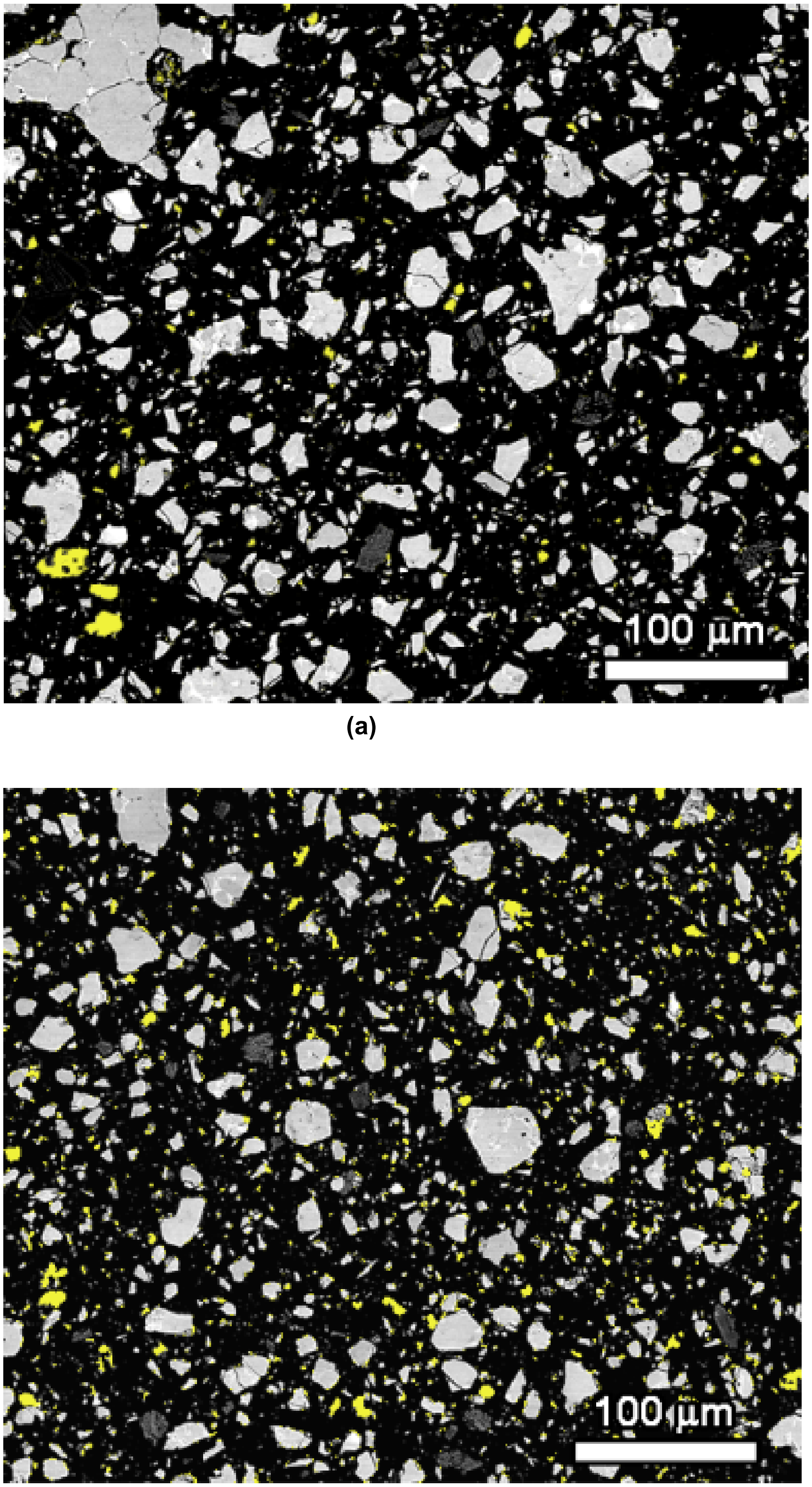


Figure 2.1 Particle size distributions for components of an interground cement. The limestone fraction is finer than ground clinker (Thomas et al. 2010b). PC refers to portland cement, and PLC refers to portland-limestone cement.



(a)

(b)

Figure 2.2 Backscattered electron micrographs of (a) a portland cement, and (b) a PLC. Limestone particles are shaded yellow (Barrett, Sun, and Weiss 2013).

When ground separately the limestone needs to be sufficiently fine; if it is too coarse, an increase in particle spacing may occur along with an increase in the voids between the particles. Barrett et al. (2013) demonstrated the role of limestone fineness on concrete performance. An increase in particle spacing can result in increased water demand and reduced strength (Cam and Neithalath 2010). Some researchers have suggested a potential benefit of intergrinding on the carboaluminate reaction, for example to reduce porosity slightly (Matschei et al. 2007a) and thereby improve durability.

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

Bucher (2009) provides a comparison of shrinkage for concretes made with cements without limestone and with 10% limestone at three different fineness levels (plotted by Bentz et al. (2009b) as shown in Figure 2.3). Restrained shrinkage was similar to the control for the finest limestone and somewhat lower for the concrete with the coarsest limestone.

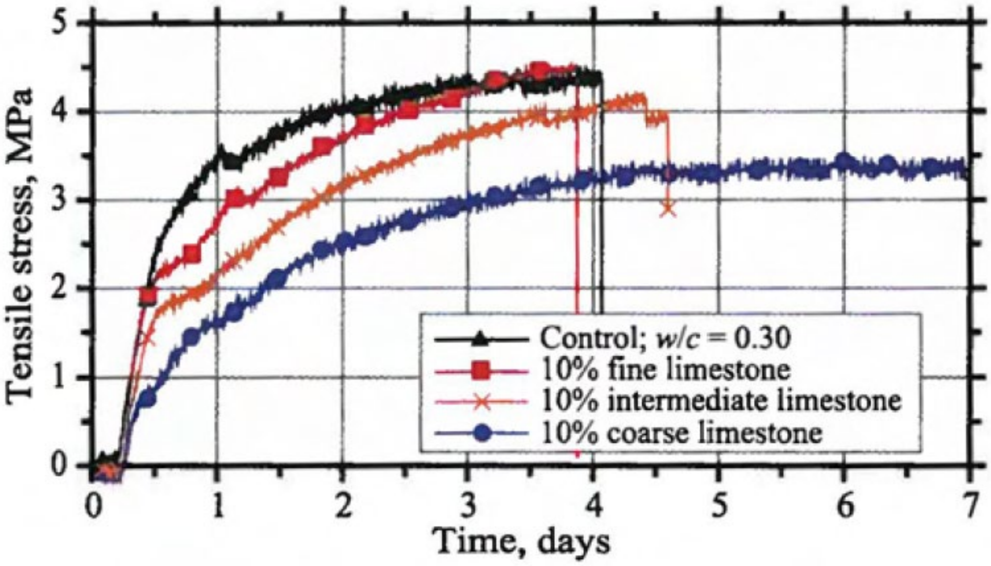


Figure 2.3 Restrained shrinkage results (Bentz et al. 2009b, quoting data from Bucher 2009) showing improved time to cracking results for low water-to-cement ratio concretes made cements with 10% limestone (and control without limestone). The coarse limestone exhibited much longer time to cracking.

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

2.2 INFLUENCE OF COMPOSITION

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

Siebel and Sprung (1991) compared the effects of characteristics of limestone in cement on concrete performance. Although no direct correlation between calcium carbonate content ($CaCO_3$), methylene blue index (MBI), or total organic carbon content (TOC) and the freeze-thaw performance of concretes made with the limestones was observed, limits on these three parameters became the basis for limestone quality for use in cements. All three parameters were included in EN 197-1 for limestones used in amounts greater than 5%.

ASTM C595 and AASHTO M 240 require a minimum of 70% $CaCO_3$ in limestone. Similarly, CSA A3001 requires limestone in portland-limestone and blended cements consist of at least 75% $CaCO_3$ and have an MBI of less than 1.2g/100 g (the same value as EN 197-1). MBI and TOC requirements were initially included in ASTM C595 and AASHTO M 240 for limestone used in Type IL and IT cements, but they were removed in 2016. This was done following a critical review of earlier work and new research (Feng and Clark 2014) that demonstrated a lack of correlation between MBI or TOC values with performance in freeze-thaw tests (ASTM C666) or hardened air void parameters (ASTM C457), along with repeatability issues with these tests in a round-robin study. Performance of concrete containing PLCs in freeze-thaw conditions is discussed further in Chapter 4.

2.3 HYDRATION CHEMISTRY

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

Calcium carbonate has been reported to react with tricalcium aluminate (C_3A) to form high and low forms of carboaluminates (Hooton et al. 2007). Tsivilis (1999a) also observed that clinker with a higher C_3A is more reactive with limestone. Matschei et al. (2007a) observed that small amounts of limestone (calcite) reacted to form various carboaluminate phases, as shown in Figure 2.3. The unreacted calcite increased with an increase in the sulfate content. This work clearly showed the relative amounts of the phases that can be present. Lothenbach et al. (2008) coupled thermodynamic calculations with experimental observations to show that the formation of monocarboaluminate stabilized ettringite, increased the volume of hydrated products, and decreased porosity. Garcia et al. (2019) presented similar findings and suggested that Al_2O_3/CO_2 and Al_2O_3/SO_3 ratios of portland-limestone blended cements could be optimized to promote these reactions and minimize formation of hemicarboaluminate and monosulfate phases. They also described the temperature-dependence of the hydration products, with gismondine (a calcium aluminosilicate hydrate) forming in PLC pastes at 5˚C, and hemicarboaluminate formation favored over monocarboaluminate in PLC pastes at 38˚C, in agreement with prior work by Voglis et al. (2005). These works provide quantitative calculations of the phases that may be present, providing a great step forward in understanding these systems.

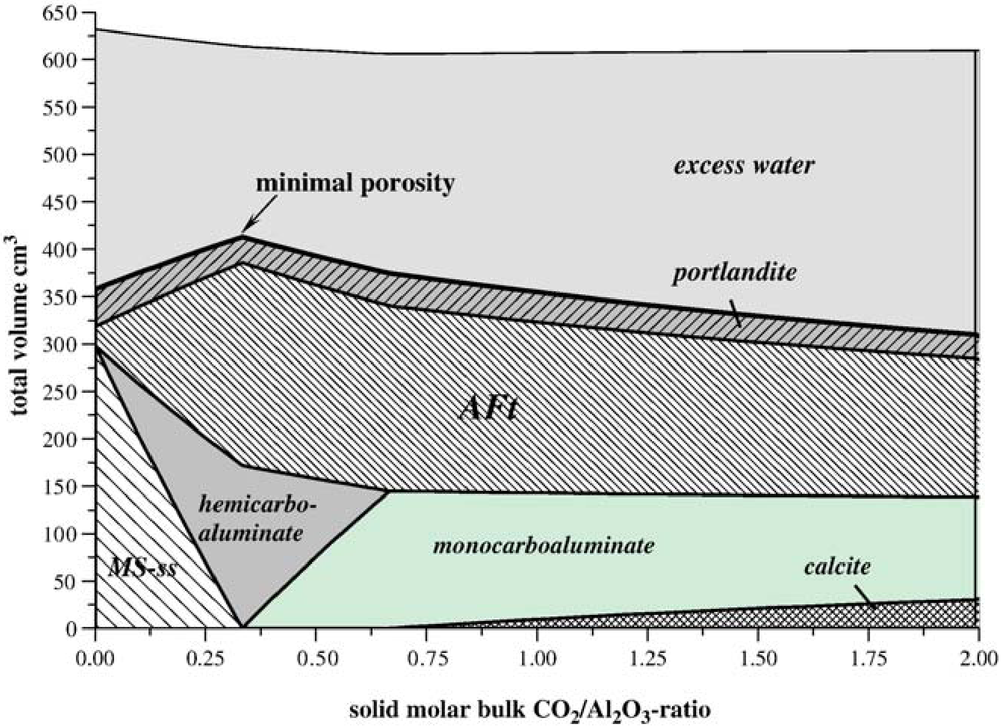


Figure 2.3 Calculated volumes of hydrate phases for a model mixture consisting of C_3A, portlandite and with fixed sulfate ratio ($SO_3/Al_2O_3=1$) as a function of carbonate ratio (CO_2/Al_2O_3) at 25°C (constant total amount of solids, $C_3A+CaSO_4+CH+Cc=3.25$ mol, reacted with 500 g water) (Matschei et al. 2007a).

Additionally, there may be a chemical effect that accelerates the hydration of tricalcium silicate in the presence of calcium carbonate. Pera et al. (1999) reported an acceleration of the C_3S reaction in the presence of limestone. Kurtis et al. (2017) also noted synergistic effects of limestone on the reactivity of SCMs, with some PLC-SCM systems exhibiting pore refinement 3 to 7 days sooner than PC-SCM systems.

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

Ye et al. (2007) reported that limestone filler used as additions to portland cement in self-consolidating cement pastes (33% and 43% of the total powder) did not participate in chemical reactions, according to backscattered SEM observations and analysis of TGA and DTA data. However, the limestone did appear to accelerate hydration reactions of the portland cement as measured by isothermal calorimetry. Garcia et al. (2019) noted that hydration studies on cements with up to 30% interground limestone, only a small fraction of the limestone participated in hydration reactions. Kurtis et al. (2017) provided a semi-quantitative estimate based on hydration studies of five Type IL cements with 8% to 12% limestone, stating that 10% to 20% of calcium carbonate could participate in early hydration reactions. This percentage would likely be much lower for limestone contents exceeding 30%, and any reaction of limestone in those binder systems could be more challenging to detect.

2.4 MICROSTRUCTURE

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

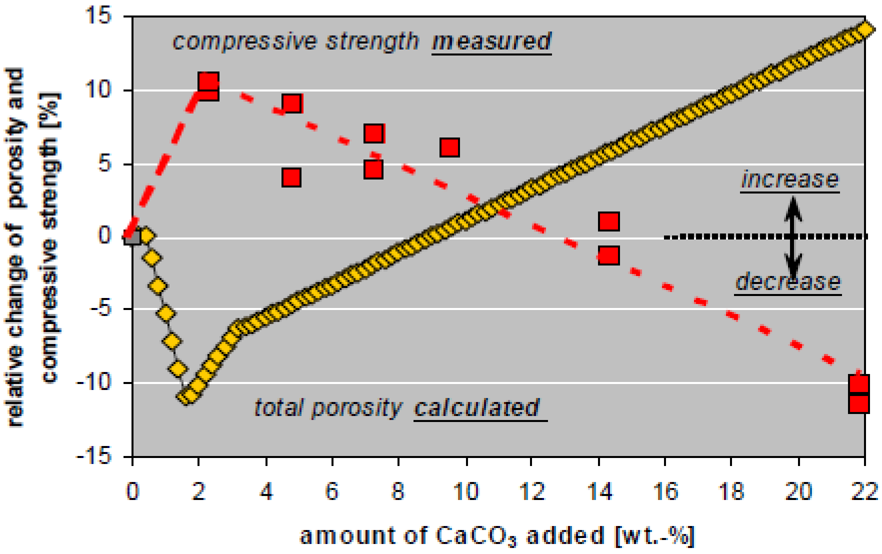


Figure 2.4 A correlation between porosity and 1-year mortar compressive strength with limestone (Matschei et al. 2007b). Note that this figure may not represent all materials.

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

De Weerdt et al. (2011) observed that limestone led to the formation of mono- or hemi-carboaluminate hydrates instead of monosulfoaluminate hydrates. This effect helped to stabilize ettringite, leading to an increase in the volume of the hydrates and a reduction in porosity. This is similar to the findings of Lothenbach et al. (2008). They observed that fly ash could beneficially be blended with this system to obtain even greater porosity reductions. However, this was reported for relatively low limestone additions (<5%). Matschei et al. (2007b) reported that if additional aluminates are available from supplementary materials, reducing the carbonate-to-aluminate ratio, improvements in porosity and strength shown in Figs. 2.3 or 2.4 could occur at higher limestone contents.

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

Bharadwaj et al. (2021) noted that porosity of PLC mortars was consistently about 5% higher than portland cement mortars made at the same plant, whether or not the systems included supplementary cementitious materials (SCMs). This is because small amounts of limestone have been added to modern portland cements, which reduces the porosity of modern portland cements compared to historical ones (Weiss et al. 2023). However, the electrical resistivity measurements of those PLC mortars were between 10% and 30% higher than their portland cement counterparts, and therefore the permeability would be expected to be lower. Adding SCMs increased resistivity compared to the systems without SCMs, and the increase in resistivity was generally greater for PLC and PLC with SCMs than it was for portland cement or portland cement with SCMs. This would imply lower permeability and better performance for the PLC systems, and the authors attributed this behavior to lower pore connectivity, likely due to refinement of the pore structure in the PLC and PLC with SCM systems.

2.5 REFERENCES

Barcelo, L.; Thomas, M.D.A.; Cail, K.; Delagrave, A.; and Blair, B., "Portland Limestone Cement: Equivalent Strength Explained," *Concrete International*, Vol. 35, No. 11, November 2013, pages 41 to 47.

Barrett, T. J.; Sun, H.; and Weiss., W. J., *Performance of Portland Limestone Cements: Cements Designed to Be More Sustainable That Include up to 15% Limestone Addition*. Publication FHWA/IN/JTRP-2013/29. Joint Transportation Research Program, Indiana Department of Transportation and Purdue University, West Lafayette, Indiana, 2013. Doi:10.5703/1288284315335.

Bharadwaj, K.; Chopperla, K.; Choudhary A.; Glosser, D.; Ghantous, R.; Vasudevan, G.; Ideker, J.; Isgor, O.; Trejo, D.; and Weiss, J., *Impact of the Use of Portland-Limestone Cement on Concrete Performance as Plain or Reinforced Material*, Oregon State University, Corvallis, Oregon, 2021, 320 pages.

Bentz, D. P., "Replacement of Coarse Cement Particles by Inert Fillers in Low w/c Ratio Concretes II. Experimental Validation, Communication," *Cement and Concrete Research*, Vol. 35, 2005, pages 185 to 188.

Bentz, D.P., "Modeling the Influence of Limestone Filler on Cement Hydration using CEMHYD3D," *Cement and Concrete Composites,* Vol. 28, 2006, pages 124 to 129.

Bentz, D. P. and Conway, J. T., "Computer Modeling of the Replacement of "Coarse" Cement Particles by Inert Fillers in Low W/C Ratio Concretes: Hydration and Strength," *Cement and Concrete Research*, Vol. 31, No. 3, 2001, pages 503 to 506.

Bentz, D. P.; Irassar, E. F.; Bucher, B. E.; and Weiss, W. J., "Limestone Fillers Conserve Cement, Part 1. An Analysis Based on Powers' Model," *Concrete International*, November 2009a, pages 41 to 46.

Bentz, D. P.; Irassar, E. F.; Bucher, B. E.; and Weiss, W. J., “Limestone Fillers Conserve Cement, Part 2: Durability Issues and the Effects of Limestone Fineness on Mixtures,” *Concrete International*, December 2009b, pages 35 to 39.

Bucher, B., *Shrinkage and Cracking and its Relation to Cement Composition*, MSCE thesis, Purdue University, West Lafayette, Indiana, December 2009, 187 pages.

Cam, H. T. and Neithalath, N., “Moisture and Ionic Transport in Coarse Limestone Powder Modified Concretes,” *Cement and Concrete Composites*, Vol. 32, Issue 7, 2010, pages 486 to 496.

Campiteli, V. C. and Florindo, M. C., “The Influence of Limestone Additions on Optimum Sulfur Trioxide Content in Portland Cements,” *Carbonate Additions to Cement*, ASTM STP 1064, P. Klieger and R. D Hooton Eds. American Society for Testing and Materials, Philadelphia Pennsylvania, 1990, pages 30 to 40.

De Weerdt, K.; Kjellsen, K.O.; Sellevold, E.; and Justnes, H., “Synergy between Fly Ash and Limestone Powder in Ternary Cements,” *Cement and Concrete Composites*, Vol. 33, No. 1, 2011, pages 30 to38.

Deniz, V., “The Effect of Mill Speed on Kinetic Breakage Parameters of Clinker and Limestone,” *Cement and Concrete Research*, Vol. 34, 2004, pages 1365 to 1371.

Garcia, J.E., N.B. Tiburzi, K.J. Folliard, T. Drimalas, M.D.A. Thomas, *Laboratory and Outdoor Exposure Site Evaluations of Portland Limestone Cements*, Center for Transportation Research, Report No. FHWA/TX-18/0-6858-1, Austin, Texas, October 2019, 316 pages. http://library.ctr.utexas.edu/ctr-publications/0-6858-1.pdf

Hooton, R. D.; Nokken, M.; and Thomas, M.D.A.T, *Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A 3000*, SN3053, Cement Association of Canada, Toronto, Ontario, Canada, 2007, 60 pages.

Kurtis, K. E.; Kahn, L. F.; Shalan, A.; Zaribaf, B.; and Nadelman, E., *Assessment of Limestone Blended Cements for Transportation Applications*, Georgia DOT Research Project 13-09: Final Report, Report No. FHWA-GA-17-13-09, September 2017, 265 pages.

PCA, *Determining Base Cement Chemistry for Cements with Processing Additions or Limestone*, IS336, Portland Cement Association, Skokie, Illinois, USA, 2009, 4 pages.

PCA, *Determination of Limestone Content of Portland Cements*, IS539, Portland Cement Association, Skokie, Illinois, USA, 2006, 4 pages.

Liu, S. and Yan, P., “Effect of Limestone Powder on Microstructure of Concrete,” *Journal of Wuhan University of Technology-Mater. Sci. Ed.*, Vol. 25, No. 2, April 2010, pages 328 to 331.

Lothenbach, B.; Le Saout, G.; Gallucci, E.; and Scrivener, K.; “Influence of Limestone on the Hydration of Portland Cements,” *Cement and Concrete Research*, Vol. 38, 2008, pages 848 to 860.

Matschei, T.; Lothenbach, B.; and Glasser, F.P., “The Role of Calcium Carbonate in Cement Hydration,” *Cement and Concrete Research,* Vol. 37, 2007a, pages 551 to 558.

Matschei, T.; Glasser, F. P.; Herfort, D.; and Lothenbach, B., “Relationships of Cement Paste Mineralogy to Porosity and Mechanical Properties,” presentation at *International Conference on Modelling of Heterogeneous Materials with Applications in Construction and Biomedical Engineering*, Prague, Czech Republic, 25-27 June 2007b.

Pera, J.; Husson, S.; and Guilhot, B., “Influence of Finely Ground Limestone on Cement Hydration,” *Cement and Concrete Composites,* Vol. 21, 1999, pages 99 to 105.

Schmidt, M.; Middendorf, B.; Vellmer, C.; and Geisenhanslueke, C., “Blended Cements,” Chapter 9.2 in *Innovations in Portland Cement Manufacturing*, SP400, Portland Cement Association, Skokie, Illinois, USA, 2004, pages 1107 to 1148.

Schmidt, M., “Cement with Interground Additives – Capability and Environmental Relief,” *Zement-Kalk-Gips*, Vol. 45, Nos. 2 and 6, 1992, pages 64 to 69 and 296 to 301.

Siebel, E. and Sprung, S., “Einfluβ des Kalksteins im Portlandkalstein zement auf die Dauerhaftigkeit von Beton,” (“Influence of the Limestone in the Portland-Limestone Cement on the Durability of Concrete,”) [In German.] *Beton*, 1991, pages 171 to 191.

Thomas, M. D. A.; Cail, K.; Blair, B.; Delagrave, A.; and Barcelo, L., "Equivalent Performance with Half the Clinker Content using PLC and SCM," *2010 Concrete Sustainability Conference*, National Ready Mixed Concrete Association, April 13 to 15, 2010b, Tempe, Arizona.

Turker, P. and Erdoğdu, K., "Effects of Limestone Addition on Microstructure and Hydration of Cements," *Proceedings of the Twenty Second International Conference on Cement Microscopy* , L. Jany and A. Nisperos, Eds., Montreal, Quebec, Canada, April 29 to May 4, 2000, pages 265 to 283.

Tsivilis, S.; Batis, G.; Chaniotakis, E.; Grigoriadis, Gr.; and Theodossis, D., "Properties and Behavior of Limestone Cement Concrete and Mortar," *Cement and Concrete Research*, Vol. 30, 2000, pages 1679 to 1683.

Tsivilis, S.; Chaniotakis, E.; Badogiannis, E.; Pahoulas, G.; and Ilias, A., "A Study on the Parameters Affecting the Properties of Portland Limestone Cements," *Cement and Concrete Composites*, Vol. 21, 1999a, pages 107 to 116.

Tsivilis, S.; Chaniotakis, E.; Batis, G.; Meletiou, C.; Kasselouri, V.; and Kakali, G., "The Effect of Clinker and Limestone Quality on the Gas Permeability, Water Absorption and Pore Structure of Limestone Cement Concrete," *Cement and Concrete Composites*, Vol. 21, 1999b, pages 139 to 146.

Tsivilis, S.; Chaniotakis, E.; Kakali, G.; and Batis, G.; "An Analysis of the Properties of Portland Limestone Cements and Concrete," *Cement and Concrete Composites,* Vol. 24, 2002, pages 371 to 378.

Voglis, N., Kakali, G., Chaniotakis, E., and Tsivilis, S. "Portland-limestone cements. Their properties and hydration compared to those of other composite cements," *Cement and Concrete Composites*, Vol. 27, No. 2, 2005, pages 191 to 196.

Ye, G.; Liu, X.; De Schutter, G.; Poppe, A.-M.; and Taerwe, L.; "Influence of Limestone Powder used as Filler in SCC on Hydration and Microstructure of Cement Pastes," *Cement and Concrete Composites*, Vol. 29, 2007, pages 94 to102.

Zelić, J.; Jozić, D.; and Krpan-Lisica, D., "Synergistic Action of a Ternary System of Portland Cement – Limestone – Silica Fume in Concrete," *Proceedings of the Third International Symposium on Nanotechnology in Construction, NICOM3,* Prague, Czech Republic, May 31 to June 2, 2009, Zdeněk Bittnar, Peter J. M. Bartos, J. Němeček, V. Šmilauer, and J. Zeman, Eds., Springer-Verlag, Berlin, pages 425 to 434.

CHAPTER 3 EFFECTS ON FRESH CONCRETE PROPERTIES

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

Some important points should be considered when evaluating results from literature. First, in some laboratory studies, ground limestone is added to conventionally manufactured cement; however, other studies use commercially produced PLCs in which limestone is interground. A subtle difference between the resulting materials is that intergrinding likely results in clinker and limestone particles with a different size distribution, as was illustrated in Fig. 2.1. Further, some have argued that the intergrinding of cement and limestone may alter the properties of the component grains through mechanical activation (Tsivilis 1998). In addition, in commercially manufactured portland-limestone blended cements, the sulfate content and particle size distribution can be optimized considering the impacts of the limestone.

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

3.1 WORKABILITY AND FINISHABILTY

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

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

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

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

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

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

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

Much of the data and user feedback indicates that finishability is not significantly impacted when mixes with PLC are used as replacements for portland cement mixes. The same types of admixtures are used, at similar dosages, to control fresh concrete properties, including workability and finishing characteristics. Where slight changes in finishability may arise as a result of using PLC, the usual use of admixtures or finishing aids are sufficient and established technology to address the needs of installers.

Chapter 6 includes details of several case studies of pavements constructed with PLCs in Canada and the U.S. using both fixed form and slipform methods. Similar slumps were achieved for PLC mixtures as portland cement controls for fixed-form placements, and the PLC concretes were referred to as "readily constructible" for slipform placements (Van Dam and Smartz, 2010).

3.2 BLEEDING AND FINISHING

In general, the bleeding rate is dependent on the surface area of the cement and/or limestone. As such increasing the fineness of the cement or limestone generally decreases both the amount of bleeding and the rate at which it occurs. A comprehensive study conducted at the BRE (1993) showed that bleeding behavior was based on the specific surface area (Blaine fineness) of the cement and was similar for both control cements and cements containing limestone (Fig. 3.1).

Some field reports note that bleeding in PLC mixtures can be different than for portland cement mixtures, sometimes requiring finishers to adjust their practices. For instance, the usual visual cues that help determine when to start finishing a surface may have different timing for PLC mixtures or may occur to a lesser degree or not at all. This underscores the importance of communication between suppliers and contractors, and the use of trial batching when materials or mix designs are changed.

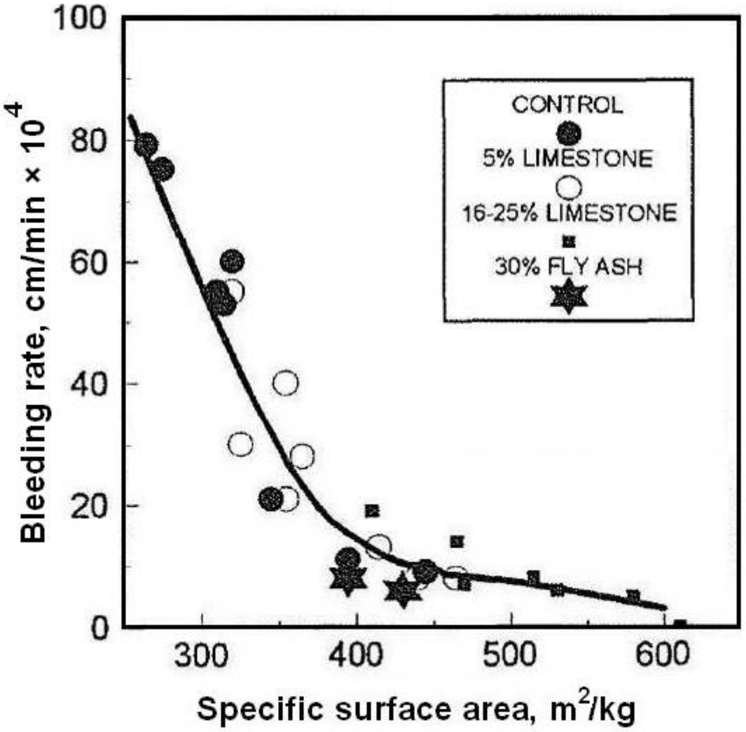


Figure 3.1 The influence of specific surface area on the bleeding rate (Moir and Kelham 1997, quoting BRE 1993).

3.3 SETTING TIME

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

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

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

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

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

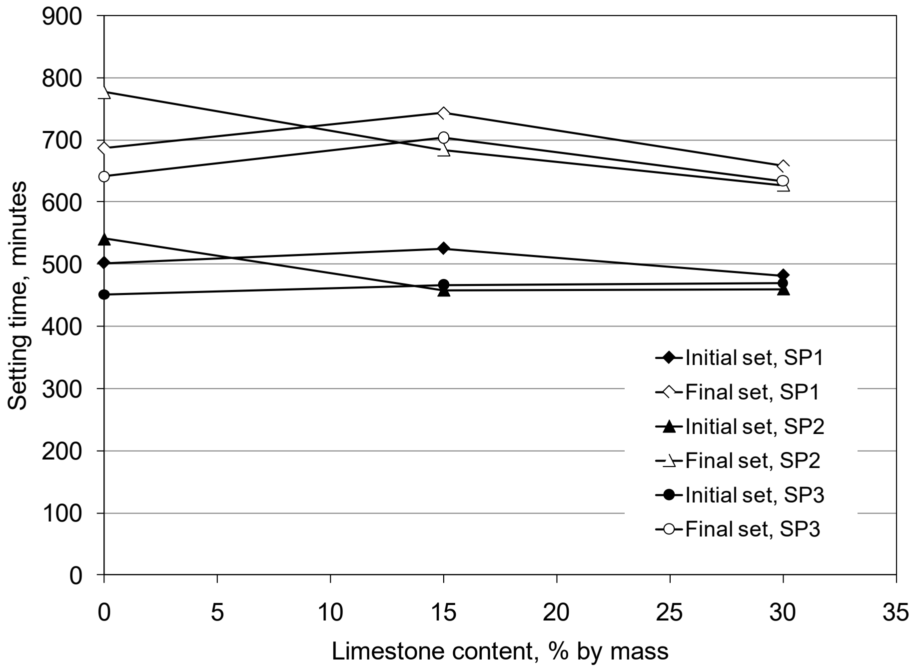
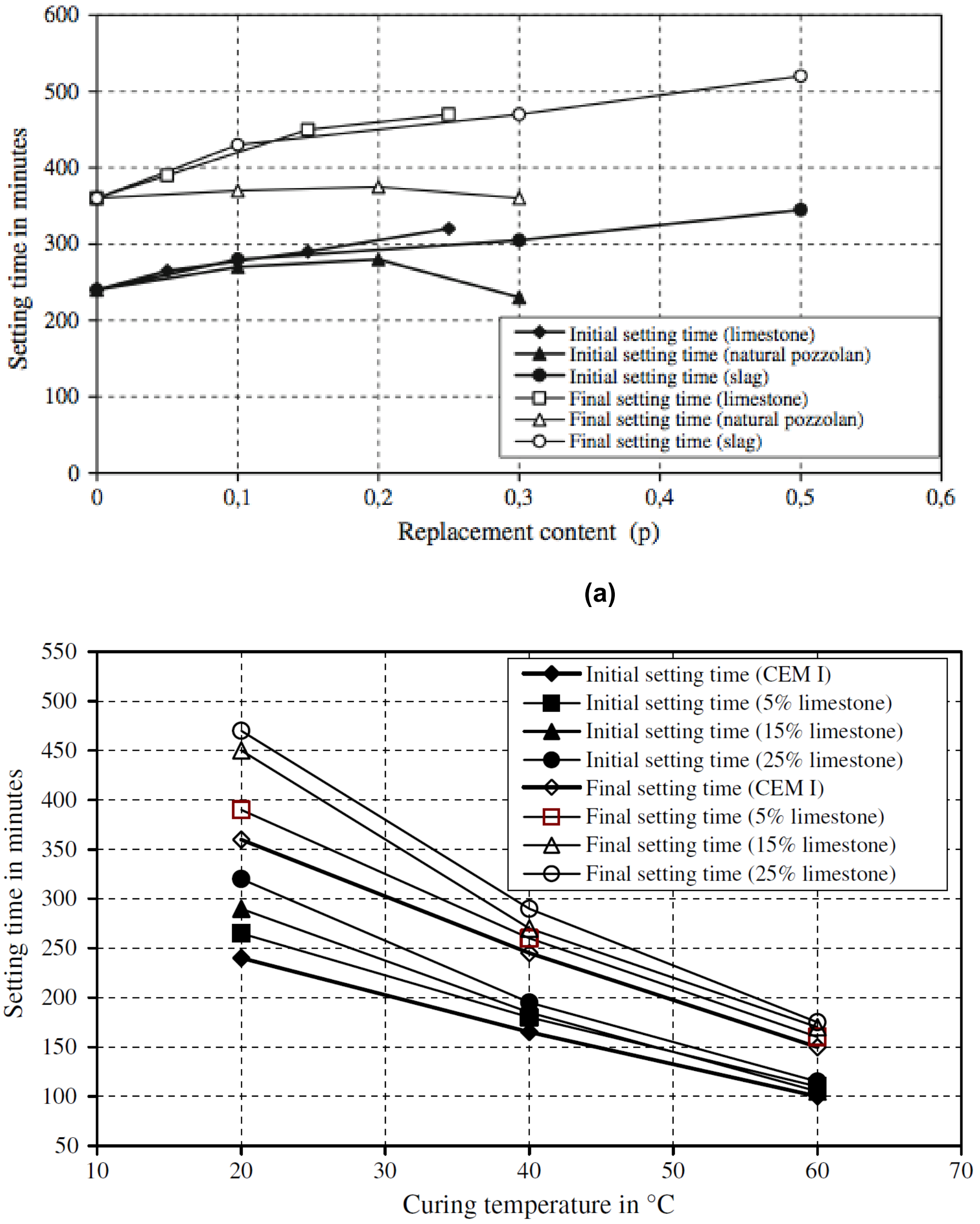


Figure 3.2 Effects of a limestone (added as a cement replacement) on setting time of mortars with three different superplasticizers (SP) (after Sahmaran et al. 2006).

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

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



(a)

(b)

Figure 3.3. (a) Influence of limestone addition on initial and final setting at 20˚C. (b) Influence of limestone addition on initial and final setting at 20˚C through 60˚C (Ezziane 2010).

Ezziane et al. (2010) reported that the replacement of cement with limestone increased the time of set of mortars. The limestone was added to the cement and not interground and was similar in fineness to the portland cement (340 m^2/kg and 310 m^2/kg respectively). This was related to the dilution effect considering the cement as the primary reactive particles. It should be noted however that this is similar to the delay in set reported for slag additions, as shown in Figure 3.3. The data also indicate that there is less of an influence of limestone addition on setting time as the temperature increases from 20˚C to 60˚C. They reported an 'optimal' limestone content of 15% as the activation energy remained constant for initial set when the limestone content was increased from 15% to 25%.

Gurney et al. (2012) identified practical constructability limitations for low clinker mixtures including: retardation of early age reactions, delays in setting and finishing, and lower early-age strengths. They showed that setting times are linearly correlated with the surface area supplied by the limestone (i.e., the use of fine limestone could offset slow setting). They showed that the small particle size accelerated hydration due to nucleation and additional calcium ions.

3.4 INFLUENCES ON HYDRATION AND HEAT OF HYDRATION

The specific effects of limestone on heat of hydration in a particular cement will be related to the particle size distribution of the limestone and the ground clinker, the chemistry of the binder system, and temperatures encountered during curing. The limestone is not completely inert (i.e., simple dilution effect), but rather, can act as a site for nucleation of cement hydrates and thereby increase heat of hydration at early ages. As discussed in Section 2.3, some of the limestone can also participate in hydration reactions to form carboaluminate phases, which may contribute to greater heat of hydration than other phases and may accelerate setting times. When limestone is added to cement, manufacturers generally optimize the limestone content and fineness of blends to compensate for the dilution effect. They may also seek to optimize the chemistry of the blend (most notably, the sulfate content), to achieve desired properties in concrete.

While one early study (Hooton 1990) indicated that for commercially produced cements manufactured from the same clinker, comparing a portland cement to a cement with 5% limestone, there was no consistent effect of the limestone on the heat of hydration, more recently, Bharadwaj et al. (2021) found that a slightly lower heat release occurs with PLCs (higher limestone contents – from 10% to 15%) when compared with portland cements that have up to 5% limestone. They show that more of the clinker reacts in those systems, indicating that the blended cement system leads to more efficient hydration.

In general, the influence of limestone on heat of hydration can be observed at early ages (up to 48 hours), which is generally attributed to dilution or nucleation effects. Kurtis et al. (2017) studied five cements with approximately 10% limestone content (actual 8.7% to 11.8%) with either coarser or finer limestone particles and related limestone particle size to the dilution and nucleation effects (Fig. 3.4) They note that limestone fillers may promote hydration of cement clinker at earlier ages more effectively than other fillers. They found that for the first 24 hours, the rate of hydration was directly related to the relative fineness of the filler: finer fillers increased the heat released (filler effect dominates) and coarser fillers reduced the heat released (dilution effect dominates). The filler effect leads to both wider dispersion of cement grains and better particle packing. After the first 24 hours, however, the rate of heat evolution for all Type IL cement pastes was lower than their Type I/II counterparts, which confirmed that dilution dominates during that time. Depending on how fine or coarse the cement is, nucleation may compensate for dilution at earlier ages, but longer term (beyond about 7 days), dilution appears to have the more significant effect on heat of hydration.

Garcia et al. (2019) studied the heat evolution of cement pastes and found that as the limestone content increased, the heat flow peaks decreased with respect to the Type I or I/II counterpart and that the cumulative heat evolved up to 72 hours decreased for both high- and moderate-C_3A cements. They attributed this to the dilution effect. They found that for high-C_3A

cement with limestone content greater than 20%, there was a shorter time to the main heat generation peak (hydration was faster) for all except one cement (13.6% limestone content), which they suggested may not have been optimized to the same degree as the other high-C_3A cements. The cement with the highest limestone content (30.6%) exhibited an increased rate of reaction during the acceleration stage compared to the lower limestone content cements (nominal 5%, 10%, 20%) owing to better nucleation and growth of C-S-H.

Barrett et al. (2013) studied heat evolution of several commercial PLC blends vs. their portland cement counterparts and also looked at blends of cement with either coarse or fine limestone powders to better understand dilution, the filler effect, and nucleation. The commercial PLCs had between 10% and 14% limestone, and the cement plus limestone blends had 15% limestone content. For interground PLCs (the commercial cements), the heat evolution was slightly less (up to 10%) or in some cases developed more heat than the portland cement counterpart mortar at 7 days. (It is important to note that the portland cement in several cases also contained up to 5% limestone). Researchers suggest this meant that additional clinker reactions in the PLC systems overcome the effects of dilution. De La Varga et al. (2018) demonstrated that additional nucleation could account for approximately 30 J/g and the effects of increased cement particle spacing which allowed more hydration products to form could account for approximately 20 J/g of cement. Bharadwaj et al. (2022) also showed that the heat of hydration associated with limestone aluminate reactions was typically greater than other reactions. They also found the secondary heat peaks to be more distinct for all PLCs, suggesting that reactions involving sulfates may be altered due to the presence of limestone, indicating the importance of optimizing sulfate content. Chemical shrinkage and non-evaporable water content testing showed that the PLCs meet or exceed the degree of hydration of the reference portland cement during the first 7 days, but the cements blended with limestone had a rate of hydration that was dependent on the fineness of the limestone particles, with the finer particles having the potential to achieve a higher degree of hydration. Further, the results showed that the PLC and portland cement have similar activation energies, implying the maturity method can be used with similar activation energies. Barrett et al. (2013) showed that when cements were blended (not interground) with either coarse or fine limestone, the heat release over that time was up to 15% less, indicating that dilution was a factor in these systems.

Earlier research also provided evidence of nucleation site and dilution effects on early hydration, depending on the properties of the blended system and w/cm used. Bonavetti et al. (2000) reported results from a study on concrete in which an increase in the rate of hydration occurred when limestone (10% and 20%) was added to cement. Xiong and Van Breugel (2003) noticed that limestone additions (using limestone that was relatively coarse as compared to the cement) in cement paste resulted in a slight acceleration of hydration measured by isothermal calorimetry; however, this effect decreased in higher water-to-cement ratio mixtures. Ezziane et al. (2010) also suggested that limestone replacement of up to 25% of portland cement in mortars provided both nucleation sites and dilution behavior, based on Vicat setting time results and calculated activation energies; as noted in 3.3, set times increased with limestone content, so the dilution effects in this study were greater than the nucleation site effects. It should be noted that commercially produced interground PLCs typically have more finely ground clinker and limestone than the materials studied by Ezziane and coworkers.

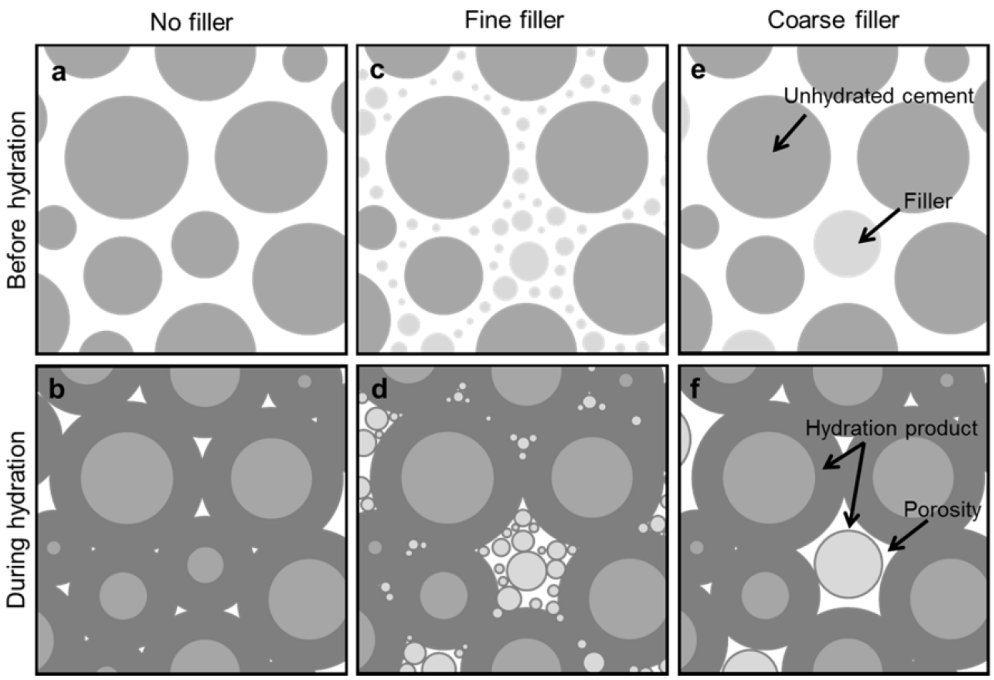


Figure 3.4 Schematic representation of the effect on cement hydration of a filler replacing 10% by volume of the cement. Finely ground fillers (c & d) lead to filler effects dominating, while coarsely ground fillers (e & f) cause dilution effects to dominate (Nadelman 2016).

Poppe and DeSchutter (2005) observed that high addition rates of limestone powder fillers influenced cement hydration in pastes. The induction period was shortened and both a greater peak rate and cumulative heat were generated for each mixture with limestone filler in the concrete, compared to the control mixture without limestone (Fig 3.5). Similarly, Heikal et al. (2000) reported that using limestone as a filler produced a carboaluminate reaction.

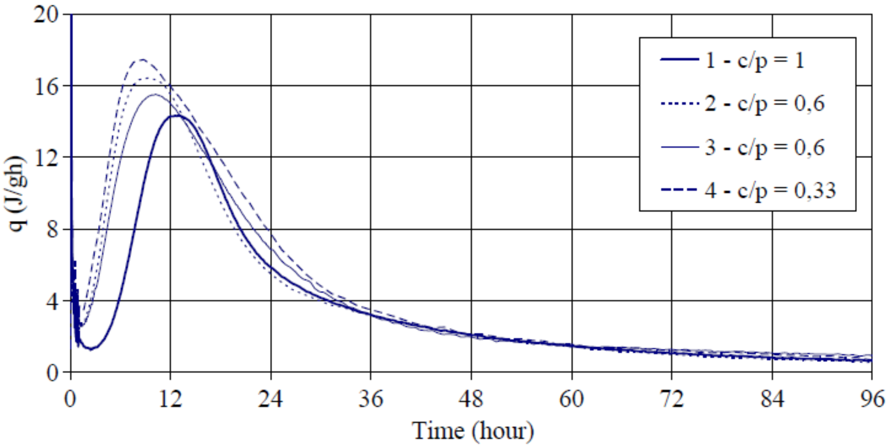


Figure 3.5 Rate of heat evolution for mixtures with a CEM I 52.5 cement and high limestone contents at 20°C. "c/p" refers to the cement/powder (cement+limestone) ratio (Poppe and De Schutter 2005).

3.5 REFERENCES

Barrett, T. J.; Sun, H.; and Weiss, W. J., *Performance of Portland Limestone Cements: Cements Designed to Be More Sustainable That Include up to 15% Limestone Addition*. Publication FHWA/IN/JTRP-2013/29. Joint Transportation Research Program, Indiana Department of Transportation and Purdue University, West Lafayette, Indiana, 2013. Doi:10.5703/1288284315335.

Bharadwaj, K.; Chopperla, K.; Choudhary A.; Glosser, D.; Ghantous, R.; Vasudevan, G.; Ideker, J.; Isgor, O.; Trejo, D.; and Weiss, J., *Impact of the Use of Portland-Limestone Cement on Concrete Performance as Plain or Reinforced Material*, Oregon State University, Corvallis, Oregon, 2021, 320 pages. Doi:10.14359/51734356.

Bobrowski, G. S.; Wilson, J. L.; and Daugherty, K. E., "Limestone Substitutes for Gypsum as a Cement Ingredient," *Rock Products*, February 1977, pages 64 to 67.

Bonavetti, V.; Donza, H.; Rahhal, V.; and Irassar, E.,"Influence of Initial Curing on the Properties of Concrete Containing Limestone Blended Cement," *Cement and Concrete Research*, Vol. 30, No. 5, 2000, pages 703 to 708.

Building Research Establishment (BRE), U.K. *Seminar: Performance of Limestone-Filled Cements: Report of Joint BRE/BCA/Cement Industry Working Party*, 28 November 1989, BR245, Building Research Establishment, Garston, Watford, England, 1993.

Bucher, B.; Radlinska, A.; and Weiss, W.J., *Preliminary Comments on Shrinkage and Shrinkage Cracking Behavior of Cement Systems that Contain Limestone*, SN3051, Portland Cement Association, Skokie, Illinois, USA, 2008, 9 pages. Reprinted from *Concrete Technology Forum*, National Ready Mixed Concrete Association, Silver Spring, Maryland, USA, 2008.

De La Varga, I.; Castro, J.; Bentz, D.P.; Zunino, F.; and Weiss, J., "Evaluating the Hydration of High Volume Fly Ash Mixtures using Chemically Inert Fillers," *Construction and Building Materials*, Vol. 161, February 2018, pages 221 to 228. https://doi.org/10.1016/j.conbuildmat.2017.11.132

El Barrak, M.; Mouret, M.; and Bascoul, A., "Self-Compacting Concrete Paste Constituents: Hierarchical Classification of their Influence on Flow Properties of the Paste," *Cement and Concrete Composites,* Vol. 31, 2009, pages 12 to 21.

El Didamony, H.; Salem, T.; Gabr, N.; and Mohamed, T., "Limestone as a Retarder and Filler in Limestone Blended Cement," *Ceramics – Silikaty*, Vol. 39, No. 1, 1995, pages 15 to 19.

Ezziane, K.; Kadri, E. H.; Hallal, A.; and Duval, R., "Effect of Mineral Additives on the Setting of Blended Cement by the Maturity Method," *Materials and Structures*, Vol. 43, 2010, pages 393 to 401.

Garcia, J.; Tiburzi, N.; Folliard, K.; Drimalas, T.; and Thomas, M., "Laboratory and Outdoor Exposure Site Evaluations of Portland Limestone Cements," *Technical Report 0-6858-1*, Center for Transportation Research, The University of Texas at Austin, Austin, Texas, 2019. http://library.ctr.utexas.edu/ctr-publications/0-6858-1.pdf

Gurney, L. R.; Bentz, D. P.; Sato, T.; and Weiss, W. J., "Reducing Set Retardation in High-Volume Fly Ash Mixtures with the Use of Limestone: Improving Constructability for Sustainability," *Transportation Research Record*, Vol. 2290, No. 1, pages 139 to 146.

Heikal, M.; El-Didamony, H.; and Morsy, M.S., "Limestone-Filled Pozzolanic Cement," *Cement and Concrete Research,* Vol. 30, 2000, pages 1827 to 1834.

Hooton, R. D. and Thomas, M. D. A., "Portland-limestone Cements for Use in Concrete CSA A23.1-09 Ballot (Changes to Section 4.2.1 and Table 6)," PowerPoint presentation for the CSA Webex, April 3, 2009.

Hooton, R. D.; Nokken, M.; and Thomas, M.D.A.T, *Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A 3000*, SN3053, Cement Association of Canada, Toronto, Ontario, Canada, 2007, 60 pages. Available at: http://www.cement.org/bookstore/results_quicksearch.asp?store=main&id=&cat2ID=3&searchterm=SN3053, accessed March 30, 2011.

Hooton, R. D., "Effects of Carbonate Additions on Heat of Hydration and Sulfate Resistance of Portland Cement," in *Carbonate Additions to Cement*, ASTM STP 1064, P. Klieger and R. D. Hooton, Eds., American Society for Testing and Materials, Philadelphia, 1990, pages 73 to 81.

Ingram, K. D. and Daugherty, Kenneth E., "A Review of Limestone Additions to Portland Cement and Concrete," *Cement and Concrete Composites*, Vol. 13, 1991, pages 165 to 170.

Kurtis, K.; Kahn, L.; Shalan, A.; Zaribaf, B.; and Nadelman, E., *Assessment of Limestone Blended Cements for Transportation Applications*, Georgia DOT Research Project 13-09, Final Report (FHWA-GA-17-13-09), Georgia Department of Transportation, Office of Research, Forest Park, Georgia, September 2017, 265 pages.

Matthews, J. D., "Performance of Limestone Filler Cement Concrete," In *Euro-Cements – Impact of ENV 197 on Concrete Construction*, R. K. Dhir and M. R. Jones, Eds., E&FN Spon, 1994, London, pages 113 to 147.

Moir, G. K. and Kelham, S., "Developments in the Manufacture and Use of Portland Limestone Cement," *ACI Special Publication SP 172-42*, 1997, pages 797 to 819.

Mounanga, P.; Khokhar, M.; I., A.; El Hachem, R.; and Loukili, A., Improvement of the Early-Age Reactivity of Fly Ash and Blast Furnace Slag Cementitious systems using Limestone Filler, *Materials and Structures*, on-line edition, June 30, 2010. DOI: 10.1617/s11527-010-9637-1. http://www.springerlink.com/content/1380w3475567881h/fulltext.pdf.

Nadelman, E., *Hydration and Microstructural Development of Portland Limestone Cement-Based Materials*, Ph.D dissertation, Georgia Institute of Technology, 2016, 328 pages. https://smartech.gatech.edu/bitstream/handle/1853/58587/NADELMAN-DISSERTATION-2016.pdf

Nehdi, M.; Mindess, S.; and Aïtcin, P-C. "Rheology of High-Performance Concrete: Effect of Ultrafine Particles," *Cement and Concrete Research*, Vol. 28, No. 5, 1998, pages 687 to 697.

Poppe, A.-M., and De Schutter, G., "Cement Hydration in the Presence of High Filler Contents," *Cement and Concrete Research,* Vol. 35, 2005, pages 2290 to 2299.

Şahmaran, M.; Christianto, H. A.; and Yaman, İ. Ö., "The Effect of Chemical Admixtures and Mineral Additives on the Properties of Self-Compacting Mortars," *Cement and Concrete Composites*, Vol. 28, 2006, pages 432 to 440.

Schmidt, M.; Harr, K.; and Boeing, R., "Blended Cement According to ENV 197 and Experiences in Germany," *Cement, Concrete, and Aggregates*, Vol. 15, No. 2, 1993, pages 156 to 164.

Tsivilis, S.; Batis, G.; Chaniotakis, E.; Grigoriadis, Gr.; and Theodossis, D., "Properties and Behavior of Limestone Cement Concrete and Mortar," *Cement and Concrete Research*, Vol. 30, 2000, pages 1679 to 1683.

Tsivilis, S.; Chaniotakis, E.; Badogiannis, E.; Pahoulas, G.; and Ilias, A., "A Study on the Parameters Affecting the Properties of Portland Limestone Cements," *Cement and Concrete Composites*, Vol. 21, 1999a, pages 107 to 116.

Tsivilis, S.; Kakali, G.; Chaniotakis, E.; and Souvaridou, A., "A Study of the Hydration of Portland Limestone Cement by Means of TG," *Journal of Thermal Analysis*, Vol. 52, 1998, pages 863 to 870.

Van Dam, T. J. and Smartz, B. W., "Use of Performance Specified (ASTM C1157) Cements in Colorado Transportation Projects: Case Studies," *TRB 2010 Annual Meeting CD-ROM*, Transportation Research Board, Washington, D.C., USA, 2010, 9 pages.

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

CHAPTER 4 EFFECTS ON HARDENED CONCRETE PROPERTIES

This chapter provides a review of the performance of concrete made with portland-limestone cements (PLCs), comparing and contrasting that with portland cement-based concrete as appropriate. Most of the information presented is for limestone contents in the maximum 15% range, but several studies have looked at higher limestone contents, too, and those findings offer insight into trends of cement blends made with limestone. Commercially produced Type IL cements meeting ASTM C595/AASHTO M 240 are generally intended to be used as 1:1 replacements for commercially produced ASTM C150/AASHTO M 85 Type I or Type I/II cements. Generally speaking, hardened concrete properties for PLC mixtures are similar to portland cement mixtures. This holds true for mechanical properties as well as durability properties. Portland-limestone cements can be used with the same dosage of SCMs as portland cements. Admixture use is comparable, though dosages may vary slightly. The same techniques used to modify hardened properties of portland cement mixtures are used to change properties of PLC mixtures. For instance, control of freeze-thaw and deicer scaling resistance is accomplished through proper air void systems (content, spacing factor); control of ASR expansion is predominantly done with SCMs; and sulfate resistance is improved through lower water-cementitious materials ratios, use of SCMs, and cements with special property designations such as (MS) or (HS).

4.1 MECHANICAL PROPERTIES

4.1.1 Strength and Strength Development

4.1.1.1 Compressive strength. Like other properties, the strength of concrete produced with portland-limestone cement (PLC) is influenced by the w/cm of the mixture, characteristics and quantity of the limestone, the clinker and other cement ingredients, and the particle size distribution of the finished cement. Limestone contents up to 15% may increase early-age strength as a combined result of improving particle packing (Sprung and Siebel 1991), increasing the rate of cement hydration (Vuk et al. 2001; Bonavetti et al. 2003), and production of calcium carboaluminates (Voglis et al. 2005). Schmidt (1992a) reported similar strengths for limestone levels up to 10%. However, Hawkins et al. (2005) showed that finer grinding is required in some cases even at lower levels of limestone (up to 8%). Figure 4.1 shows the data from Hawkins et al. (2005) indicating that comparable strengths can be achieved with PLC with up to 8% limestone, provided that the PLC is ground to a higher surface area (Blaine fineness) or an equal fraction passing the 45 μm (No. 325) sieve. Fineness values for the cements used in this study are presented in Table 4.1; in these cements, clinker, limestone, and gypsum were interground in a laboratory ball mill. Barrett et al. (2013) noted that intergrinding limestone with clinker (as opposed to blending ground limestone into cement) provides a PSD without any gaps across the distribution, which improves particle packing and leads to higher strength and improved transport properties. It should be noted that compressive strength is just one performance characteristic of concrete, and that the chemistry and particle size distribution of a PLC may be optimized to maximize other concrete performance characteristics (e.g., sulfate resistance or heat of hydration).

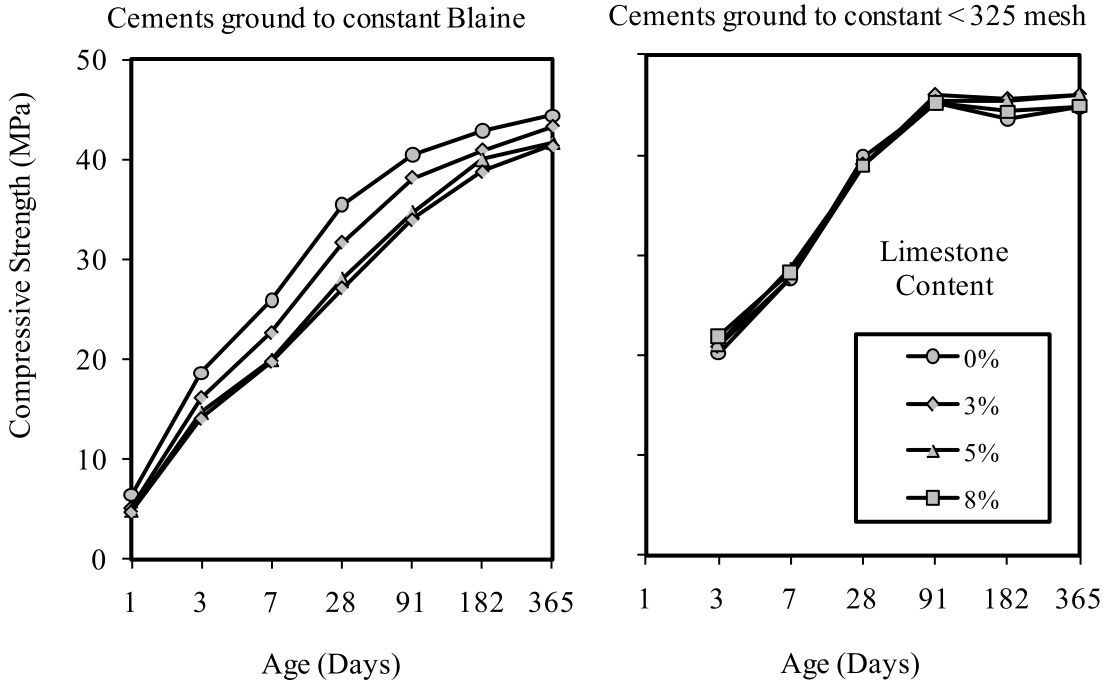


Figure 4.1 Strength development of mortars produced with portland cementand PLC ground to constant Blaine fineness (left) or constant percent passing a No. 325 (45-µm) sieve (right) (Hawkins et al. 2005).

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

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

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

limestone (blended) was equivalent to what would be expected due to a 25% replacement of the portland cement with an inert diluent.

In a number of full-scale plant trials in Canada, it has been demonstrated that comparable strength can be achieved in concrete produced with PLC containing up to 15% limestone by intergrinding the limestone with clinker (Thomas et al. 2010a; 2010b; 2010c; 2010d). The practice has been to grind the PLC to a higher fineness compared to the portland cement from the same plant. Figure 4.3 shows compressive strength data for concrete (w/cm = 0.49 to 0.51) produced with PLC (12% limestone) at a range of different Blaine fineness values. Typically, an increase in the Blaine fineness of between 8 m^2/kg/% limestone to 10 m^2/kg/% limestone is necessary to achieve the same 28-day strength (Barcelo et al. 2013). Thus for a PLC with 12% limestone, an increase in Blaine fineness on the order of 90 m^2/kg might be needed compared to a portland cement with 3% limestone from the same plant. This will vary with other cement compositional characteristics. Table 4.2 shows strength data for three series of concrete mixtures (w/cm = 0.78 to 0.80, 0.45, and 0.40) produced with portland cement (4% limestone and 380 m^2/kg Blaine) and PLC (12% limestone and 500 m^2/kg Blaine). The strength varies with w/cm and the presence of SCM, but no significant differences are observed in the 28-day strength between equivalent mixes with portland cement or PLC. The early-age strength is increased for concretes with PLC compared with portland cement.

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

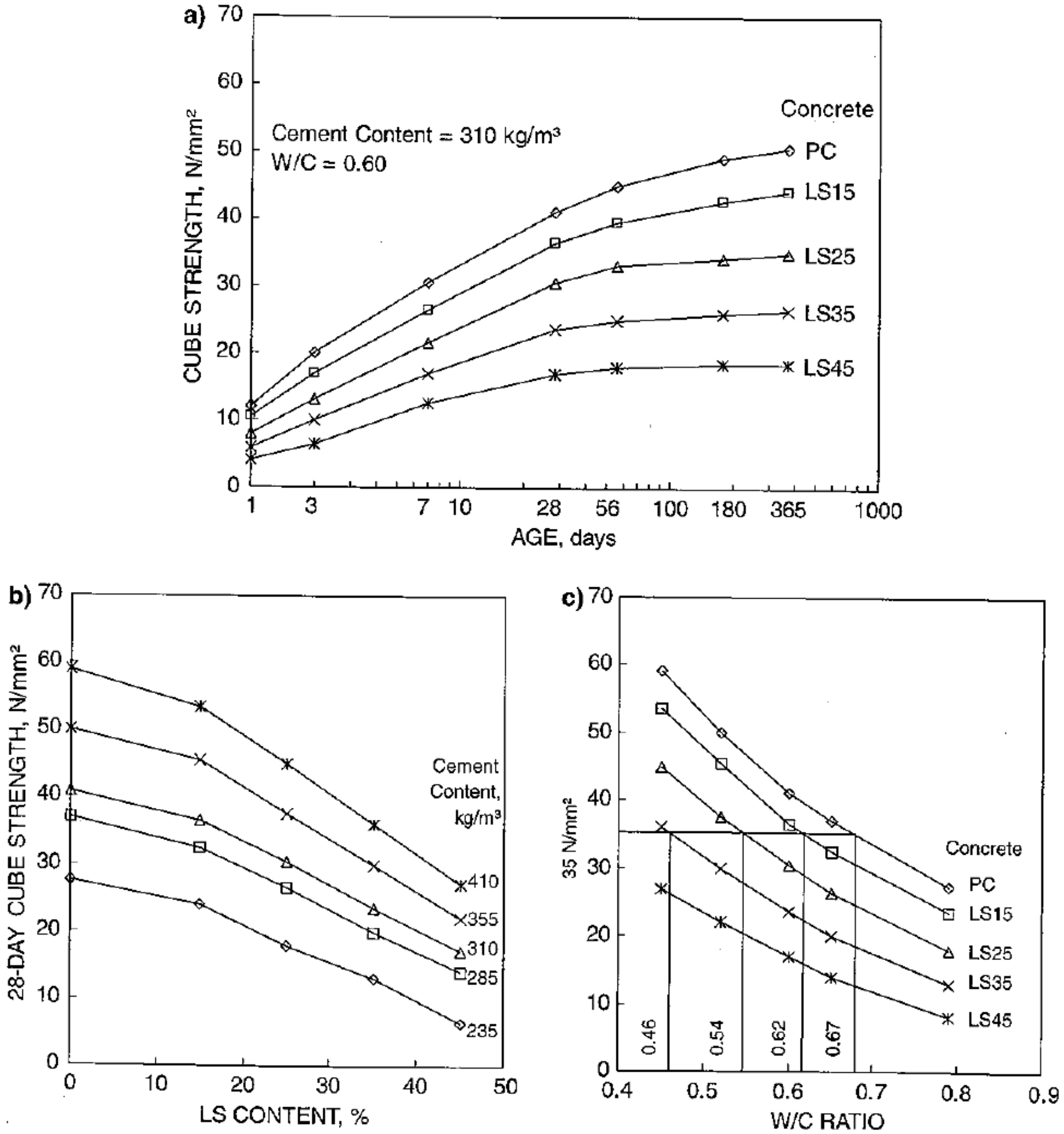


Figure 4.2 Effect of replacing cement with 15% to 45% limestone on the strength of concrete produced at a range of w/cm values (Dhir et al. 2005).

Two studies by the Georgia Department of Transportation (GDOT) investigated the potential to produce concrete meeting GDOT specifications with regionally produced Type IL cements. Kurtis et al. (2017) examined the suitability for a variety of transportation applications, while Shalan et al. (2016) focused on high-early strength concrete for prestressed concrete.

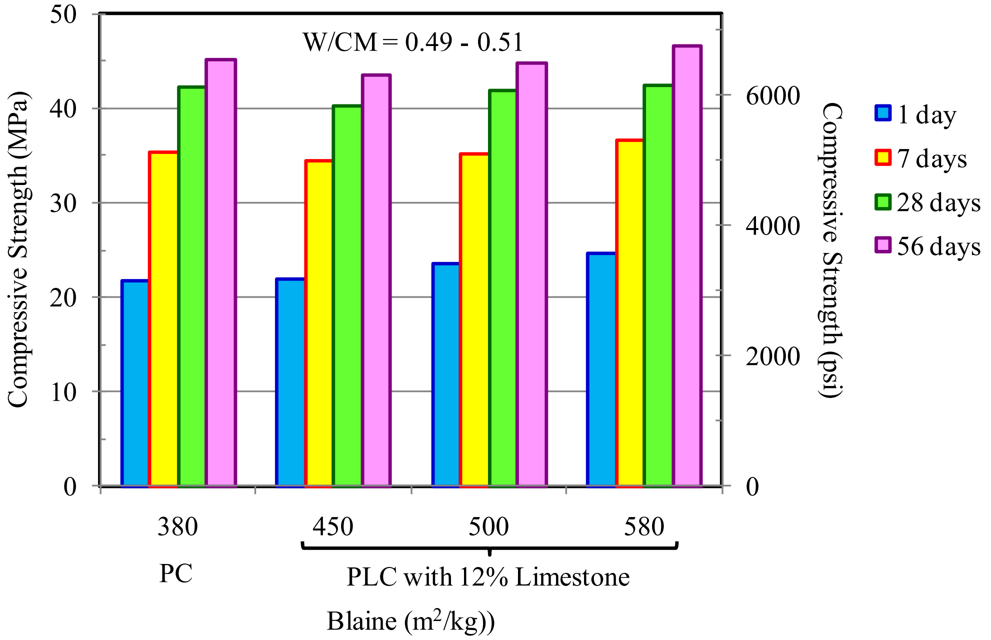


Figure 4.3 Effect of surface area (Blaine) on the strength of concrete (w/cm = 0.49 to 0.51) produced with PLC and Portland Cement from the same cement plant (Thomas et al. 2010b).

GDOT has a release strength requirement for precast pretensioned bridge members of 31 MPa (4500 psi) (at 18 hours). Shalan et al. (2016) compared two Type IL cements to Type I/II cements produced from the same plant and clinker. One Type IL cement was more finely ground and optimized to have similar hydration characteristics as the Type I/II cement, while the other was not as finely ground. Concrete with the finer Type IL cement achieved an 18-hour compressive strength of 45 MPa (6500 psi) when cured in limewater at 23 ˚C (73˚F), nearly 20% greater than the mixture with the corresponding Type I/II cement. Concrete with the coarser Type IL cement achieved an 18-hour compressive strength of 32 MPa (4600 psi) when cured in limewater at 23 ˚C (73˚F), and 46 MPa (6700 psi) when cured at 60 ˚C (140˚F) to simulate steam curing common at precast operations. In both curing conditions, concrete with the coarser Type IL cement had lower strength than concrete with the corresponding Type I/II cement. These results illustrate the importance of optimizing the particle size distribution of Type IL cements to achieve comparable early-age strength development compared to Type I/II cements that concrete producers have become accustomed to using.

Kurtis et al. (2017) found that the fineness of Type IL cements had a greater influence on the measured compressive strength of prescriptive GDOT mixture designs for higher strength class concretes than those designed for a lower strength class, when compared to the same mix designs using Type I/II cements produced from the same clinker. They suggested that coarser Type IL cements may be more suitable for higher w/cm concretes with lower strength requirements, and more finely ground Type IL cements for lower w/cm concretes with higher strength requirements.

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

Table 4.2 Concrete Mixture Proportions and Test Results for Concrete Produced with Portland Cement (4% limestone) and PLC (12% limestone) (Thomas et al. 2010b)

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

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

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

[3] Charged passed after 6 hours – ASTM C1202 "Rapid Chloride Permeability Test."

4.1.1.2 Tensile strength, flexural strength, and modulus of elasticity. Studies of tensile (cylinder splitting) and flexural strength and modulus of elasticity have been made by a number of authors (Alunno-Rossetti and Curcio 1997; Bonavetti et al. 1999; Irassar et al. 2001; Dhir et al. 2007). Data reported by Alunno-Rossetti and Curcio (1997) on splitting tensile strength, flexural strength, and modulus of elasticity are shown in Table 4.3. Generally, the trend in behavior is the same as that observed for compressive strength, and predictive equations used to estimate these properties from the compressive strength (e.g. relationships in Eurocode 2) are valid for concrete produced using PLC.

Table 4.3 Mechanical Properties of Concrete Produced with Portland Cement and PLC from Two Italian Cement Plants (Alunno-Rossetti and Curcio 1997)

	Plant B				Plant G			
Cement Content, kg/m^3	270		330		270		330	
Limestone, %	0	20	0	20	0	20	0	20
Water: cement ratio	0.65	0.64	0.55	0.53	0.63	0.62	0.54	0.53
Fineness, m^2/kg	345.0	482.5	345.0	482.5	362.0	489.5	362.0	489.5
28-day strength (MPa)								
Compression	30.7	30.0	39.7	38.0	31.6	29.1	37.5	36.5
Splitting	2.3	2.7	2.9	2.7	3.2	2.1	4.1	2.6
Flexure	5.0	4.8	6.4	5.3	3.6	4.7	4.7	4.7
28-day Modulus (GPa)	26.0	24.5	28.0	27.5	25.1	25.4	27.2	27.1
*Shrinkage (μm/m)	635	640	680	690	540	560	614	595
*Creep (μm/m)	718	1102	778	914	824	972	756	869
*Carbonation (mm)	20	10	18	13	19	21	15	16

*Shrinkage and creep were measured at 360 days. Carbonation was measured at 900 days.

Figure 4.4 shows compressive and flexural strength data for concrete mixtures produced using the three types of cement described in Table 4.4, which were manufactured in a Canadian cement plant and ground to the required fineness to give comparable performance (Thomas et al. 2010d). The clinker, gypsum, slag, and limestone were interground to produce each cement.

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

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

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

Bharadwaj et al. (2021) focused on flexural strength comparisons of PLCs to control mixtures made with Type II/V cement. They considered both interground PLCs and blends of portland cement with limestone. Mortar mixtures were proportioned to have a w/cm of 0.40; for the cement blended with limestone, the limestone was included as part of the cementitious materials content. Ball-on-ball flexural strength tests were performed on thin discs sectioned from 52-mm (2-inch) diameter mortar cylinders. They found that the addition of limestone reduced the 7-day flexural strength of all systems with and without fly ash for both portland cement and PLC; for the blended cements, the flexural strength reduction was even greater at early ages and the delay in strength gain more pronounced, but by 28 days and out to 90 days, there was little difference in flexural strength for all cements containing limestone compared to portland cement mixtures. In general, the flexural strength of mortars containing both interground PLC and blended cement was less than 5% lower than the control mixture. When slag cement was added to the PLC or blended cement mixtures, the flexural strength was up to 13% higher than the portland cement controls.

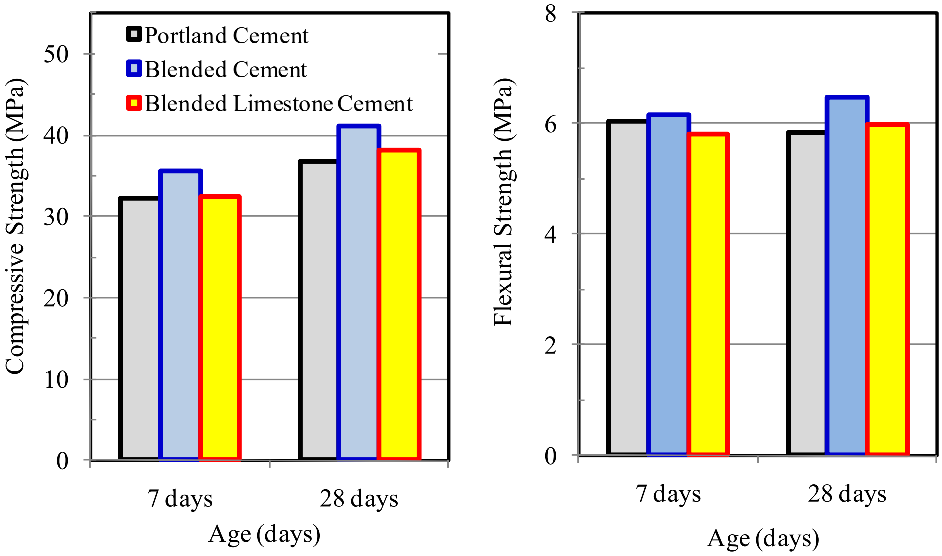


Figure 4.4 Strength data for concretes produced with different cements from the same plant (Thomas et al. 2010d).

Barrett et al. (2013) studied three pairs of commercially produced Type I/II and Type IL cements (ranging from approximately 10% to 14% interground limestone) and a fourth portland cement blended a 15% replacement of either fine or coarse limestone (PC-limestone blends). The effect of 20% Class C fly ash replacement by volume was also considered for one of the Type I/II vs. Type IL comparisons. As this study was directed at paving mixes allowed by the Indiana Department of Transportation, three water/powder (w/p) ratios for the concrete were used (0.38, 0.42, and 0.46), representing the lower, middle, and upper bounds permitted by their specification. Flexural strength of concrete beams was measured following ASTM C78. The interground PLCs achieved similar 7-day flexural strengths as the corresponding portland cement controls (+3% on average and -6% maximum). However, the PC-limestone blended cements had an average reduction in 7-day flexural strength of 9% compared to the portland cement control, and the blends with finer limestone were slightly lower strength (-12%) than the coarser limestone blends (-6%). The mixtures with Type IL and fly ash exhibited a 7% average increase in 7-day flexural strength over the corresponding mixtures containing Type I/II cement with fly ash, suggesting a synergistic effect with the combination of the interground limestone and fly ash. All mixtures produced concrete with flexural strength well above the 3.8 MPa (550 psi) requirement of the Indiana DOT specification; the mixture with the lowest average flexural strength was a Type I/II with 0.46 w/p (4.9 MPa (710 psi)).

Moduli of elasticity were also measured by Barrett et al. (2013) for the same mixtures at various ages from one day to one year. "Negligible" differences were generally observed between concretes with Type IL and Type I/II cement, although moduli increased by more than 10% at early ages (1-day and 3-days) for some mixtures with Type IL cement. An early-age reduction in modulus (approximately 5% to 10%) was observed for the PC-limestone blends, with w/p of 0.42 and 0.46, which did not appear to be correlated to limestone fineness.

Shalan et al. (2016) found similar elastic moduli and split tensile strengths for concretes made with Type IL and Type I/II cements produced from the same clinker, using mixtures specified by the Georgia DOT for prestressed concrete bridge members. The same study included production and load testing of two 9.14-m-long (30-ft-long) pretensioned precast beams, one each with Type IL cement and Type I/II cement produced from the same clinker. The Type IL cement used was previously shown to have lower strength development relative to the Type I/II cement. However, there was no difference between the two beams with respect to bond in strand pull-out tests, development length, and flexural capacity. The flexural capacities of the beams were 5% higher than predicted by the 2016 AASHTO LRFD design specification. Prestress losses were reported to be 2% lower for the beam with Type IL cement. Both beams were reported to have transfer lengths less than 30% of the predicted transfer length according to the AASHTO 2016 LRFD design specification, and development lengths were approximately 45% of the predicted value. This demonstrated that the AASHTO design procedures remained conservative for pretensioned beams containing Type IL cement.

Kurtis et al. (2017) noted the influence of cement fineness on the elastic modulus of concrete. Five pairs of Type IL and Type I/II cements were tested in concrete mixtures designed for Georgia DOT Class AAA, AA, and A concrete. The elastic moduli were largely similar when comparing Type IL and Type I/II cements made from the same clinker. One clinker source was used to produce two Type IL cements, one ground more finely than the other; modulus was increased with fineness. This study also noted that the equation given in ACI 363R-10 provided a more accurate prediction of elastic modulus based on the compressive strength than is obtained from the equation in the ACI 318 building code requirements. Equations in ACI 363R-10 for calculating elastic modulus based on compressive strength are shown below for both SI (top) and in.-lb. (bottom) units:

$$E_c = 3320\sqrt{f_c'} + 6900$$

where, E_c = modulus of elasticity (MPa), and f_c' = compressive strength (MPa).

$$E_c = 40\sqrt{f_c'} + 10{,}000$$

where, E_c = modulus of elasticity (ksi), and f_c' = compressive strength (psi).

Splitting tensile strengths were similar when comparing the Type IL and Type I/II cements in this study. The authors noted that finer Type IL cements may yield slight improvements in tensile strength.

Garcia et al. (2019) also examined the issue of predicting the elastic modulus of concrete made with PLCs based on compressive strength. They tested mixtures with w/cm of 0.40 and 0.45 using a total of seven portland cements and PLCs with up to 30% limestone, with and without 30% replacement with Class C fly ash. The equation in ACI 318 was consistently conservative when using actual 28-day strengths (not specified strengths for design). The 0.45 w/cm mixtures were also tested for splitting tensile strength (ASTM C496). PLC concretes exhibited similar or slightly higher ratios of tensile/compressive strengths than portland cement concretes. However, the splitting tensile strength ratios were all between 8% and 10.5% of the compressive strengths, which is well within the commonly accepted range of 8% to 14% of compressive strength.

4.1.2 Volume Stability

Several studies of creep and shrinkage behavior of PLC concretes (in comparison to portland cement concretes) are reported in the literature. Controlled laboratory conditions were generally employed (20˚C to 23˚C and about 50% relative humidity). However, the specimen dimensions, mixture proportions, time of initial loading, and magnitude of loading in these studies vary. Accurate measurement of creep properties is also dependent on the apparatus used to apply and maintain the creep load, and accurate determination of the drying shrinkage component of the measured strain under sustained load.

Caution is particularly warranted when evaluating the results of creep studies. The differences in testing parameters and the overall challenge of conducting creep tests can make comparisons between studies difficult. Calculation and reporting of specific creep, normalized to the applied stress, can be useful in comparing tests on concretes with different compressive strengths.

In general, concrete containing PLC with up to 15% limestone should have similar creep characteristics as concrete containing portland cement, provided they are designed for the same strength and with essentially the same paste content. Concrete with PLC has generally been reported to have similar or less shrinkage than similarly proportioned portland cement concrete.

Creep and shrinkage behavior of concrete is influenced by the mixture proportions, compressive strength, rate of strength development, elastic modulus of the aggregate and the concrete, volume:surface area ratio of the element, humidity, temperature, age of loading, and the magnitude and duration of the applied stress. The w/cm of the paste, volume fraction of the aggregate, and volume fraction of paste are the most important mixture proportion variables. Because creep and shrinkage occur almost exclusively in the paste, increasing the amount of cement used in a concrete mixture for a given application is likely to increase creep and shrinkage.

According to the *AASHTO LRFD Bridge Design Specifications* (2014), creep strain under permanent loading is typically from 0.5 to 4.0 times the initial elastic shortening, with the primary governing variable for a given concrete mixture being the maturity of the concrete at the time of loading. In prestressed elements, creep will be one of several variables contributing to time-dependent deformation, which also include shrinkage and relaxation of prestressing steel.

Alunno-Rossetti and Curcio (1997) measured creep and shrinkage on concrete mixtures produced using four cements (2 PLC, 2 portland cement) manufactured at two cement plants. Details of the cements and the results of the tests are given in Table 4.3. The two PLCs contained 20% limestone (the maximum permitted under EN 197-1 for CEM II/B cements). As discussed in 4.1.1, the PLC mixtures were comparable in strength to the portland-cement mixtures, and the w/c were quite high, ranging from 0.53 to 0.65. The rate of shrinkage and total amount of drying shrinkage at 1 year was essentially the same for comparable concrete mixes produced with portland cement and PLC from the same plant. Creep tests were performed by loading 150 × 150 × 600 mm concrete prism specimens at an age of 28 days to a stress equal to one-third of the compressive strength; the specimens were stored at a relative humidity of 50 ± 5%. The total deformation due to creep at 360 days was 13% to 35% lower for concretes produced with portland cement compared with those produced with PLC. The authors concluded that this was due to the reduced volume of "cement gel" available to resist the compressive stress in concrete containing PLC.

Dhir et al. (2007) tested 0.60 w/c concrete mixtures with 0% to 45% ground limestone blended (not interground) with portland cement. All mixes contained 310 kg/m^3 of the blended PLC. Creep tests were conducted on 100 × 300 mm cylinders at 40% of the 28-day cube compressive strength. Drying shrinkage tests were also conducted on 75 × 75 × 300-mm prisms at

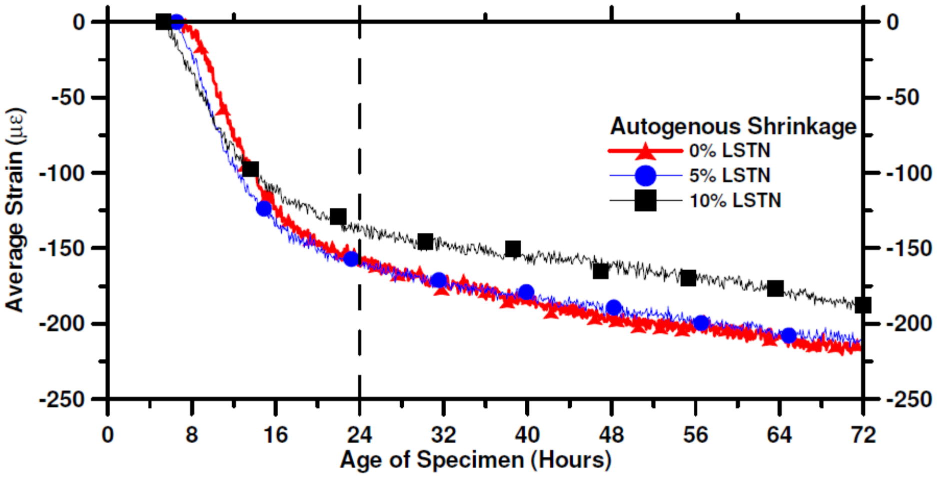
20 ˚C and 55% humidity, beginning at an age of 24 hours. Both tests were conducted for 90 days. It was not stated whether the creep values were adjusted based on the drying shrinkage (obtained from smaller prisms with a smaller volume:surface area ratio than the cylindrical creep specimens). Table 4.5 shows the data for each of the five mixtures tested. Creep was nearly constant as the limestone content increased, but the applied loading decreased with the compressive strength, so the 45% limestone concrete was subjected to only 41% of the sustained load as the 0% limestone concrete.

Table 4.5 Strength, Creep, and Shrinkage Results for Concrete with w/cm = 0.60 after 90 days (Dhir et al. 2007)

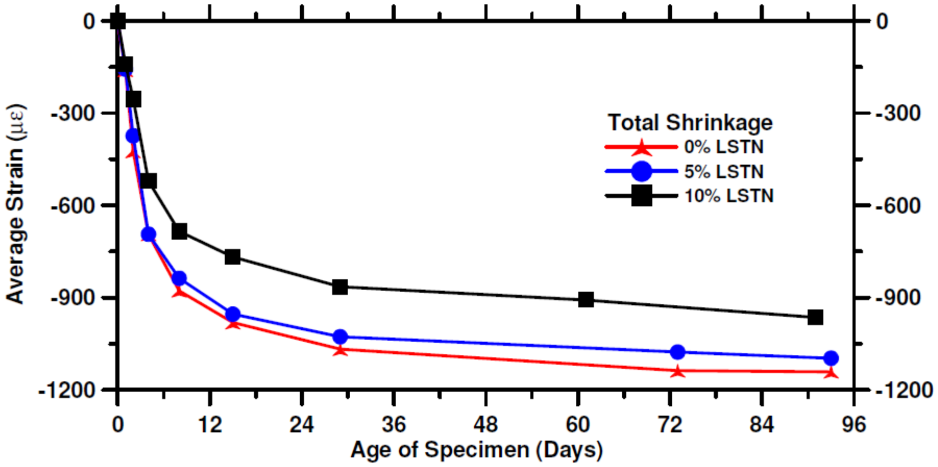
	Limestone Content, %				
	0	15	25	35	45
Cube strength (MPa)	41.0	36.5	30.5	23.5	17.0
Creep (μm/m)	790	780	775	770	760
Drying shrinkage (μm/m)	680	630	605	590	575

It is not clear why there is such a marked difference in the effect of limestone on the creep of concrete as reported by Alunno-Rossetti and Curcio (1997) and Dhir and coworkers (2007). Intuitively one would expect the creep for a given stress-strength ratio to decrease as the volume of cement paste decreases and the amount of aggregate (including filler) increases, which is consistent with the observations of Dhir et al. (2007). However, further work is required to confirm this effect. One significant difference in the two studies was that Alunno-Rossetti and Curcio used a creep load of 33% of the cube compressive strengths, which were similar for the portland cement and PLC (20% limestone) concretes, while Dhir and coworkers used a creep load of 40% of the cube compressive strengths, which were decreased at higher limestone contents (25% to 45%). Thus, the creep loads used by Dhir and coworkers decreased as limestone content increased.

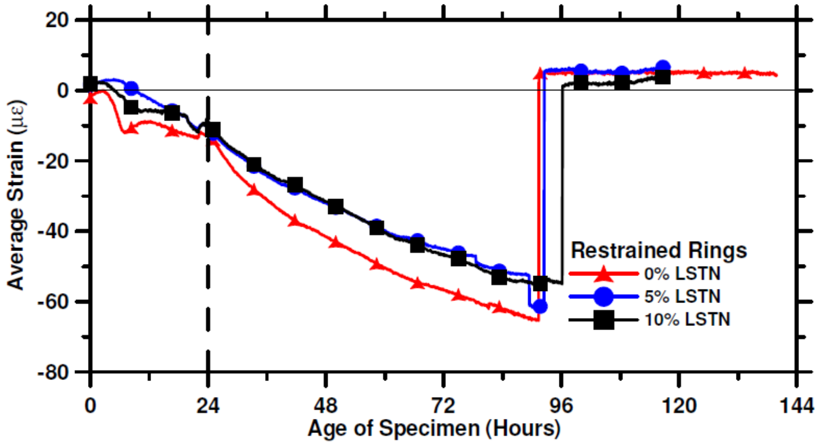
Bucher and coworkers (2008) reported shrinkage data for three cements produced with 0%, 5% and 10% limestone. Their testing included measurements of autogenous shrinkage, and unrestrained and restrained drying shrinkage of mortars (Figure 4.5 (a), (b), and (c)). The autogenous shrinkage during the first 3 days was highest for mortars without limestone (215 με) and the lowest for mortars with 10% limestone (185 με). The amount of unrestrained drying shrinkage also decreased with increasing limestone content. Restrained mortar samples produced with cement without limestone exhibited cracking at 87 hours. The presence of limestone increased the time to cracking slightly, but all samples cracked after 96 hours. Overall, the data indicate that mortars produced with PLC show slightly reduced shrinkage and a lower tendency to crack compared with equivalent mortars produced with portland cement. Bentz et al. (2009), analyzing the results of Bucher (2009), attribute these differences to particle size distribution and note that cements with coarser limestones resulted in less shrinkage and a lower potential for cracking (Fig. 2.3).



a. Autogenous shrinkage



b. Unrestrained shrinkage



c. Restrained shrinkage

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

Sait (2017) conducted a meta-analysis of the mechanical properties of PLC concretes using data sourced in a literature survey. This includes data presented above by Alunno-Rossetti and Curcio (1997) and Dhir et al. (2007), along with other data. In Figure 4.6, creep of PLC concretes is presented as a percentage of portland cement concrete creep. Both creep and specific creep are plotted against the limestone content of the cement in the cited studies. The data markers do not indicate the identity of the source study, nor are any details of testing parameters of those studies provided.

Sait's (2017) data for concrete with more than 20% limestone appear to be solely that of the Dhir et al. (2007) study, because only one pair of data points each is shown at 25%, 35%, and 45% limestone. This suggests a trend of drastically increasing specific creep with increasing limestone content. However, specific creep values of PLC concrete are not consistently greater than 100% of the specific creep of portland cement concrete until limestone contents are at least 20%. In the range permitted for ASTM C595 Type IL cements (5% to 15% limestone), the data show similar or slightly lower specific creep for the PLC concrete relative to portland cement concrete. Specific creep was also compared against compressive strength, as shown in Figure 4.7, with the meta-analysis suggesting a similar relationship between these values for both portland cement and PLC concretes.

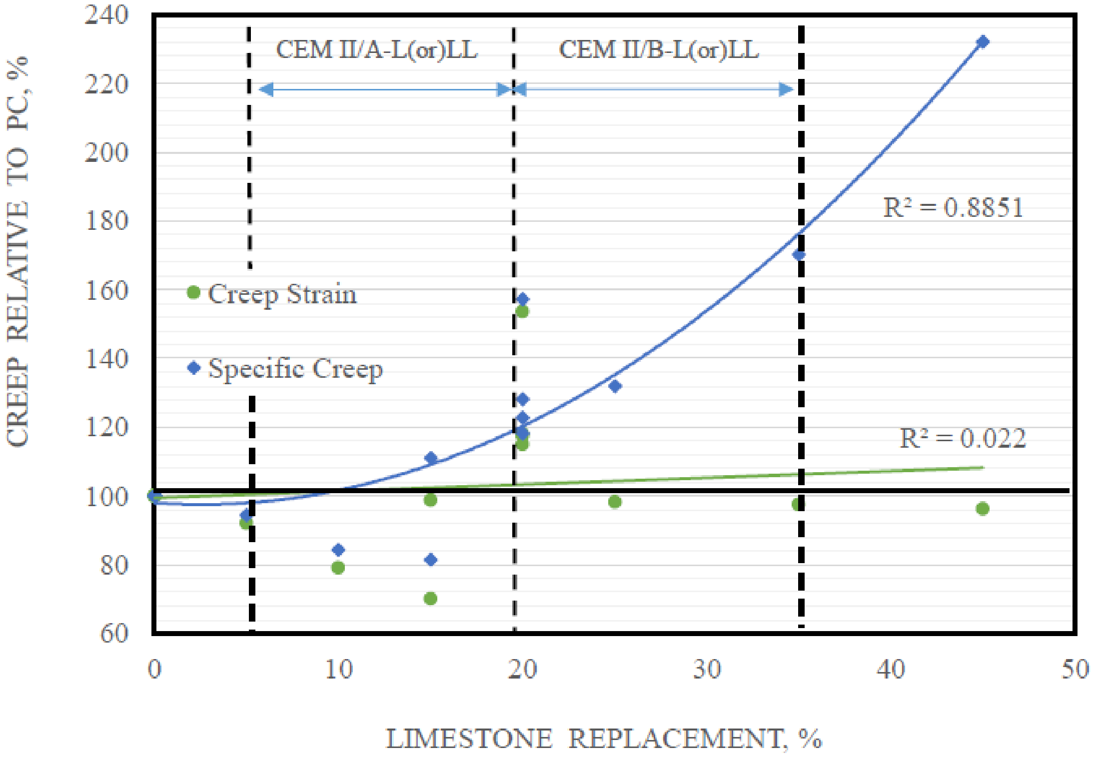


Figure 4.6 Creep and specific creep of PLC concretes as percentage of portland cement concrete creep and specific creep. Data from various sources as reported by Sait (2017).

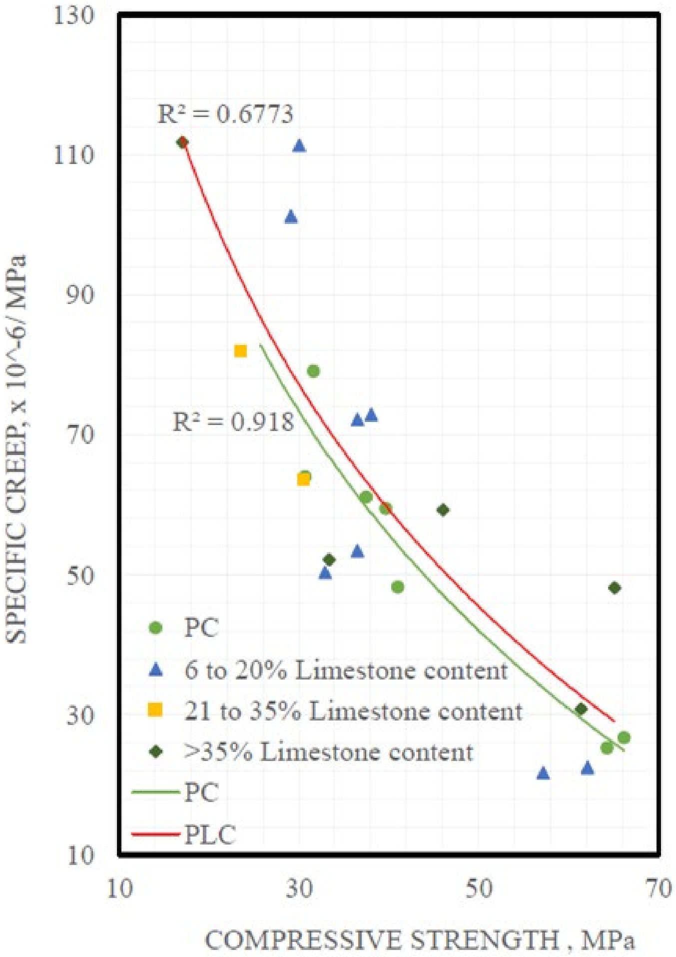


Figure 4.7 Specific creep vs. compressive strength of portland cement and PLC concretes. Data from various sources as reported by Sait (2017).

Creep experiments by Shalan et al. (2016) on prestressed concrete mixtures (see 4.1.1.1 and 4.1.1.2) demonstrated 10 to 40% less specific creep for concrete made with Type IL cements compared to concrete made with Type I/II cements produced by the same plant and based on the same clinker. The tests were reported to be conducted following ASTM C512, using a load of 40% of the 3-day compressive strength applied from 3 days of age for a total of 208 days. Drying shrinkage tests were conducted in parallel on unloaded cylinders to calculate the creep. As noted in 4.1.1.2, this seemingly large reduction in creep translated to relatively small (2%) reductions in prestress losses in tests on prestressed beams using the same pair of mixtures.

Garcia et al. (2019) noted a decrease in drying shrinkage as interground limestone content increased from 3.2% to 30.6% for cements produced at one plant, but for cements produced at a second plant with 4.9% to 15.5% limestone, there was no clear correlation between limestone content and drying shrinkage.

Kurtis et al. (2017) noted variable effects on drying shrinkage in comparing concretes made with Type IL and Type I/II cements, and that shrinkage behavior is likely to be influenced in part by the particle size distribution of the cement. The researchers suggested that more finely ground

Type IL cements may have an increased potential for chemical and autogenous shrinkage compared to those that are ground to a lower fineness. However, their data generally showed comparable chemical shrinkage for portland and PLCs from the same plants, although increased autogenous shrinkage was generally observed. Type IL cements in combination with Class C fly ashes or slag cements exhibited greater early-age shrinkage than comparable mixtures using Type I/II cements, which could indicate an increased risk of early-age cracking in structural applications.

Two other more recent studies performed comparison shrinkage testing on portland cement, PLC, and blends of cement with limestone. Bharadwaj et al. (2021) found no statistically different performance in shrinkage. Barrett et al. (2013) found that for sealed conditions, shrinkage was similar, while for unsealed conditions (50% RH), PLC mixtures had a minor increase (5%) in shrinkage strain of mortar bars at 28 days. Using a dual ring test (restrained shrinkage), researchers found that portland cement and PLC mortars behaved similarly for the first 72 hours, after which the PLC mortar exhibited less stress development. At 168 hours, specimens were cooled slowly until cracking developed, demonstrating that mixtures made with interground PLC did not exhibit an increased risk of shrinkage cracking.

Although creep and shrinkage can be evaluated empirically for a particular mix design, this testing requires time (typically 3 to 12 months), is challenging to perform, and may have minimal impact on the overall design of the structure. For structures that will be particularly susceptible to creep and shrinkage, testing of these properties may be necessary. Strategies that are effective in minimizing creep in portland cement concrete can also be effectively employed when using PLC: minimizing paste content in the mix design and allowing more strength gain before the application of long-term compressive loads (e.g., prestressing).

4.2 DURABILITY

4.2.1 Transport Properties and Chloride Resistance

As a porous medium, concrete is subject to ingress by ions. Permeability and porosity of concrete, under the broad heading of "transport properties," both play a role in how ions travel into the matrix and are potentially bound by it. Chloride ions are of considerable interest in concrete systems primarily because they can corrode reinforcing steel and prestressing strands that may be embedded in the concrete. Two common sources of chloride are deicers applied to pavements and bridges during winter weather and seawater for marine exposures.

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

The authors concluded that overall, the PLC concrete had "competitive properties" with the PC concrete. Earlier work at the same institute (Tsivilis et al. 1999b) reported that the quality and composition of both the clinker and the limestone had a significant impact on the permeability of concrete. For five of these mixtures, Tsivilis et al. (2000) conducted the "Rapid Chloride Permeability Test" (RCPT) (ASTM C1202) after 28 days of moist curing. Table 4.6 shows the RCPT results, with authors noting that for cements with up to 15% limestone, the charge passed was near 6000 C, while the concrete made with 35% limestone cement had the highest RCPT value of 6600 C despite the use of a lower w/cm (0.62) than the mixtures with 20% or less limestone (0.70). All five mixtures would be classified as high permeability, likely due to the high w/cm ratio.

Table 4.6 Permeability Test Results for Concretes Produced with PLC (Tsivilis et al. 2000, 2003a)

Cement Properties			Concrete Properties						
Lime-stone (%)	Blaine fineness (m^2/kg)	Strength at 28d (MPa)	W/CM	Strength at 28d (MPa)	K_g (10^{-17} m^2)	K_w (10^{-12} m/s)	*S* (mm/ $min^{0.5}$)	*P* (%)	*RCPT (coulombs)*
0	260	51.1	0.70	31.9	2.26	2.39	0.237	12.5	6100
10	340	47.9	0.70	27.4	2.65	2.30	0.238	12.3	5800
15	366	48.5	0.70	27.3	2.80	2.22	0.226	12.3	6000
20	470	48.1	0.70	28.0	2.95	2.00	0.220	13.1	6400
20	325	39.8	0.62	28.2	3.03	1.81	0.228	12.9	-
25	380	40.0	0.62	26.5	2.82	2.07	0.229	13.6	-
35	530	32.9	0.62	26.6	2.10	2.23	0.224	14.6	6600

Hooton et al. (2010) noted that ASTM C1202 testing of concrete cylinders made with a range of cementitious materials, including portland cement and PLCs with and without slag cement, at a w/cm of 0.40, indicated no impact of PLC with 10% limestone on permeability at 56 and 85 days. Table 4.7 provides their data. Those authors do note that slag cement does have a significant beneficial impact. Based on C1202 guidance, these concretes made with portland cement and PLC (alone) would be classified as having moderate permeability, while those made with slag cement would be classified as having low or very low permeability.

Table 4.7 Rapid Chloride Permeability Test (ASTM C1202) Results, Coulombs (Hooton et al. 2010)

		GU 100%	PLC10 100%	PLC15 100%	GU 70% Slag 30%	PLC10 70% Slag 30%	PLC15 70% Slag 30%
56 Days	Top	3220	3220	3130	1050	980	1270
	Middle	3050	2910	3130	1090	1140	1340
	Average	3135	3065	3130	1070	1060	1305
85 Days	Top	2500	2510	2850	900	970	900
	Middle	2230	2510	2750	920	970	990
	Average	2365	2510	2800	910	970	945

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

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

Irassar et al. (2001) immersed concretes, which were produced with cements with 0%, 10% or 20% limestone, into 3% NaCl solution. Chloride profiles were determined after various exposure periods, and chloride diffusion coefficients were calculated from the profiles. The results are summarized in Table 4.8. Generally, significant increases in the chloride diffusion coefficient are observed with either increasing w/cm or limestone content. Concrete produced with the highest w/cm and limestone content showed very low resistance to chloride ion penetration. However, Hooton et al. (2010) performed ASTM C1556 chloride bulk diffusion tests on samples moist cured for 28 days and found that 10% interground limestone did not change diffusion coefficients appreciably, with or without 30% slag replacement, as shown in Table 4.9.

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

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

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

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

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

Table 4.2 shows strength and durability data for three series of concrete mixtures (w/cm = 0.78-0.80, 0.45 and 0.40) produced with portland cement (4% limestone and 380 m^2/kg Blaine) and PLC (12% limestone and 500 m^2/kg Blaine). The results from the "Rapid Chloride Permeability Test" (ASTM C1202) are plotted in Figure 4.8. It is clear from these data that w/cm, age, and supplementary cementitious materials (SCM) content have a profound impact on the permeability, but that the impact of the level of limestone in the cement (4% to 12%) is not significant. For transport properties, Bharadwaj et al. (2021) found that PLC concrete displayed 5% greater porosity than portland cement concrete whether SCMs were used or not, yet the resistivity of PLC concrete was 5% to 10% greater on average for both the systems with and without SCMs. In addition, the PLC samples with SCMs had a higher resistivity than those without SCMs due to reduced pore connectivity.

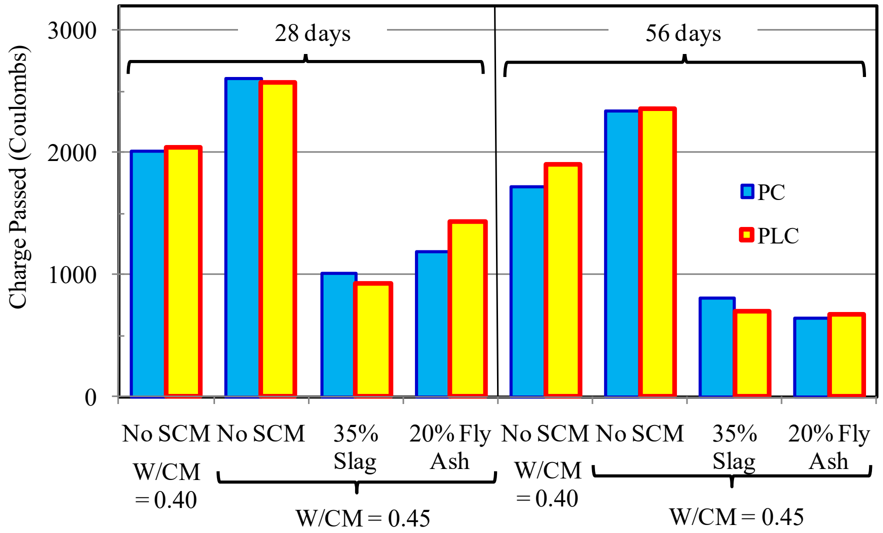
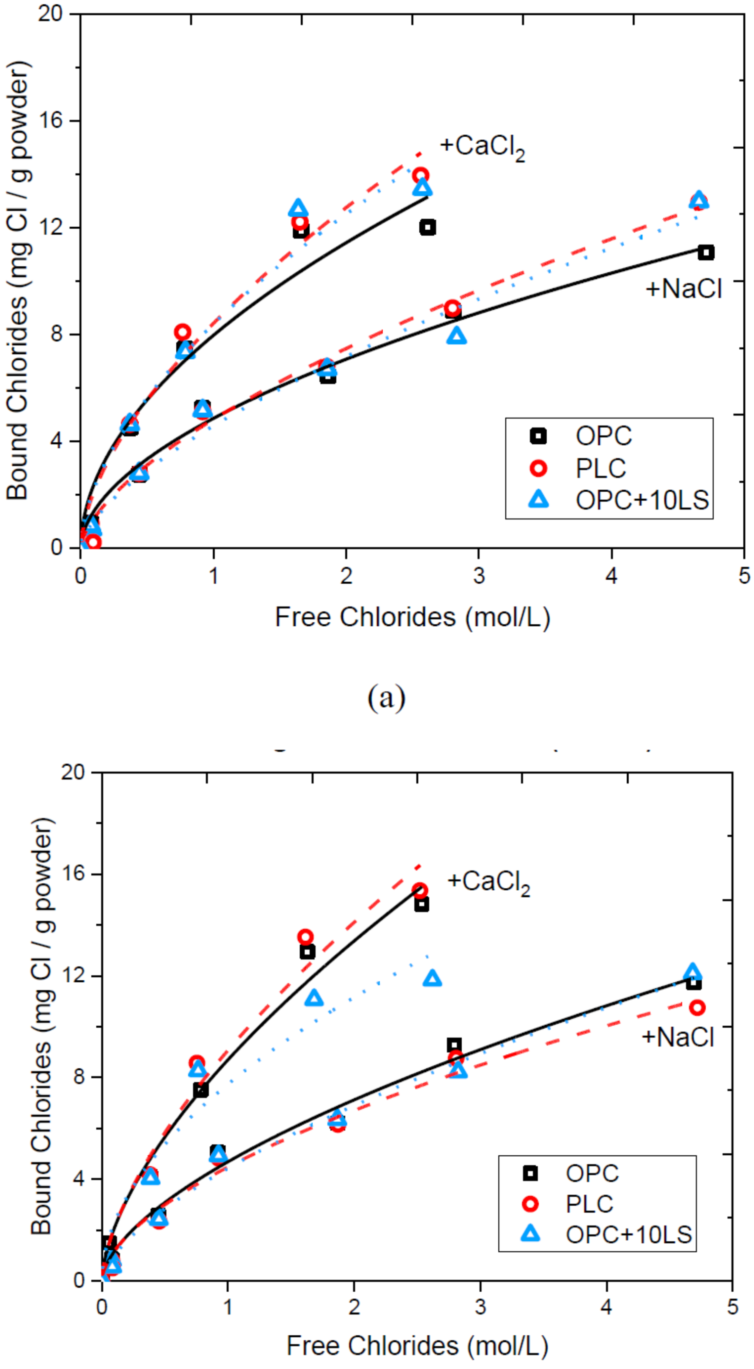


Figure 4.8 "Rapid Chloride Permeability Test" (ASTM C1202) data for portland cement and PLC concrete with and without SCM (Thomas et al. 2010b).

Bharadwaj et al. (2021) developed chloride binding isotherms to relate the free chloride content vs. the bound chloride content. These isotherms are used in service life predictions to account for the corrosion of steel reinforcement. Researchers wanted to understand how the limestone in PLC contributes to chloride binding. Chlorides can either be bound chemically or by physical adsorption on, for instance, C-S-H. The pH of the pore solutions and type of deicer both have an effect. No statistical difference was found between the chlorides bound by portland cement or PLC, leading researchers to conclude that the binders can be used as a direct substitute for one another. While the chloride binding of mixtures that contained fly ash, silica fume, or natural pozzolans were unaffected by the presence of limestone up to 15%, PLC mixtures that contained slag cement outperformed portland cement mixtures with slag cement. Researchers concluded that limestone should be considered part of the cementitious system for comparison with chloride content limits for concrete mixtures set by ACI 318. As shown in Figure 4.9, PLC cementitious systems can bind greater amounts of chloride than portland cement systems, possibly as a result of higher alumina contents. Fly ash, silica fume, and natural pozzolans do not affect the chloride binding capacity in cementitious systems containing up to 15% limestone.



(a)

(b)

Figure 4.9 Example chloride binding isotherms comparing Type V portland cement (OPC) to portland-limestone cements made from the same clinker source (PLC) and concrete with limestone added mixes for exposure to $CaCl_2$ solutions (a) Concrete mixtures made with no SCM; and (b) Concrete mixtures made with 20% fly ash and 5% silica fume. (Bharadwaj et al. 2021)

Bharadwaj et al. (2021) also looked at resistance to chloride ingress in concrete, finding that PLC and portland cement mixes have nearly identical chloride profiles. The porosity, chloride binding, and formation factor (AASHTO PP 84, now AASHTO R 101) of PLC samples are similar to their portland cement counterparts and all mixes with SCMs have a higher formation factor due to a refined microstructure. Formation factor, the ratio of concrete resistivity to its pore solution resistivity, is inversely related to the product of the total porosity and the connectivity of the pores. At a 20-year exposure and 50 mm depth, which is a typical depth/cover for reinforcing bars, the chloride content of PLC samples is either similar to, or slightly lower than, the portland cement samples.

One way to use the chloride ingress information on assessing the potential for corrosion of reinforcing steel is via a parameter known as the critical chloride threshold, Cl_{crit}, defined as the concentration of chlorides at the steel-concrete interface that is required to initiate corrosion. As such, Cl_{crit} can be used to estimate the service life of reinforced concrete. Though higher Cl_{crit} values indicate longer service life, there is not a lot of agreement on these values. Oregon State University developed a new test method and similar metric to quantify critical chloride threshold values, OC_{crit}, intended to offer a faster accelerated corrosion test than other options. While time to corrosion has not been correlated with this value, the relationship between PLC and portland cement systems indicates that PLC systems without SCMs will have similar performance to portland cement systems without SCMs. Likewise, both PLC and portland cement systems containing 25% fly ash exhibited a longer time to corrosion than the controls without fly ash, which agrees with the higher Cl_{crit} values compared to control specimens. Although specimens made with 50% slag reached corrosion initiation in a short time, if all other factors are the same, the PLC concrete had higher Cl_{crit} mean values than the control, indicating longer time to corrosion, or better performance.

The balance of evidence would seem to indicate concrete produced with PLC up to 15% can provide similar resistance to the penetration of fluids. portland cement and PLC concretes may be expected to give similar performance when they are proportioned to give the same compressive strength at 28 days.

4.2.2 Freeze/Thaw and Deicer Salt Scaling

Prior to the introduction of PLC standards in the U.S. and Canada, the primary source of data on the effect of limestone on freeze-thaw and deicer-salt scaling resistance of concrete came from European studies on non-air-entrained concretes. Some of these studies indicate that freeze-thaw resistance is decreased by the incorporation of limestone (Matthews 1994; Barker and Matthews 1994; Dhir et al. 2007) and others indicate that PLC concrete can achieve comparable performance to portland cement concrete provided equal strength is obtained, the limestone content is limited, and the clay and organic content of the limestone are limited (Sprung and Siebel 1991; Siebel and Sprung 1991; Albeck and Sutej 1991; Schmidt et al. 1993).

Since that time, several researchers have studied various aspects of freezing and thawing performance to assess if the inclusion of limestone affects durability. Kurtis et al. (2017) tested five commercially available Type IL cements from the southeastern U.S. in concrete mixtures designed to meet Georgia DOT specifications and found good freeze-thaw resistance when the concrete was adequately air entrained. In addition, Ghazy et al. (2018) looked at the physicomechanical properties and microstructural features of concrete made with either portland cement or PLC, with or without SCMs, exposed to freeze-thaw cycles combined with different concentrations of chloride-based deicing salts ($MgCl_2$ and $CaCl_2$). They found that the resistance of concrete exposed to deicing salts is a function of three factors: physical penetrability of the concrete, C_3A content of the cement, and content of portlandite available for chemical reactions in the hydrated paste. Mixes included either portland cement or PLC as the primary binder, with SCM dosages of fly ash at 0%, 20%, or 30%, and nanosilica at 0% or 6%. Deicer solutions investigated were moderate (about 13% +/-1% mass of solids) and high (about 20% +/-1% mass of solids) concentrations each of $MgCl_2$ and $CaCl_2$. The presence of limestone in the concrete matrix as PLC provided better resistance to moderate and high concentrations of deicing salts: lower expansion, less mass loss, and higher retention of dynamic modulus. The fly ash + nanosilica mixes resulted in a denser matrix. Fly ash concrete was more durable than the reference concretes, especially when used at a 30% dosage, as a result of lower penetrability and low initial portlandite phase/content. Nanosilica concrete mixtures exhibited no features of damage due to freeze-thaw as a result of the filler effect, pozzolanic reactivity, and reduction of water volume in the matrix, which was absorbed on the surface of ultrafine silica agglomerates.

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

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

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

Table 4.2 (Thomas et al. 2010b) shows strength and durability data for three series of concrete mixtures (w/cm = 0.78-0.80, 0.45 and 0.40) produced with portland cement (4% limestone and 380 m^2/kg Blaine) and PLC (12% limestone and 500 m^2/kg Blaine). The results from cyclic freeze-thaw (ASTM C666 Procedure A) and deicer salt scaling (ASTM C672) are shown in Figure 4.11. All of the concrete mixtures tested showed excellent resistance to cyclic freeze-thaw tests. Some scaling was observed for concrete with fly ash or slag in the accelerated laboratory salt scaling tests, however, mass losses were less than maximum values specified by state transportation departments (e.g., typically mass loss $\leq$ 800 g/m^2 to 1000 g/m^2). There was no consistent difference between the scaling behavior of equivalent mixes with portland cement or PLC.

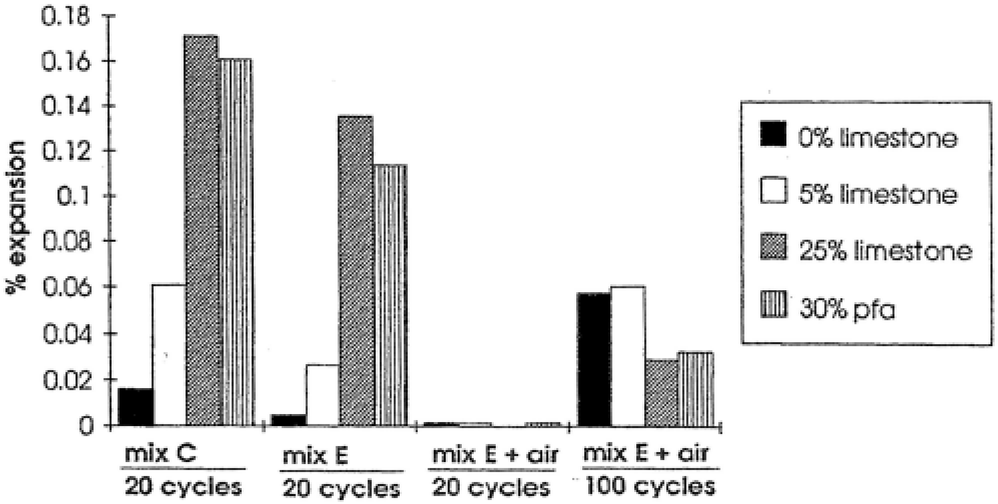
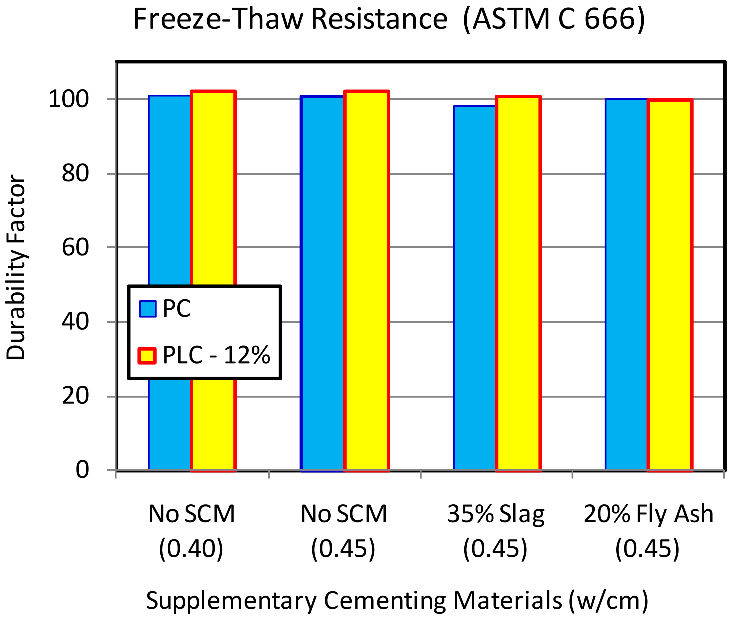


Figure 4.10 Effect of air entrainment on the freeze-thaw resistance of portland cement and PLC concrete (Matthews 1994).



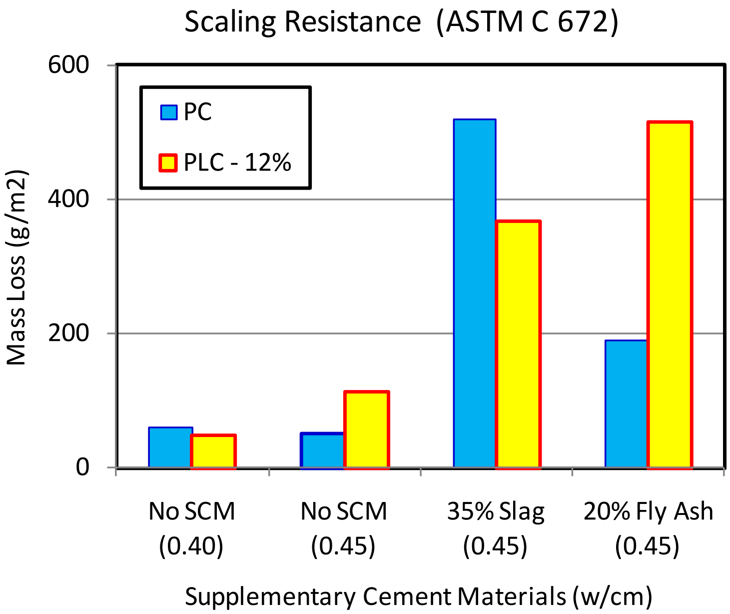


Figure 4.11 Results of freeze-thaw (top) and deicer-salt scaling tests for portland cement and PLC concretes with and without SCM (Thomas et al. 2010b).

4.2.3 Carbonation

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

Barker and Matthews (1994) studied the effect of limestone (0%, 9%, 15%, and 24% interground with the portland cement) on the carbonation of two series of concretes; Series A was produced to the same w/cm (0.60) and Series B was proportioned to achieve the same 28-day compressive strength (44 MPa; cube strength). Figure 4.12 confirms the findings of Matthews (1994) that concretes of equal strength carbonate at similar rates even when the concretes are produced with PLC with varying limestone contents.

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

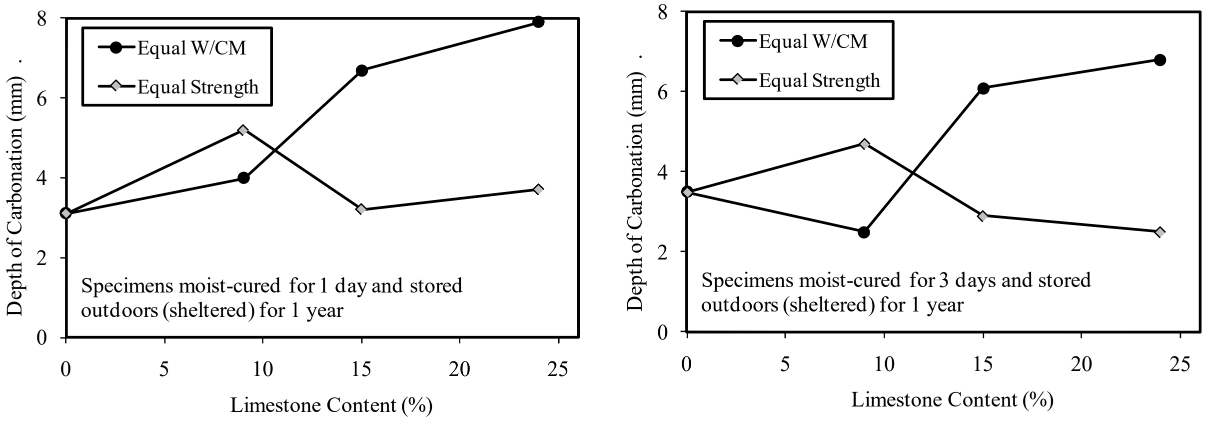
Collepardi et al. (2004) showed that substitution of 15% or 25% of the portland cement by ground limestone, fly ash or slag (added at the concrete mixer) led to an increase in carbonation rate when concrete was compared at equal w/cm, but that the rate was similar for concretes of equal strength. The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

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

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

Garcia et al. (2019) conducted carbonation tests on concrete prisms in outdoor exposure, unsheltered and sheltered in a Stevenson Screen (per EN 12390-10), using seven cements produced at two cement plants with interground limestone contents ranging from 3.2% to 30.6%, and w/cm of 0.40, 0.45, and 0.50. Data after 24 months of exposure in Austin, Texas for 0.45 w/cm showed a general increase in the carbonation rate with increased limestone content; however, it should be noted that cements in this study were not all optimized to yield similar strength development characteristics. Trends are similar to those shown in Figure 4.12 by Barker and Matthews (1994). Carbonation rates in 0.50 w/cm concretes using the non-optimized 21% and 30.6% limestone cements were concluded to be problematic for reinforcing steel at 1.5 inches depth. Concretes with 0.40 w/cm, however, had substantially lower carbonation rates, although data were only available for 12 months of exposure. Similar trends, although with reduced carbonation rates, were observed for the 0.45 w/cm mixtures at a second test site on the Texas Gulf Coast. The overall reduction in carbonation rates was attributed to higher humidity and precipitation at this test site compared to the Austin site.

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



(a) (b)

Figure 4.12 Effect of the limestone content of PLC on the carbonation of concrete mixes produced at equal w/cm or equal 28-day strength for specimens cured (a) 1 day or (b) 3 days (Barker and Matthews 1994).

4.2.4 Sulfate Resistance

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

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

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

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

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

Matthews (1994) exposed 100-mm concrete cubes (w/cm = 0.62 to 0.66) to three sulfate solutions consisting of either Na_2SO_4 (1.5% SO_3) or $MgSO_4$ (0.35% or 1.5% SO_3) for up to 5 years. Portland cement from five different sources was blended or interground (in one case) with 5% or 25% limestone. The sulfate resistance of the concrete was strongly dependent on the C_3A content of the cement with no consistent difference in performance being attributed to the limestone content (Figure 4.13). It should be noted that of the five cements used, only two had C_3A contents consistent with Type II cement requirements (<8%), and none had C_3A contents below 5%, as would be required for a Type V cement.

Irassar and coworkers (Gonzáles and Irassar 1998; Irassar et al. 2000, 2005) compared the performance of three cements (one Type II and two Type V) with varying C_3A and C_3S levels, and limestone contents of 0%, 10% and 20%, in ASTM C1012 mortar tests. Generally, the presence of 10% limestone had little impact on the performance of mortars stored in 5% Na_2SO_4 compared with control mortars without limestone, but 20% limestone resulted in increased expansion. Additionally, mortars containing the low C_3S content Type V cement performed better than those with the high C_3S Type V cement. Figure 4.14 shows the expansion results for mortars with 0% and 20% limestone.

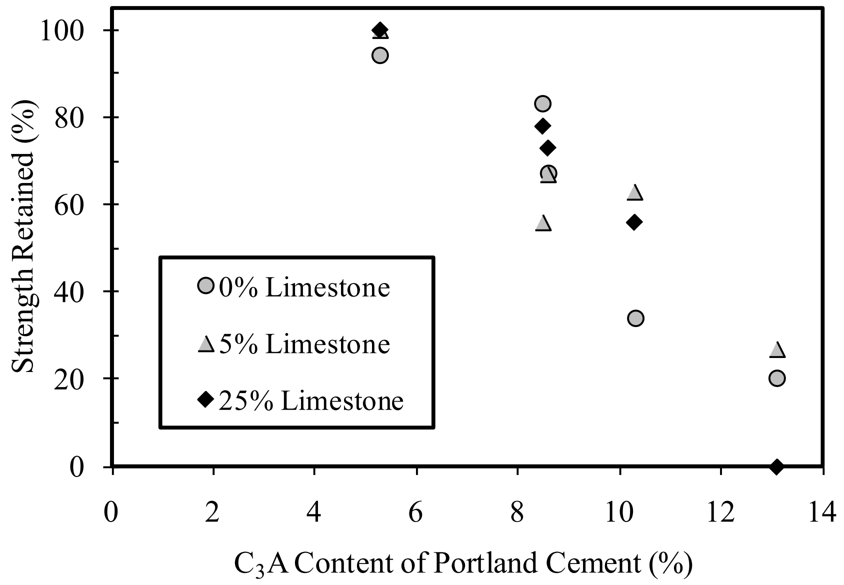
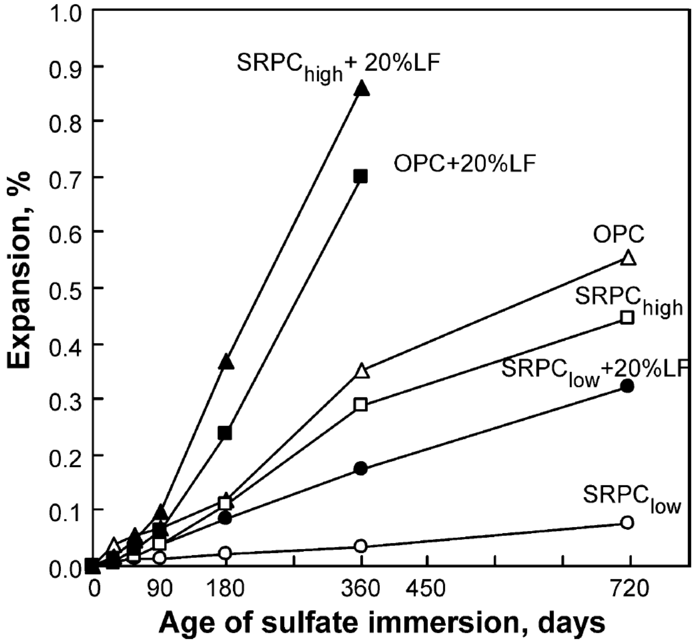


Figure 4.13 Strength retained after 2 years in $MgSO_4$ (1.5% SO_3) solution (Matthews 1994).



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

Figure 4.14 Effect of limestone on the expansion of mortars stored in 5% Na_2SO_4 (Irassar et al. 2005). OPC = Type II cement; SRPC$_{low}$ = Low C_3S Type V cement; SRPC$_{high}$ = High C_3S Type V cement.

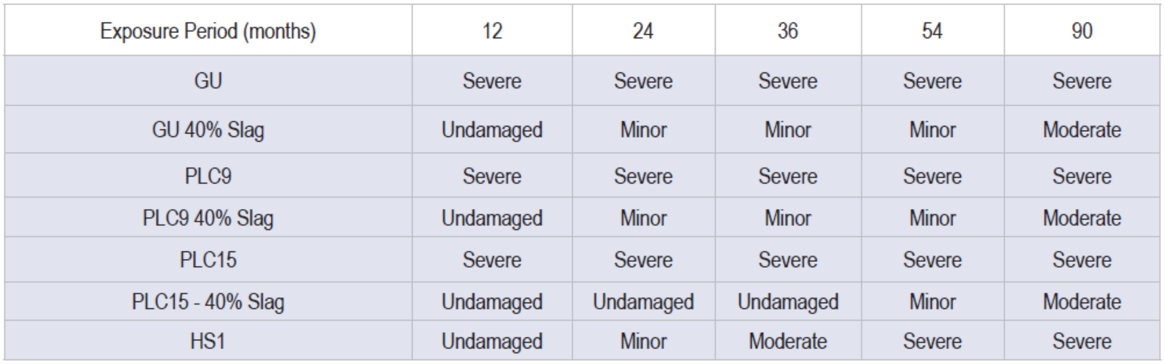
When PLCs were initially introduced in CSA A3001 and ASTM C595 / AASHTO M 240, these specifications did not include provisions for sulfate-resistant PLCs or sulfate-resistant blended cements containing PLCs and SCMs, because these materials had not yet been sufficiently studied in sulfate exposures, particularly at low temperatures that might favor thaumasite formation (discussed further in 4.2.4.1).

ASTM C1012 was developed for use with blended cements and cementitious systems with SCMs. This test is also used to evaluate sulfate resistance of PLCs and qualify Type IL cements for the moderate and high sulfate-resistance designations under ASTM C595. It is a relatively severe test: Some Type V cements will not satisfy the 6-month 0.05% expansion limit in ASTM C1012 testing for high sulfate resistance in ASTM C595 (Gagatek and Hooton, 2019).

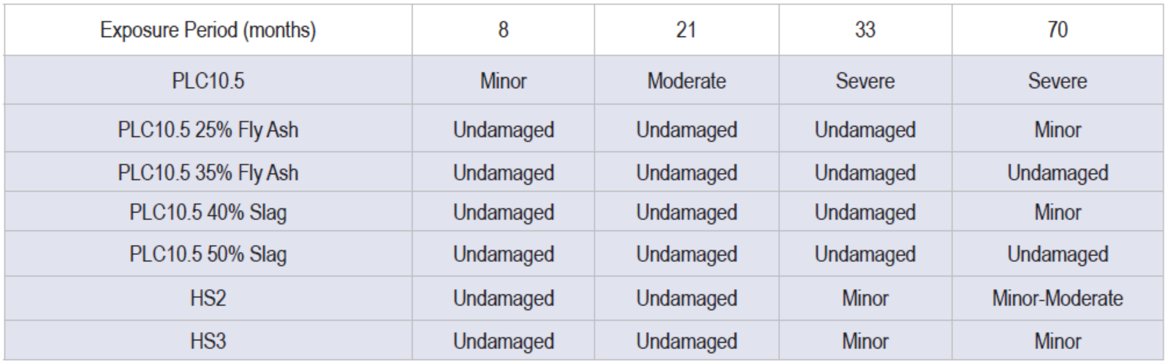
Hooton and Thomas (2016) investigated the suitability of PLCs and PLC-SCM blends containing 5% to 15% limestone for use in sulfate exposures. Their study included both standard laboratory mortar expansion tests and tests of concrete prisms in simulated severe sulfate field exposure conditions for up to five years. A key finding of this study was that PC-SCM and PLC-SCM mixtures exhibited similar performance for the same w/cm, exposure conditions, and SCM replacement level. That is, the replacement of portland cement with PLC did not prevent the production of sulfate-resistant concrete. The use of SCMs in combination with PC or PLC produced concretes that exceeded the performance of CSA Type HS portland cements in severe exposures. An update two years later (Hooton and Thomas 2018) with additional outdoor exposure monitoring (up to 90 months exposure) further illustrates that PLCs in combination with SCMs can be used to produce exceptional sulfate resistance in severe exposures capable of damaging concrete produced with CSA Type HS portland cements. Tables 4.13 and 4.14 present a summary of the visual ratings of the different mixtures. The sulfate concentrations in the outdoor exposure tests were sufficiently high to be classified as S3, or very severe, by ACI 318 (2019) and ACI

201.2R (2016); Type V or HS portland cements are not recommended for use without an SCM in S3 exposures. The low-temperature testing aspects of this study and recommendations for cement standards are discussed in 4.2.4.1 on the thaumasite form of sulfate attack (TSA).

Table 4.13 Visual ratings of 0.40 w/cm concrete in outdoor exposure in sodium sulfate solution (15,000 ppm SO_4^{2-} concentration). (CAC 2021, adapted from Hooton and Thomas, 2018).



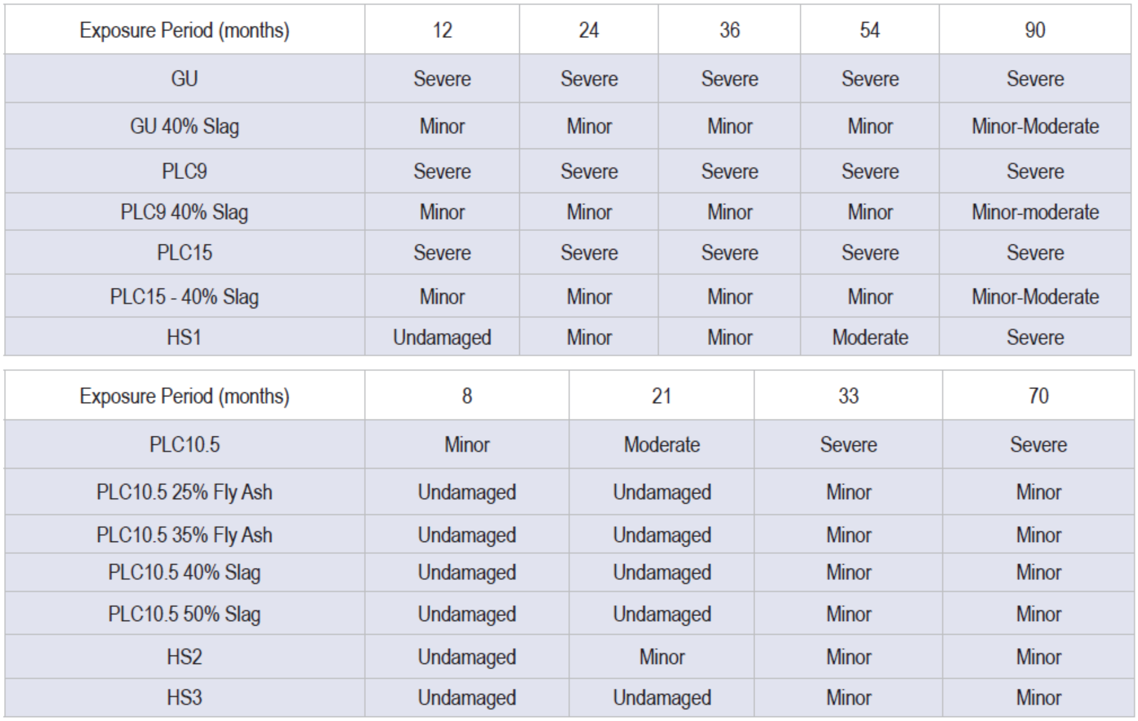
Exposure Period (months)	12	24	36	54	90
GU	Severe	Severe	Severe	Severe	Severe
GU 40% Slag	Undamaged	Minor	Minor	Minor	Moderate
PLC9	Severe	Severe	Severe	Severe	Severe
PLC9 40% Slag	Undamaged	Minor	Minor	Minor	Moderate
PLC15	Severe	Severe	Severe	Severe	Severe
PLC15 - 40% Slag	Undamaged	Undamaged	Undamaged	Minor	Moderate
HS1	Undamaged	Minor	Moderate	Severe	Severe



Exposure Period (months)	8	21	33	70
PLC10.5	Minor	Moderate	Severe	Severe
PLC10.5 25% Fly Ash	Undamaged	Undamaged	Undamaged	Minor
PLC10.5 35% Fly Ash	Undamaged	Undamaged	Undamaged	Undamaged
PLC10.5 40% Slag	Undamaged	Undamaged	Undamaged	Minor
PLC10.5 50% Slag	Undamaged	Undamaged	Undamaged	Undamaged
HS2	Undamaged	Undamaged	Minor	Minor-Moderate
HS3	Undamaged	Undamaged	Minor	Minor

Elahi and Shearer (2018) tested PLC mortars in both sodium sulfate and magnesium sulfate solutions following ASTM C1012. The cements included both laboratory blends of portland cements (Type I/II or V) and limestone powder, and interground Type IL cements. With one exception, the cements would not meet requirements for moderate or high sulfate resistance, including the Type V cement itself. Mixtures with 20% Class F fly ash (13% CaO content) replacement performed somewhat better. The authors recommended that the South Dakota DOT permit the use of Type IL cements in sulfate exposure provided they meet ASTM C1012 expansion requirements for moderate or high sulfate-resistance designations, with annual testing to verify this performance. They also recommended the use of 20 to 25% Class F fly ash in sulfate-exposed concrete, with ASTM C1012 testing to verify that sulfate resistance of the system is sufficient.

Table 4.14 Visual ratings of 0.40 w/cm concrete in outdoor exposure in magnesium sulfate solution (15,000 ppm SO_4^{2-} concentration). (CAC 2021, adapted from Hooton and Thomas, 2018).



Exposure Period (months)	12	24	36	54	90
GU	Severe	Severe	Severe	Severe	Severe
GU 40% Slag	Minor	Minor	Minor	Minor	Minor-Moderate
PLC9	Severe	Severe	Severe	Severe	Severe
PLC9 40% Slag	Minor	Minor	Minor	Minor	Minor-moderate
PLC15	Severe	Severe	Severe	Severe	Severe
PLC15 - 40% Slag	Minor	Minor	Minor	Minor	Minor-Moderate
HS1	Undamaged	Minor	Minor	Moderate	Severe

Exposure Period (months)	8	21	33	70
PLC10.5	Minor	Moderate	Severe	Severe
PLC10.5 25% Fly Ash	Undamaged	Undamaged	Minor	Minor
PLC10.5 35% Fly Ash	Undamaged	Undamaged	Minor	Minor
PLC10.5 40% Slag	Undamaged	Undamaged	Minor	Minor
PLC10.5 50% Slag	Undamaged	Undamaged	Minor	Minor
HS2	Undamaged	Minor	Minor	Minor
HS3	Undamaged	Undamaged	Minor	Minor

Garcia et al. (2019) present the results of ASTM C1012 mortar bar tests on cements containing up to 30% limestone, with and without SCMs. Four cements were produced using clinker intended for Type I cement, three were produced using moderate C_3A clinker intended for Type I/II cement, and a low C_3A Type V cement was also tested for comparison. Two of the cements had limestone contents between 5 and 15% as permitted for Type IL cements. Table 4.15 summarizes the results of tests involving mortars without SCMs, with a Class F fly ash, with a Class C fly ash (22.6% CaO), and with slag cement. The results are presented as whether the mortar bar expansions would satisfy requirements for the moderate sulfate-resistance (MS) or high sulfate-resistance (HS) designations in ASTM C595 / AASHTO M 240.

The data demonstrate that clinker chemistry may be an important factor in whether a PLC can meet sulfate-resistance requirements of cement specifications but may not alone be sufficient. When the Type I/II-based cements were tested without SCMs, mortar bars with the portland cement and the 11.6% limestone cement had expansions less than 0.10% at 180 days, while the 15.5% limestone cement expanded more than 0.5% at 180 days and samples exhibited some warping. Mixtures with 35% slag cement were highly effective, followed by 30% Class F fly ash, 20% Class F fly ash, and 40% Class C fly ash. The authors also tested mixtures with 20% Class C fly ash and 5% silica fume, and a second Class C fly ash (27.7% CaO) at 20% and 40% replacement levels; all of these combinations exceeded 0.10% expansions at 180 days and in some cases performed worse than without any SCM. Similar trends were observed in testing of concrete prisms stored in ASTM C1012 conditions.

The work by Garcia et al. (2019) further demonstrates that SCMs improve the sulfate resistance of PLCs. It also shows that some PLCs may be capable of meeting sulfate-resistance requirements on their own, without SCMs. XRD studies of the mortars with and without exposure to sodium sulfate in ASTM C1012 conditions also suggested that the SO_3/Al_2O_3 and CO_2/Al_2O_3 ratios of cement-SCM combinations were an important factor in sulfate resistance and could be optimized in a blended cement. Higher ratios favored stabilization of ettringite and monocarbonate phases in the paste over hemicarbonate and monosulfate.

Table 4.15 Performance of combinations of cements and SCMs in ASTM C1012 testing, relative to ASTM C595 / AASHTO M 240 requirements for sulfate-resistant designations (after Garcia et al. 2019).

Clinker Type	Limestone Content	No SCM	20% Class F Fly Ash	30% Class F Fly Ash	40% Class C Fly Ash #1	35% Slag Cement
Type I	3.2%	X	X	n/a	MS	HS
	13.4	X	X	n/a	n/a	HS
	21.0	X	MS	HS	MS	HS
	30.6	X	X	HS	MS	HS
Type I/II	4.9%	MS	HS	n/a	n/a	HS
	11.6%	MS	n/a	n/a	n/a	n/a
	15.5%	X	X	n/a	n/a	HS
Type V	2.9%	HS	n/a	n/a	n/a	n/a

Key: MS = less than 0.10% at 180 days, HS = less than 0.05% at 180 days or less than 0.10% at 1 year, X = greater than 0.10% at 180 days, n/a = not tested.

Bharadwaj et al. (2021) also found no significant difference in sulfate expansion of mortar bars made with PLC vs. portland cement for clinkers used to make Type II/V cements. The presence of SCMs (fly ash, slag cement, silica fume, and natural pozzolan) significantly reduced expansions at 6 months and 1 year when used alone or in various combinations relative to the mixtures that contained no SCM. For mixtures that contained both fly ash and slag cement, the PLC-based mortars performed slightly better than the portland cement-based mortars; the authors suggested that improved pore refinement with PLC was likely the reason.

In summary, the sulfate resistance of concrete produced with PLCs with up to 15% limestone is largely determined by the chemistry of the portland cement clinker, the w/cm, and the type and dosage of SCM (if used). Practitioners should ensure these are appropriate for the exposure conditions. ACI 318 (2019) contains code requirements for buildings with sulfate exposures; these provisions and the recommendations of ACI 201.2R (2016) may be useful for other structures as well.

4.2.4.1 Thaumasite form of sulfate attack (TSA). The sulfate-resistance data discussed above were generated by studies conducted at normal laboratory temperature (e.g., 20°C to 23°C). There was increased concern in the decade or so preceding the introduction of Type IL cements in ASTM C595 and AASHTO M 240 about the performance of concrete exposed to sulfates at lower temperatures which favors the thaumasite form of sulfate attack (TSA) especially when the concrete contains a source of carbonate ions.

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

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

In 1998 BRE initiated a combined field and laboratory trial to investigate the performance of concrete containing limestone aggregates in sulfate-bearing ground (Crammond et al. 2003). Concrete specimens were buried in sulfate-bearing clay at a site in Central England (Shipston on Stour). Concretes cast with high-C_3A portland cement with and without 15% limestone all showed some surface deterioration when half the samples were retrieved after 3 years. Concretes with carbonate aggregates showed more deterioration than concretes with siliceous aggregates; however, the results reported give no indication of the comparative performance of concretes with and without limestone as an ingredient in cement. The remaining samples were scheduled to be retrieved in 2008 (10 years); however, no follow-up study appears to have been published.

Tsivilis and coworkers (Tsivilis et al. 2007; Kakali et al. 2003; Skaropoulou et al. 2009a) ran a series of tests using cement with 6.7% C_3A interground with 15% and 30% limestone and reported separately on the effect of various supplementary cementitious materials (SCM) on the performance of the cement with 15% limestone (Tsivilis et al. 2003b; Skaropoulou et al. 2009b). Mortar bars (40 mm × 40 mm × 53 mm) were produced at w/cm = 0.50 and after 28 days of curing, the bars were placed in a solution of 1.8% $MgSO_4$ at both 5°C and 25°C. Mortars were produced both with a siliceous sand and a calcareous sand. After 11 months visual inspection showed no cracking of the mortar without limestone, expansion and cracking of the mortar with 15% limestone, and expansion and spalling of the mortar with 30% limestone (Tsivilis et al. 2007). After 60 months both mortars with 15% and 30% limestone were reported (Skaropoulou et al. 2009a) to have completely disintegrated (damage rating 9) and the mortar with no limestone in the cement was exhibiting cracking and spalling (damage rating 5 and 6). Figure 4.15 shows the changes in mass of the mortars over 5 years. Thaumasite was found in all the specimens at 5 years, including the specimen produced without limestone in the cement and with siliceous sand.

Specimens produced with the cement with 15% limestone plus SCM showed variable performance and the changes in mass are shown in Figure 4.16 (Skaropoulou et al. 2009b). The use of 20% natural pozzolan increased the rate of deterioration with visible deterioration occurring after just 7 months compared with 8 months for the specimens without SCM. Signs of deterioration appeared at 11 months for specimens containing 30% fly ash, 16 to 30 months for specimens with 10% metakaolin and 30 months for specimens with 50% slag. Generally, the performance of the mortar with 15% limestone in the cement plus 50% slag was similar or slightly better than the mortar produced with cement without limestone or SCM (compare data in Skaropoulou et al. 2009a with Skaropoulou et al. 2009b).

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

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

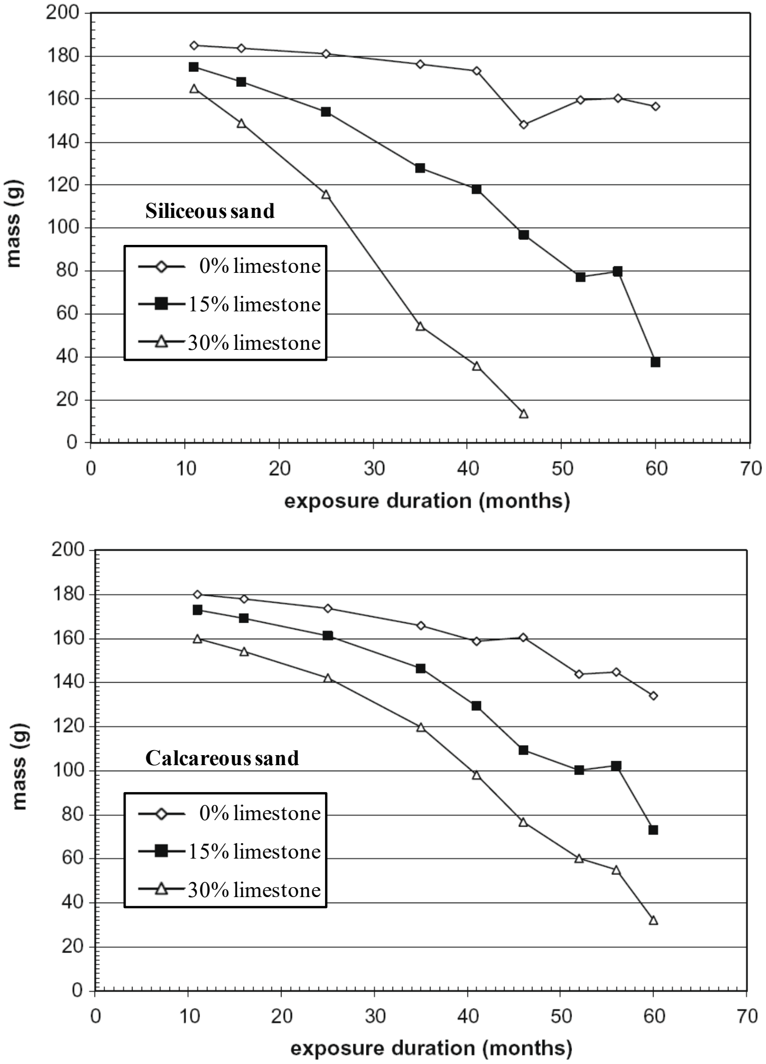


Figure 4.15 Change in mass of mortars with siliceous sand (top) or calcareous sand (bottom) stored in 1.8% $MgSO_4$ solution at 5°C (Skaropoulou et al. 2009a).

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

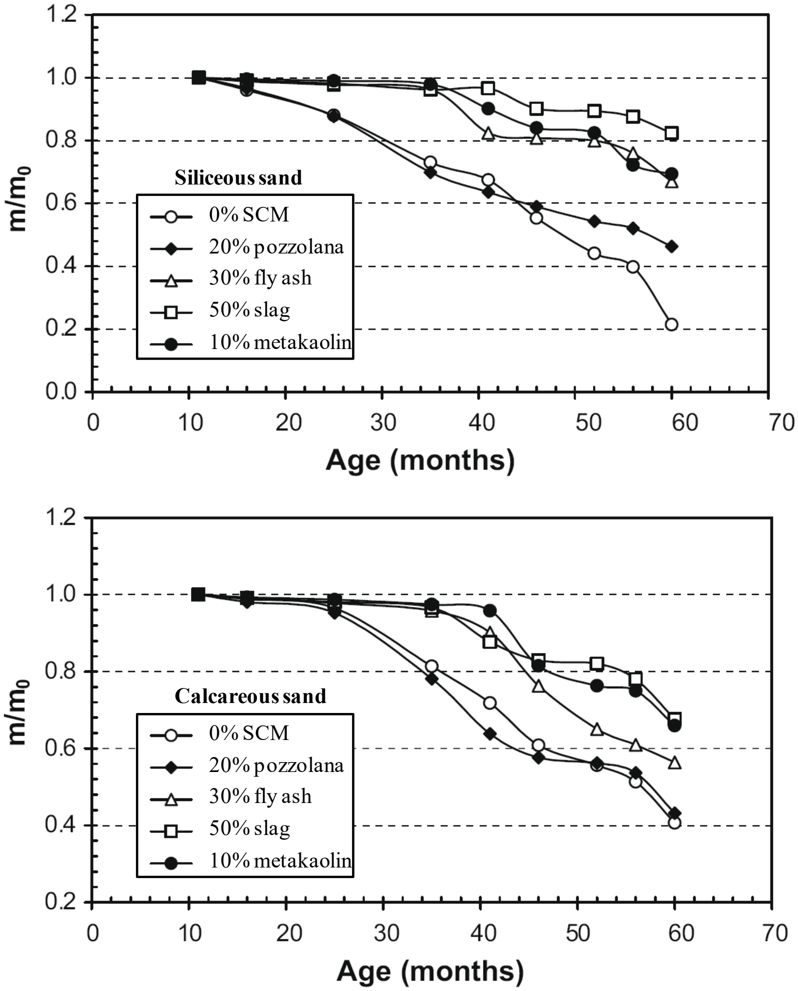


Figure 4.16 Relative mass change of mortars with siliceous sand (top) or calcareous sand (bottom) and SCM stored in 1.8% $MgSO_4$ solution at 5°C (Skaropoulou et al. 2009b).

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

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

In an extensive review of research into thaumasite, Irassar (2009) concluded that risk of TSA is minimized by limiting ingress of sulfate ions with low water-to-cement ratios (and the use of SCMs), the use of sulfate-resistant (low C_3A content) cements, sufficient cementitious materials contents to permit full compaction of the mixture, and sufficient curing. In other words, following established sulfate-resistant concrete practice such as that described in ACI 201.2R (2016) will minimize risk of TSA. Irassar (2009) also noted that when TSA occurs, the thaumasite likely forms on ettringite crystals in the paste. Thus, preventing ettringite formation from classical external sulfate attack helps prevent damaging thaumasite formation.

The long-term testing program by Thomas and Hooton (2016) concluded that ASTM C1012 conducted at normal temperatures (23˚C) is suitable for evaluating the resistance of PLC and PLC-SCM mixtures to both classical and thaumasite forms of sulfate attack. They found that the low-temperature version of the test conducted at 5˚C (CSA A3004-C8, Procedure B) did not provide a reliable prediction of the performance of concrete containing either portland cement or PLC combined with SCMs. Additionally, PC-SCM and PLC-SCM concretes in low-temperature sulfate exposure in both the laboratory and simulated field conditions exhibited similar performance. The concretes with SCMs also exhibited superior performance to sulfate-resistant portland cements (i.e. Type II or V) at the same w/cm and in the same exposure conditions. They recommended that ASTM permit Type IL and Type IT cements containing up to 15% limestone to be designated as having moderate (MS) or high sulfate (HS) resistant properties based on performance in the traditional 23˚C ASTM C1012 mortar bar test, without an additional requirement for low-temperature test performance. This change was ultimately adopted in ASTM C595 and AASHTO M 240. CSA has also removed the requirement for the 18-month expansion in the low-temperature mortar bar test to evaluate resistance of PLC and blended PLCs to TSA, as well as the low-temperature test method.

4.2.5 Alkali-Silica Reaction

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

Figure 4.17 (from Thomas et al. 2010b) shows the expansion of mortar bars and concrete prisms containing an alkali-silica reactive aggregate (siliceous limestone from the Spratt quarry in Ontario). Expansion results are reported at 14 days for the accelerated mortar bar test (AMBT) (ASTM C1260), 1 year for the concrete prism test (CPT) (ASTM C1293) and 3 months for the accelerated concrete prism test (ACPT) (this test is similar to the CPT except specimens are stored at 60°C (140°F)). The data show that there is no consistent difference between expansions produced with portland cement compared with PLC.

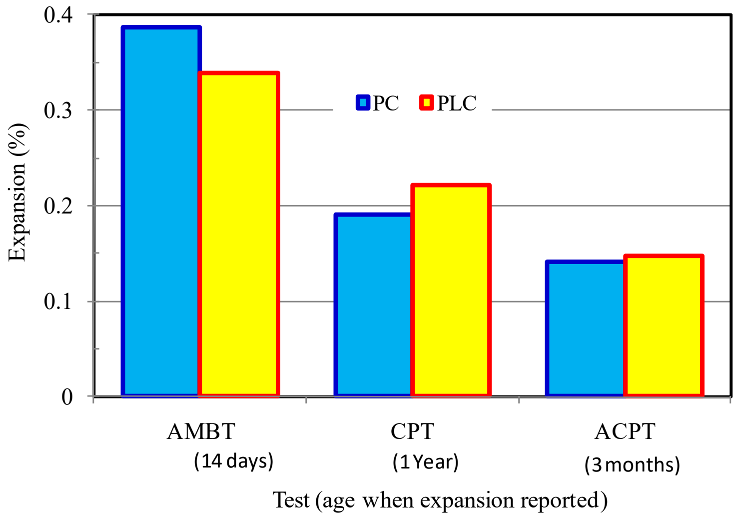


Figure 4.17 Expansion of mortar and concrete containing an alkali-silica reactive aggregate (Thomas et al. 2010b).

To better understand if current (California Department of Transportation) ASR mitigation measures would be appropriate with PLCs, Bharadwaj et al. (2021) studied the influence of PLCs with SCMs on ASR potential. First, it was found that in general replacing a portion of the clinker with limestone reduces the alkali loading. Second, the research indicates that PLCs perform similar to, or better than, their respective portland cements in reducing expansion associated with ASR, especially when SCMs were used. Several test methods were used to verify expansion: ASTM C441, a test to assess relative effectiveness of SCMs to reduce ASR expansion; ASTM C1260, a rapid test on mortar bars to determine aggregate reactivity; ASTM C1567, a test designed to evaluate effectiveness of SCMs using the ASTM C1260 testing procedure; AASHTO T 380, a miniature concrete prism test; and ASTM C1293, a concrete prism test run for a year. Bharadwaj et al. (2021) found similar trends to those measured by Thomas (2011) on ASR mitigation in portland cement-based mixtures. The SCM dosage required to mitigate ASR increased with the CaO and equivalent alkali contents of the SCM and with an increase in the reactivity of the aggregate. The SCM dosage required typically decreases with an increase in the SiO_2 content and the Al_2O_3 content of the SCM.

4.2.6 Abrasion Resistance

Dhir et al. (2007) conducted abrasion tests on two series of concrete mixtures (w/cm = 0.52 and 0.65) produced with cements containing between 0% and 45% limestone. The results, shown in Figure 4.18, indicate that for concrete compared at equal w/cm the depth of abrasion increases with increasing limestone content although the difference between concretes with 0% and 15% limestone is small. Concretes of the same 28-day strength have similar abrasion resistance irrespective of the limestone content of the cement.

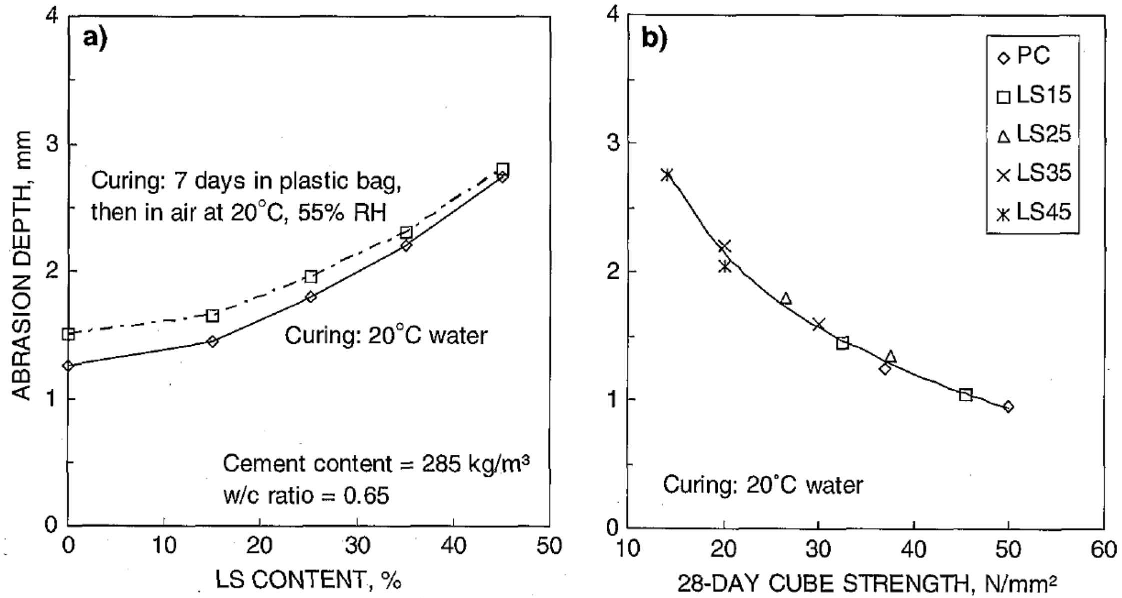


Figure 4.18 Effect of the limestone (LS) content of portland-limestone cement on the abrasion resistance of concrete (Dhir et al. 2007).

4.3 REFERENCES

AASHTO LRFD Bridge Design Specifications, 7th edition, American Association of State Highway and Transportation Officials, 2014.

AASHTO - R 101, Standard Practice for Developing Performance Engineered Concrete Pavement Mixtures, American Association of State Highway and Transportation Officials, January 1, 2022, 13 pages.

ACI 201.2R-16, *Guide to Durable Concrete*, American Concrete Institute, 2016, Farmington Hills, Michigan. 86 pages

ACI 318-19, *Building Code Requirements for Structural Concrete and Commentary*, 2019, American Concrete Institute, Farmington Hills, Michigan.

ACI 363R-10, *Report on High-Strength Concrete*, 2010, American Concrete Institute, Farmington Hills, Michigan. 65 pages.

Alunno-Rosetti, V. and Curcio, F., "A Contribution to the Knowledge of the Properties of Portland-Limestone Cement Concretes, with Respect to the Requirements of European and Italian Design Code," *Proceedings of the 10th International Congress on the Chemistry of Cement,* Gothenburg, Sweden, June 2-6, 1997, Ed. H. Justnes, pages 3v026 to 3v032.

Barcelo, et al., "Portland Limestone Cement Equivalent Strength Explained," *Concrete International*, November 2013, pages 41 to 47.

Barker, A. P. and Hobbs, D. W., "Performance of Portland Limestone Cements in Mortar Prisms Immersed in Sulfate Solutions at 5°C," *Cement and Concrete Composites*, Vol. 21, 1999.pages 129 to 137.

Barker, A. P. and Matthews, J. D., "Concrete Durability Specification by Water/Cement or Compressive Strength for European Cement Types," *Proceedings 3rd International Conference on the Durability of Concrete*, ACI SP-145, American Concrete Institute, Detroit, 1994, pages 1135 to 1160.

Barrett, T. J.; Sun, H.; and Weiss, W. J. *Performance of Portland Limestone Cements: Cements Designed to Be More Sustainable That Include up to 15% Limestone Addition*. Publication FHWA/IN/JTRP-2013/29. Joint Transportation Research Program, Indiana Department of

Transportation and Purdue University, West Lafayette, Indiana, 2013. doi:10.5703/1288284315335.

Bentz, D. P.; Irassar, E. F.; Bucher, B. E.; and Weiss, W. J., "Limestone Fillers Conserve Cement, Part 2: Durability Issues and the Effects of Limestone Fineness on Mixtures," *Concrete International*, December 2009, pages 35 to 39.

Bharadwaj, K.; Chopperla, K.; Choudhary A.; Glosser, D.; Ghantous, R.; Vasudevan, G.; Ideker, J.; Isgor, O.; Trejo, D.; and Weiss, J., *Impact of the Use of Portland-Limestone Cement on Concrete Performance as Plain or Reinforced Material*, Oregon State University, Corvallis, Oregon, 2021, 320 pages.

Bonavetti, V.; Donza, H.; Menéndez, G.; Cabrera, O.; and Irassar, E. F., "Limestone Filler Cement in Low w/c Concrete: A Rational Use of Energy," *Cement and Concrete Research*, Vol. 33, 2003, pages 865 to 871.

Bonavetti, V.; Dounz, H.; Rahhal, V.; and Irassar, E., "Influence of Initial Curing on the Properties of Concrete Containing Limestone Blended Cement," *Cement and Concrete Research*, Vol. 30, No. 5, 2000, pages 703 to 708.

Bucher, B., *Shrinkage and Cracking and its Relation to Cement Composition*, MSCE thesis, Purdue University, West Lafayette, Indiana, December 2009, 187 pages.

Bucher, B.; Radlinska, A.; and Weiss, J., *Preliminary Comments on Shrinkage and Shrinkage Cracking Behavior of Cement Systems that Contain Limestone*, SN3051, Portland Cement Association, Skokie, Illinois, USA, 2008, 9 pages. Reprinted from *Concrete Technology Forum,* National Ready Mixed Concrete Association, Silver Spring, Maryland, USA, 2008.

CAC, *A Technical Introduction to Portland-Limestone Cement for Municipal and Provincial Construction Specifications*, Cement Association of Canada, Ottawa, Ontario, May 2021, 26 pages.

Collepardi, M.; Collepardi, S.; Ogoumah Olagot, J. J.; and Simonelli, F., "The Influence of Slag and Fly Ash on the Carbonation of Concrete," *Proceedings 8th CANMET/ACI Internationals Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete*, SP-221, American Concrete Institute, Detroit, 2004, pages 483 to 493.

Crammond, N., "The Thaumasite Form of Sulfate Attack in the U.K.," *Cement and Concrete Composites,* Vol. 25, 2003, pages 809 to 818.

Dhir, R. K.; Limbachiya, M. C.; McCarthy, M. J.; and Chaipanich, A., "Evaluation of Portland Limestone Cements for Use in Concrete Construction," *Materials and Structures*, Vol. 40, 2007. Pages 459 to 473.

Elahi, M. A.; Shearer, C. R., "Development of Specifications for Portland-Limestone Cement, Study SD2016-04, Draft Final Report, November 2018, 141 pages.

EN 12390-10:2008, Testing hardened concrete – Part 10: Determination of the relative carbonation resistance of concrete, 2008.

Gagatek, D. and Hooton, R. D., "Assessing Performance of Sulfate-Resistant Portland Cements," *ACI Materials Journal*, Vol. 116, No. 6, 2019. Pages 227-233.

Garcia, J. E.; Tiburzi, N. B.; Folliard, K. J.; Drimalas, T.; and Thomas, M. D. A., *Laboratory and Outdoor Exposure Site Evaluations of Portland Limestone Cements*, Center for Transportation Research, Report No. FHWA/TX-18/0-6858-1, Austin, Texas, October 2019, 316 pp. http://library.ctr.utexas.edu/ctr-publications/0-6858-1.pdf

Ghazy, A.; Bassuoni, M. T.; and Islam, A. K. M. R., "Response of Concrete with Blended Binders and Nanosilica to Freezing–Thawing Cycles and Different Concentrations of Deicing Salts," *Journal of Materials in Civil Engineering*, American Society of Civil Engineers, Reston, Virginia, USA, 2018.

González, M.A. and Irassar, E.F., "Effect of Limestone Filler on the Sulfate Resistance of Low C_3A Portland Cement," *Cement and Concrete Research*, Vol. 28, No. 11, 1998, pages 1655 to 1667.

Hartshorn, S. A.; Sharp, J. H.; and Swamy, R. N., "The Thaumasite Form of Sulfate Attack in Portland-Limestone Cement Mortars Stored in Magnesium Sulfate Solution," *Cement and Concrete Composites*, Vol. 24, 2002, pages 351 to 359.

Hartshorn, S. A.; Sharp, J. H.; and Swamy, R. N., "Thaumasite Formation in Portland Limestone Cement Pastes," *Cement and Concrete Research*, Vol. 29, 1999, pages 1331 to 1340.

Hawkins, P.; Tennis, P. D.; and Detwiler, R. J., *The Use of Limestone in Portland Cement: A State-of-the-Art Review*, EB227, Portland Cement Association, Skokie, Illinois, USA, 2003, 44 pages.

Hobbs, D.W., "Possible Influence of Small Additions of Pfa, Gbfs and Limestone Flour Upon Expansion Caused by the Alkali-Silica Reaction," *Magazine of Concrete Research*, Vol. 35, No. 122, 1983, pages 55 to 58.

Hooton, D.; Ramezanianpour, A.; and Schutz, U., "Decreasing the Clinker Component in Cementing Materials: Performance of Portland-Limestone Cements in Concrete in Combination with SCMs," *2010 Concrete Sustainability Conference*, National Ready Mixed Concrete Association, April 13 to 15, 2010, Tempe, Arizona.

Hooton, R. D. and Thomas, M. D. A., *Sulfate Resistance of Mortar and Concrete Produced with Portland-Limestone Cement and Supplementary Cementing Materials*: *Recommendation for ASTM C595/AASHTO M 240,* SN3285a, Portland Cement Association, Skokie, Illinois, USA, 2016, 28 pages.

Hooton, R.D. and Thomas, M. D. A., Sulfate Resistance of Mortar and Concrete Produced with Portland-Limestone Cement and Supplementary Cementing Materials: Recommendation for CSA A3000, Portland Cement Association, SN3285b, 2016, 28 pages. Data updated for 2018.

Irassar, E. F., "Sulfate Attack on Cementitious Materials Containing Limestone Filler – A Review," *Cement and Concrete Research*, Vol. 39, No. 3, March 2009, pages 241 to 254.

Irassar, E. F.; Bonavetti, V. L.; Trezza, M. A.; and González, M. A.; "Thaumasite formation in Limestone Filler Cements Exposed to Sodium Sulphate Solution at 20°C," *Cement and Concrete Composites*, Vol. 27, 2005, pages 77 to 84.

Irassar, E. F.; Bonavetti, V. L.; Menhdez, G.; Donza, H.; and Cabrera, O., "Mechanical Properties and Durability of Concrete Made with Portland Limestone Cement," *Proceedings 3rd CANMET/ACI International Symposium on Sustainable Development of Concrete*, SP-202, American Concrete Institute, Detroit, 2001, pages 431 to 450.

Irassar, E.F.; Gonzalez, M.; and Rahhal, V., "Sulphate Resistance of Type V Cements with Limestone Filler and Natural Pozzolana," *Cement and Concrete Composites*, Vol. 22, 2000, pages 361 to 368.

Kakali, G.; Tsivilis, S.; Skaropoulou, A.; Sharp, J.H.; and Swamy, R. N., "Parameters Affecting Thaumasite Formation in Limestone Cement Mortar," *Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials*, Building Research Establishment, U.K., 2002. (Also, in *Cement and Concrete Composites*, Vol. 25, No. 8, 2003, pages 977 to 981.)

Kurtis, K.E.; Kahn, L. F.: Shalan, A.; Zaribaf, B.; and Nadelman, E., *Assessment of Limestone Blended Cements for Transportation Applications*, Georgia DOT Research Project 13-09: Final Report, Report No. FHWA-GA-17-13-09, September 2017, 265 pp.

Lipus, K. and Puntke, S., "Sulfate Resistance of Concretes with Different Compositions," *Beton*, Vol. 2, 2003, pages 169 to 180.

Matthews, J. D., "Performance of Limestone Filler Cement Concrete," in *Euro-Cements –Impact of ENV 197 on Concrete Construction*, (Ed. R. K. Dhir and M. R. Jones), E&FN Spon, London, 1994, pages 113 to 147.

Sait, M.A.W.S., "Eurocode 2: Deformation properties of structural concrete made with BS EN 197 -1 Portland limestone cement," MSc Individual Research Project, University of Birmingham, 2017. 28 pages.

Schmidt, M., "Cement with Interground Additives - Capabilities and Environmental Relief: Part 1," *Zement-Kalk-Gips*, Vol. 45, No. 2, 1992a, pages 64 to 69 (English part in Vol. 45, No. 4, page 87 to 92.).

Schmidt, M., “Cement with Interground Additives - Capabilities and Environmental Relief: Part 2,” *Zement-Kalk-Gips*, Vol. 45, No. 6, 1992b, pages 296 to 301.

Shalan, A.; Kahn, L.F.; Kurtis, K.; and Nadelman, E., *Assessment of High Early Strength Limestone Blended Cement for Next Generation Transportation Structures*, Georgia DOT Research Project 14-33: Final Report, Report No. FHWA-GA-17-1433, December 2016, 85 pp.

Siebel, E., and Sprung, S. “Influence of Limestone in Portland Limestone Cement on the Durability of Concrete,” *Beton*, Vol. 41, No. 3, 1991, pages 113 to 117. (In German. English translation by Susan U. Lauer available from Portland Cement Association Library, Skokie, Illinois, USA.)

Soroka, I., and Stern, N., “Effect of Calcareous Fillers on Sulfate Resistance of Portland Cement,” *Bulletin of the American Ceramic Society*, Vol. 55, No. 6, 1976, pages 594 to 595.

Soroka, I., and Setter, N. “Effect of Mineral Fillers on Sulfate Resistance 0f Portland Cement Mortars,” in *Durability of Building Materials and Components*, ASTM STP 691, 1980, pages 326 to 335.

Skaropoulou, A.; Tsivilis, S.; Kakali, G.; Sharp, J. H.; and Swamy, R. N., “Long Term Behavior of Portland Limestone Cement Mortars Exposed to Magnesium Sulfate Attack,” *Cement and Concrete Composites*, Vol. 31, 2009a, pages 628 to 636.

Skaropoulou, A.; Tsivilis, S.; Kakali, G.; Sharp, J. H.; and Swamy, R. N., “Thaumasite Form of Sulfate Attack in Limestone Cement Mortars: A Study on Long Term Efficiency of Mineral Admixtures,” *Construction and Building Materials*, Vol. 23, 2009b, pages 2338 to 2345.

Sprung, V. S., and E. Siebel, E., “Assessment of the Suitability of Limestone for Producing Portland Limestone Cement,” *ZKG International*, Vol. 1, 1991, pages 1 to 11. (In German. English text in No. 3, 1991, pages 43 to 48.)

Tezuka, Y.; Gomes, D.; Martins, J.; and Djanikian, J. G., “Durability Aspect of Cement with High Limestone Filler Content,” *Proceedings of the 9th International Congress on the Chemistry of Cements*, New Delhi, India, Vol. V., 1992, pages 53 to 59.

Thomas, M., “The effect of supplementary cementing materials on alkali-silica reaction: A review,” Cement and concrete research, Vol. 41, No. 12, 2011, pages 1224 to 1231.

Thomas, M. D. A.; Hooton, R. D.; Cail, K.; Smith, B. A.; De Wal, J.; and Kazanis, K. G., “Field Trials of Concretes Produced with Portland Limestone Cement,” *Concrete International*, January 2010a, pages 35 to 41.

Thomas, M. D. A.; Cail, K.; Blair, B.; Delagrave, A.; and Barcelo, L., “Equivalent Performance with Half the Clinker Content using PLC and SCM,” *2010 Concrete Sustainability Conference*, National Ready Mixed Concrete Association, April 13 to 15, 2010b, Tempe, Arizona.

Thomas, M. D. A.; Cail, K.; Blair, B.; Delagrave, A.; Masson, P., and Kazanis, K., “Use of Low-CO_2 Portland Limestone Cement for Pavement Construction in Canada,” *International Conference on Sustainable Concrete Pavements,* Sacramento, September 2010c.

Thomas, M. D. A.; Kazanis, K.; Cail, K.; Delagrave, A.; and Blair, B., “Lowering the Carbon Footprint of Concrete by Reducing the Clinker Content of Cement,” *Transportation Association of Canada Annual Conference*, Halifax, September 2010d.

Torres, S. M.; Sharp, J. H.; Swamy, R. N.; Lynsdale, C. J.; and Huntley, S. A., “Long-term durability of portland limestone cement exposed to magnesium sulfate attack.” Proceedings of the 1st International Conference on Thaumasite in Cementitious Materials, Building Research Establishment, U.K., 2002. (Also, in *Cement and Concrete Composites*, Vol. 25, No. 8, 2003, pages 947 to 954.)

Torres, S. M.; Lynsdale, C. J.; Swamy, R. N.; and Sharp, J. H., “Microstructure of 5-Year-Old Mortars Containing Limestone Filler Damaged by Thaumasite,” *Cement and Concrete Research*, Vol. 36, 2006, pages 384 to 394.

Tsivilis, S.; Sotiriadis, K.; and Skaropoulou, A., “Thaumasite Form of Sulfate Attack (TSA) in Limestone Cement Pastes,” *Journal of the European Ceramic Society*, Vol. 27, 2007, pages 1711 to 1714.

Tsivilis, S.; Tsantilas, J.; Kakali, G.; Chaniotakis, E.; and Sakellariou, A., “The permeability of Portland limestone cement concrete,” *Cement and Concrete Research*, Vol. 33, No. 9, 2003a, pages 1465 to 1471.

Tsivilis, S.; Kakali, G.; Skaropoulou, A.; Sharp, J. H.; and Swamy, R.N., “Use of mineral admixtures to prevent thaumasite formation in limestone cement mortar,” *Cement and Concrete Composites*, Vol. 25, No. 8, 2003b, page 969 to 976.

Tsivilis, S.; Batis, G.; Chaniotakis, E.; Grigoriadis, Gr.; and Theodossis, D., “Properties and Behavior of Limestone Cement Concrete and Mortar,” *Cement and Concrete Research*, Vol. 30, No. 10, 2000, pages 1679 to 1683.

Tsivilis, S.; Chaniotakis, E.; Badogiannis, E.; Pahoulas G.; and Ilias, A., “A Study on the Parameters Affecting the Properties of Portland Limestone Cements,” *Cement and Concrete Composites*, Vol. 21, No. 2, 1999a, pages 107 to 116.

Tsivilis, S.; Chaniotakis, E.; Batis, G.; Meletiou, C.; Kasselouri, V.; Kakali, G.; Sakellariou, A.; Pavlakis, G.; and Psimadas. C., “The Effect of Clinker and Limestone Quality on the Gas Permeability, Water Absorption and Pore Structure of Limestone Cement Concrete,” *Cement and Concrete Composites,* Vol. 21, No. 2, 1999b, pages 139 to 146.

Voglis, N.; Kakali, G.; Chaniotakis, E.; and Tsivilis, S., “Portland-Limestone Cements. Their Properties and Hydration Compared to those of Other Composite Cements,” *Cement and Concrete Composites*, Vol. 27, 2005, pages 191 to 196.

Vuk, T.; Tinta, V.; Gabrovšek, R.; and Kaučič, V., “The Effects of Limestone Addition, Clinker Type and Fineness on Properties of Portland Cement,” *Cement and Concrete Research*, Vol. 31, No. 1, 2001, pages 135 to 139.

CHAPTER 5 SPECIFICATION REQUIREMENTS FOR PORTLAND-LIMESTONE CEMENTS

This chapter reviews specification requirements for cements with more than 5% limestone in the U.S., Canada, and Europe. Provisions for limestone characteristics and finished cement are reviewed.

5.1 REQUIREMENTS FOR LIMESTONE

Limestones used in ASTM C595 and AASHTO M 240 blended cements are required to consist of a minimum of 70% $CaCO_3$ by mass and to be "naturally occurring." While somewhat arbitrary, this provision is intended to limit potential impurities in the limestone and was believed to have some correlation to concrete performance based on research used to substantiate a similar limit in European standards (Sprung and Seibel 1991). It is the manufacturer's responsibility to determine $CaCO_3$ content of the limestone and certify that it complies with this requirement. The $CaCO_3$ content of the limestone is determined by measuring the CaO content of the limestone, and multiplying by a factor of 1.785, the molecular weight ratio of $CaCO_3$/CaO.

Limestone requirements in European and Canadian standards for cements containing more than 5% limestone include limits on total organic carbon (TOC) in Europe, and limits on methylene blue index (MBI) in Canada and Europe, which are summarized in Table 5.1 below. Although the EN 197-1 and EN 197-5 standards contain the most extensive requirements for limestone, it is important to note that limestone can be used in significantly higher amounts than in the US or Canada (see Chapter 1).

The TOC and MBI requirements are intended to ensure concrete performance, particularly durability in freeze-thaw exposure environments (Sprung and Seibel 1991). Organic carbon has the potential to interfere with air entraining admixtures, which could in turn affect freeze-thaw durability if the dosage is not adjusted during development of a specific concrete mix design. Methylene blue is a chemical with a strong affinity for clays, and the MBI is an indicator of the clay content of a limestone. Certain clays can absorb substantial amounts of water, increasing the saturation of the concrete and potentially degrading freeze-thaw durability.

Table 5.1 Summary of Limestone Property Requirements in European and Canadian Standard Specifications (when used in amount greater than 5% by mass of the cement).

Property	EN 197-1	EN 197-5	CSA A3001
Maximum Limestone Content, %	35 (CEM II/B)	20 (CEM II/C-M)	15
$CaCO_3$ content, min %	75	40	75
$CaCO_3$ + $MgCO_3$, min %	--	75	--
TOC, max %	0.20 (LL); 0.50 (L)	0.20 (LL); 0.50 (L)	--
MBI, max g/100 g limestone	1.20	1.20	1.20

Similar requirements for TOC and MBI were originally included in ASTM C595 and AASHTO M 240 when Type IL cements were introduced in 2012, but they were removed in 2016 following a critical review of the original research and field performance of concrete containing up to 15% limestone, as well as additional research (Feng and Clark 2014) demonstrating a lack of correlation between TOC, MBI, and freeze-thaw performance. CSA A3001 also initially contained a limit on TOC of limestone in portland-limestone and blended portland-limestone cements (PLCs), but this was removed for the same reasons. See 2.2 (Influence of Composition) and 4.2.3 (Freeze-thaw and Deicer Salt Scaling) for further detail on these studies.

5.2 REQUIREMENTS FOR CEMENT

5.2.1 U.S. Standards

ASTM C595 and AASHTO M 240 permit up to 15% limestone in both Type IL portland-limestone cements (PLCs) and Type IT ternary blended cements. Type IL and Type IT cements have identical requirements for soundness, time of set, mortar air content, and mortar strength, except for Type IT($S \geq 70$) cements, which have lower strength requirements. There are no physical requirements for fineness or density, but these must be measured and reported on the mill certificate. These blended cement specifications also permit the use of special property designations for sulfate resistance (MS, HS), heat of hydration (MH, LH), high early strength (HE), and air entrainment (A) for both Type IL and Type IT cements, which carry additional physical requirements related to those properties. Table 1.1 in Section 1.2.2.1 compares Type IL cements with special property designations to ASTM C150 and AASHTO M 85 portland cement types with similar performance characteristics. Table 5.2 summarizes the physical requirements of ASTM C595 and AASHTO M 240 for Type IL and Type IT cements and special property designations.

Chemical requirements are summarized in Table 5.3. These include a loss-on-ignition (LOI) limit of 10.0% for Type IL cement and Type IT cement if limestone is part of the ternary blend. There is a default SO_3 limit of 3.0% for Type IL and most Type IT cements, or 4.0% for Type IT cements that contain at least 70% slag cement ($S \geq 70$) or more pozzolan than limestone ($P \geq L$). The default SO_3 limit may be exceeded if mortar expansion in water (ASTM C1038) is less than 0.020% at 14 days. Type IT($P \geq L$) cements have a limit of 6.0% MgO. Type IT cements that contain less limestone than slag cement and less than 70% total limestone and slag cement ($L < S < 70\%$) are limited to 2.0% sulfide (S^{2-}).

Sulfate resistance of ASTM C595 and AASHTO M 240 blended cements is determined by the ASTM C1012 expansion test. The test immerses mortar bars in 50 g/L Na_2SO_4 solution at 23°C. If specified by a purchaser, moderate or high sulfate resistance is indicated as a special property designation appended to the type of cement. For example, Type IL(10)(MS) would indicate a PLC with 10% limestone and moderate sulfate resistance. A blended cement qualifies for the moderate sulfate-resistance designation (MS) with a maximum expansion of 0.10% at 6 months. The high sulfate-resistance designation (HS) requires a maximum expansion of 0.05% at 6 months, or, if that value is exceeded, a maximum of 0.10% at 12 months.

Table 5.2 Summary of Physical Requirements for ASTM C595 and AASHTO M 240 Cements containing between 5% and 15% limestone

Property and ASTM Test Method(s)	Type (Special Property)	Limit	Notes
Fineness, Blaine (C204)	IL, IT	None	Report
Fineness, 45 µm sieve (C430 or C1891)	IL, IT	None	Report
Density (C188)	IL, IT	None	Report
Time of initial set, Vicat, minimum minutes (C191)	IL, IT	45	
Time of initial set, Vicat, maximum minutes (C191)	IL, IT	420	
Air Content of Mortar, volume %, maximum (C185)	IL, IT	12	Except with (A) special property
	(A)	22	
Air Content of Mortar, volume %, minimum (C185)	(A)	16	No minimum without (A) special property designation
Compressive Strength*, MPa [psi], minimum (C109/C109M), at:			
1 day	(HE)(A)	10.0 [1450]	
	(HE)	12.0 [1740]	
3 days	(A), (MH)	10.0 [1450]	
	IL, IT(S<70), (MS), (HS)	13.0 [1740]	
	(HE)(A)	19.0 [2760]	
	(HE)	24.0 [3480]	
7 days	IT(S≥70)	5.0 [720]	
	(LH)	11.0 [1600]	
	(A)	16.0 [2320]	
	(MH)	17.0 [2470	
	IL, IT(S<70), (MS), (HS)	20.0 [2900]	
28 days	IT(S≥70)	11.0 [1600]	
	(LH)	21.0 [3050]	
	(A), (MH)	22.0 [3190]	
	IL, IT(S<70), (MS), (HS)	25.0 [3190]	
Water requirement, maximum % weight of cement (C109/C109M)	(LH)	64	
Sulfate resistance, maximum % expansion at 6 months (C1012/C1012M)	(MS)	0.10	
	(HS)	0.05	0.10% at 1 year if exceeding 0.05% at 6 months.

*The lowest 7-day minimum strength applies when multiple special property designations are used, other than HE or HE(A). When HE or HE(A) is used, those strength requirements govern.

Table 5.3 Chemical requirements for ASTM C595 / AASHTO M 240 portland-limestone cements (IL) and ternary blended cements (IT) (L = limestone content, S = slag content, P = pozzolan content)

	Type			
Property	IL, IT(L ≥ S) IT(L ≥ P)	IT(L<S<70%)	IT(P ≥ L)	IT(S ≥ 70%)
Magnesium oxide (MgO), max %	--	--	6.0	--
Sulfate reported as SO_3, max %[#]	3.0	3.0	4.0	4.0
Sulfide reported as S^{2-}, max %	--	2.0	--	2.0
Loss on ignition, max %*	10.0	10.0*	10.0*	10.0*

* Lower limits apply when limestone is not part of the ternary blend.

[#] Default sulfate limit may be exceeded if expansion in water following ASTM C1038 does not exceed 0.020% at 14 days.

5.2.2 Canadian Standards

A distinction between U.S. and Canadian cement standards is that ASTM C595 and AASHTO M 240 define PLC as a blended cement, whereas CSA A3001 defines PLCs as a separate category of cement, which is neither a portland cement nor a blended cement. Both portland cements and PLCs can be used to make blended cements, which are categorized as either portland blended cements or portland-limestone blended cements. These designations are predominantly differences in nomenclature, with differences in requirements between the U.S. and Canadian specifications generally being minor.

As described in Section 1.2.2.2 (Table 1.2), PLCs in CSA A3001 have designations similar to Canadian portland cement types (or ASTM C1157 cement types), except an "L" is appended to the designation. Thus, Type GUL (general use), Type MSL (moderate sulphate-resistant), Type HSL (high sulphate-resistant), and Type HEL (high early strength) are PLC types. Blended cements based on portland cement and SCMs are designated with a suffix of "b;" for example Type GUb is a blended cement intended for general concrete construction. Blended cements based on PLCs (that include SCMs as well as between 5% and 15% limestone) are denoted with both "L" and "b" suffixes: for example, GULb.

Identical requirements for minimum compressive strengths, maximum range of initial setting times, and maximum fineness (% retained on 45-µm sieve) apply to both portland and PLCs (see Table 5.4) in CSA A3001.

Chemical requirements for cements with between 5% and 15% limestone are relatively similar between PLCs in CSA A3001 (Table 5.3) and ASTM C595. All types of PLCs have maximum loss-on-ignition (LOI) limits of 10.0% by mass. The higher LOI limit (compared to portland cements in CSA, and ASTM/AASHTO) is specifically to accommodate the higher loss due to the presence of limestone, which loses about half its mass at ignition temperatures (approximately 1000 °C).

Portland-limestone cements in CSA A3001 have 3.0% maximum SO_3 content limits by default or can exceed that limit if mortar expansion (CSA A3004-C5, similar to ASTM C1038) is less than 0.020% at 14 days. CSA A3001 PLCs also have a maximum MgO content of 5.0%. Portland-limestone cements in CSA A3001 are required to be interground.

The CSA requirements for sulfate-resistant portland-limestone and portland-limestone blended cements are aligned with the requirements for Type MSb and HSb blended cements. Type MSL and MSLb have a maximum expansion limit of 0.10% expansion at 6 months for mortar bars immersed in $NaSO_4$ solutions (50 g/L, as in ASTM C1012). Type HSL and HSLb cements have a maximum limit of 0.05% expansion at 6 months at 23°C, but they may exceed this limit if the expansion is less than 0.10% at 1 year.

Table 5.3 Summary of Compositional Requirements in CSA A3001 (% by mass)

Requirement	Types	Limit (maximum)	Notes
MgO	GU, MS, HE, HS GUL, MSL, HEL, HSL	5.0	
Sulfate, SO_3*	HS	2.5	
	GU, MS, GUb, MSb, HEb, HSb, GUL, MSL, HEL, HSL, GULb, MSLb, HELb, HSLb	3.0	3.5 for Type GU if C_3A content is >8.0%
	HE	3.5	4.5 for Type HE if C_3A content is >8.0%
Sulfide, S^{2-}	GUb, MSb, HEb, HSb,	2.0	Only applies to blended cements made with slag cement if SO_3 limit exceeded.
Loss on ignition (LOI)	GU, MS, HE, HS	3.0 / 3.5	Without / With Limestone
	GUb, MSb, HEb, HSb	3.0	For blended cements produced with slag.
	GUb, MSb, HEb, HSb,	3.5	For blended cements produced with silica fume
	GUb, MSb, HEb, HSb,	6.0	For blended cements produced with fly ash, and ternary and quaternary hydraulic blended cements.
	GUL, MSL, HEL, HSL	10.0	
	GUb, MSb, HEb, HSb GULb, MSLb, HELb, HSLb	10.0	For blended cements produced with natural pozzolans and ternary and quaternary blended cements. For blended portland-limestone cements produced with slag.
	GULb, MSLb, HELb, HSLb	10.5	For blended portland-limestone cements produced with silica fume
	GULb, MSLb, HELb, HSLb	13.0	For blended portland-limestone cements produced with fly ash, and ternary and quaternary blended cements containing portland-limestone cement.
	GULb, MSLb, HELb, HSLb	17.0	For blended portland-limestone cements produced with natural pozzolan
Insoluble residue (IR)	GU, MS, HE, HS	1.5	
Tricalcium aluminate, C_3A	MS	8	
	HS	5	

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

Table 5.4 Physical Requirements in CSA A3001, % by mass unless otherwise stated

	Types	Limit	Notes
Fineness, maximum 45 µm sieve	GU, MS, HS GUL, MSL, HSL	28	
	GUb, MSb, HEb, HSb, GULb, MSLb, HELb, HSLb	24	
Sulfate resistance, maximum % expansion at 14 days	MS	0.050	Requirement based on CSA A3004-C6 is similar to ASTM C452
	HS	0.035	
Sulfate resistance, Maximum % expansion at 6 months	MSL, MSb, MSLb	0.10	Requirement based on CSA A3004-C8 is similar to ASTM C1012.
	HSL, HSb, HSLb	0.05	If expansion is greater than 0.05% at 6 months, limit is 0.10% at 1 year.
Initial time of set, minutes	GU, MS, HE, HS, GUL, MSL, HEL, HSL GUb, HEb GULb, HELb	minimum 45	
	MSb, HSb MSLb, HSLb	minimum 60	
	HE, HEL, HEb, HELb	maximum 250	
	GU, MS, HS GUL, MSL, HSL	maximum 375	
	GUb, MSb, HSb GULb, MSLb, HSLb	maximum 480	
Heat of hydration, Maximum kJ/kg at 7 days	All types	None	For all types, report at the request of the purchaser.
Compressive strength, minimum MPa* at:			Strength at any age shall not be less than that of the preceding age.
1 day	HE, HEL, HEb, HELb	13.5	
3 days	GU, MS, HS, GUb, MSb, HSb, GUL, MSL, HSL GULb, MSLb, HSLb	14.5	
	HE, HEb, HEL, HELb	24.0	
7 days	GU, MS, HS, GUb, MSb, HSb GUL, MSL, HSL	20.0	
28 days	GU, MS, HS, GUb, MSb, HSb, GUL, MSL, HSL GULb, MSLb, HSLb	26.5	

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

5.2.3. European Standards

EN 197-1 outlines requirements for 27 basic cement types based on composition. These are also classified into three ranges of 28-day compressive strength, with minimum strengths of 32.5, 42.5 and 52.5 MPa (each of these has three further divisions of low, normal, or rapid strength gain). CEM II/A-L or CEM II/A-LL cements with between 6% and 20% limestone, and CEM II/B-L or CEM II/B-LL with 21% to 35% limestone, have the same physical requirements (compressive strength, initial setting time, and soundness) within each class as other cement types, as noted in Table 5.5. Sulfate contents for CEM II cements are 3.5% or 4.0% maximum, depending on the strength class, and all cements have an additional requirement of 0.10% maximum chloride content. Although CEM I and CEM III cements have loss-on-ignition requirements and insoluble residue requirements, CEM II cements do not.

Table 5.5 Basic Physical Requirements of European Cements*

Strength Class	Compressive Strength, MPa (per EN 196-1)				Initial setting time, min	Soundness (expansion) mm
	Early strength		Later Strength			
	2 days	7 days	28 days			
32.5N	–	≥ 16.0	≥ 32.5	≤ 52.5	≥ 75	≤ 10
32.5R	≥ 10.0	–				
42.5N	≥ 10.0	–	≥ 42.5	≤ 62.5	≥ 60	
42.5R	≥ 20.0	–				
52.5N	≥ 20.0	–	≥ 52.5	–	≥ 45	
52.5R	≥ 30.0	–				

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

The EN 197-5 standard, introduced in 2021, lists five blended cement types, two of which may contain between 6% and 20% limestone as an ingredient. CEM II/C-M portland-composite cements contain 36% to 50% of up to two ingredients other than clinker and gypsum; these may be SCMs or limestone, with limestone subject to a limit of 6% to 20% by mass. CEM VI composite cements are ternary blends with clinker and blast-furnace slag as required ingredients; the third ingredient may be between 6% and 20% limestone, with the cement designated CEM VI(S-L) or CEM VI(S-LL) depending on the total organic carbon content of the limestone. Physical requirements for initial setting time, soundness, and strength of these cements reference EN 197-1. All EN 197-5 cements also use the low-early strength requirements defined in EN 197-1, and low heat of hydration as defined in EN 197-1 may also be specified with the notation "LH". Chemical requirements for EN 197-5 cements include a 4.0% maximum sulfate content and 0.10% maximum chloride content.

European cement standards handle sulfate resistance differently than North American standards and do not include performance test requirements. EN 197-1:2011 lists seven "sulfate resisting common cements." Three are CEM I portland cements, two are CEM III blast-furnace (slag) cements, and two are CEM IV pozzolanic cements; none are PLCs in the CEM II family. Sulfate resistance among these cements is designated by an -SR suffix and are met primarily through compositional requirements (SO_3 and C_3A content). Some CEN member countries consider additional cement types as sulfate resisting under their national standards, which are listed in Annex A of EN 197-1:2011. This listing includes CEM II PLCs in Italy (all four types) and Portugal (CEM II/A-L and CEM II/A-LL only), and CEM II portland-composite cements (CEM II/A-M and/or CEM II/B-M) in several countries. Annex A is informative in nature and does not capture changes that may have occurred in national standards since 2011.

5.3 REFERENCES

ASTM C1012, Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Sulfate Solution

ASTM C150/C150M, Standard Specification for Portland Cement

ASTM C595/C595M, Standard Specification for Blended Hydraulic Cements

AASHTO M 85, Standard Specification for Portland Cement

AASHTO M 240, Standard Specification for Blended Hydraulic Cements

CSA A3001, "Cementitious Materials for Use in Concrete," in *A3000 Cementitious Materials Compendium*, Canadian Standards Association, Mississauga, Ontario, Canada L4W 5N6.

CSA A3004-C5, Test method for determination of expansion of hydraulic cement mortar bars due to internal cement sulphate attack, in *A3000 Cementitious Materials Compendium*, Canadian Standards Association, Mississauga, Ontario, Canada L4W 5N6.

CSA A3004-C6, Test method for determination of expansion of portland cement mortar bars due to external sulphate, in *A3000 Cementitious Materials Compendium*, Canadian Standards Association, Mississauga, Ontario, Canada L4W 5N6.

CSA A3004-C8, Test methods for determination of expansion of blended hydraulic cement mortar bars due to external sulphate attack, in *A3000 Cementitious Materials Compendium*, Canadian Standards Association, Mississauga, Ontario, Canada L4W 5N6.

EN 197-1, *Cement - Part 1: Composition, specifications and conformity criteria for common cements,* European Committee for Standardization, Brussels, Belgium, B-1050.

EN 197-5, *Cement – Part 5: Portland-composite cement CEM II/C-M and Composite cement CEM VI*, European Committee for Standardization, Brussels, Belgium, B-1000.

Feng, X., and Clark, B., *Portland-Limestone Blended Cement: Effects of Limestone Characteristics*, SN3241, Portland Cement Association, Skokie, Illinois, USA, 2014, 62 pages.

Sprung, S. and Siebel, E., "Assessment of the Suitability of Limestone for Producing Portland Limestone Cement (PKZ)," *Zement-Kalk-Gips*, No. 1, 1991, pages 1 to 11. (In German. English text translation: No. 3, 1991, pages 43 to 48.)

CHAPTER 6 FIELD STUDIES AND PROJECT EXAMPLES

This chapter provides data from two series of field studies in which cements with up to 15% limestone have been used. The first series is comprised of three sets of pavements placed in different Canadian provinces and covers a wide range of both fresh and hardened concrete properties. The second series summarizes several test pavements in three U.S. states that used cements with 10% limestone as an ingredient. Selected examples of projects in the U.S. using portland-limestone cement in various types of construction are also presented in 6.3.

6.1 CANADIAN STUDIES

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

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

Location of trial	Cement type	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O_{eq.}$	SO_3	LOI	Blaine (m^2/kg)
Quebec[1]	PC[2]	20.53	4.63	2.77	62.7	2.48	0.21	3.23	2.26	373
	PLC[3]	19.23	4.4	2.64	61.45	2.41	0.20	3.4	5.25	453
	Fly ash	36.53	19.39	5.27	18.62	4.92	5.69	2.06	0.30	
	Slag	35.75	9.72	0.50	35.66	13.05	0.33	2.93	-	
Alberta	PC[2]	20.17	4.31	2.65	61.48	4.48	0.62	2.79	2.86	399
	PLC[3]	18.76	4.04	2.47	61.05	4.29	0.55	2.58	5.77	510
	Fly ash	56.4	24.1	3.5	10.0	1.1	3.14	0.2	0.26	
Nova Scotia	PC-slag[4]	22.9	5.9	1.9	59.3	3.2	0.89	4.10	0.6	453
	PLC-slag[5]	22.4	5.7	1.8	57.1	3.4	0.85	3.96	6.15	532
	Fly ash	48.02	20.65	7.92	6.68		1.48*	3.08	1.43	

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

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

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

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

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

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

*Available alkali reported (ASTM C311) not total alkali

Table 6.2 Details of Concrete Mixtures used in Field Trials

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

*F=Type F fly ash, CI=Type CI fly ash, CI/S=Type CI fly ash blended with slag cement.

** Note: 1 kg/m^3 = 1.686 lb/yd^3)

6.1.1 Paving at Ready-Mixed Concrete Plant, Quebec

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

The test data for concrete specimens cast during the trial are presented in Table 6.3. As expected, the inclusion of SCM significantly influenced concrete properties and generally an increase in the SCM content reduced the early-age strength but increased the resistance to chloride ingress. The SCM content did not impact the freeze-thaw durability as measured by ASTM C666, but increased mass losses were observed for concrete with 40% or 50% SCM when tested in deicer-salt scaling tests. However, the scaling mass losses were significantly below the maximum limits for acceptance specified by provincial agencies in Canada (e.g. 800 g/m^2 to 1000 g/m^2).

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

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

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

	No SCM		25% SCM		40% SCM		50% SCM	
	PC	PLC	PC	PLC	PC	PLC	PC	PLC
W/CM	0.45	0.44	0.44	0.45	0.44	0.44	0.44	0.44
Plastic air content, %	6.8	6.0	6.2	6.6	6.8	6.0	6.8	6.5
Slump, mm	100	80	75	100	95	80	95	95
Slump, in.	3.9	3.1	3.0	3.9	3.7	3.1	3.7	3.7
Hardened air content								
Air content, %	5.3	5.6	4.9	5.4	5.6	5.3	5.6	6.6
Spacing factor, μm	173	187	148	149	164	165	150	147
Spacing factor, in.	0.0068	0.0074	0.0058	0.0059	0.0065	0.0065	0.0059	0.0058
Strength, MPa								
1 day	24.2	25.2	21.7	20.7	18.9	19.2	15.3	15.6
7 days	30.2	30.5	29.8	29.6	30.3	31.1	29.4	28.8
28 days	37.7	38.2	41.3	39.8	43.5	43.5	43.0	42.5
56 days	41.3	40.9	45.4	44.7	48.6	48.3	48.7	46.5
Cores at 35 days	39.7	35.3	35.7	35.5	42.3	43.2	37.6	39.4
Strength, psi								
1 day	3510	3650	3150	3000	2740	2780	2220	2260
7 days	4380	4420	4320	4290	4390	4510	4260	4180
28 days	5470	5540	5990	5770	6310	6310	6240	6160
56 days	5990	5930	6580	6480	7050	7000	7060	6740
Cores at 35 days	5760	5120	5180	5150	6130	6260	5450	5710
[1]Durability factor, %	101	100	101	104	101	103	102	100
[2]Scaling mass C672, g/m^2	40	10	30	50	80	230	400	320
[2]Scaling mass C672, oz/yd^2	1.17	0.29	0.88	1.46	2.34	6.73	11.71	9.36
[3]Scaling mass BNQ, g/m^2	39	114	273	127	106	142	380	497
[3]Scaling mass BNQ, oz/yd^2	1.14	3.34	7.99	3.72	3.10	4.16	11.12	14.54
[4]RCPT, Coulombs								
28 days	3446	3734	2004	1765	1145	1056	1052	932
56 days	2781	2964	1233	1317	733	666	548	474
Cores at 35 days	2395	2345	1410	1308	570	617	491	520
[5]Diff. coeff., D_a, × 10^{-12} m^2/s	15.0	11.9	3.77	2.91	1.51	1.22	1.25	1.81

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

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

[3] Mass loss after 56 freeze-thaw cycles ponded with salt solution – BNQ "Salt Scaling Test."

[4] Charged passed after 6 hours – ASTM C1202 "Rapid Chloride Permeability Test."

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

6.1.2 Paving at Cement Plant, Alberta

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

Figure 6.2 Paving at a cement plant in Alberta.

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

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

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

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

Results of tests performed on test specimens produced on site are presented in Table 6.4. Generally, increasing levels of fly ash were found to decrease the early-age strength but increase the later-age strength, increase the set time, and increase the resistance to chloride ion penetration (as evidenced by a decrease in the charge passed in ASTM C1202). For concrete with a given level of fly ash, the use of PLC decreased the set time by 5 to 10% for mixes with fly ash and increased the early-age strength compared with portland cement with and without fly ash; otherwise, the PLC concrete gave comparable performance as the portland cement concrete.

6.1.3 Paving at Cement Plant, Nova Scotia

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

Figure 6.3 Paving at a cement plant in Nova Scotia.

Table 6.5 presents data from tests conducted on specimens cast on site. For concrete mixes with 15% and 20% fly ash, there was no consistent significant difference between the strength of mixes cast with the blended PC-slag versus PLC-slag, except that PC-slag mixes had slightly higher 90-day strengths. For the mixes without fly ash, the strengths were similar at 3 days, but the mix with PLC-slag showed lower strengths (by about 10%) at the later ages. It should be noted that the mix with PLC-slag had a slightly higher w/cm (by 0.02) and significantly higher air content (by 0.8%) compared to the mix with PC-slag and this could partially explain the lower strengths (note a 1% increase in air can reduce the strength by approximately 5.5%).

RCPT tests conducted on concrete samples at an age of 90 days show that the partial replacement of either blended cement with fly ash has a profound effect on the charge passed. Mixes without fly ash are classed as concrete with high chloride penetrability by the criteria in ASTM C1202, mixes with 15% fly ash are classed as low-to-intermediate penetrability, and mixes with 20% fly ash are classed as low penetrability. Comparing mixes with the same fly ash content, those produced with blended PLC-slag showed lower chloride ion penetrability compared with mixes with PC-slag; the differences are considered to be significant. Calculated chloride diffusion coefficients indicate that partially replacing 20% of the cement with fly ash increases the resistance of the concrete to chloride ion penetration. However, there is no consistent difference between the chloride diffusion coefficient of concrete produced with either blended PC-slag or blended PLC-slag cement.

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

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

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

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

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

Results from deicer scaling tests indicate no consistent difference with fly ash content. At each level of fly ash, the scaled mass loss is slightly higher for the blended PLC-slag cement compared with the PC-slag cement. However, differences are small, and in all cases, the scaled mass loss can be considered very low and well below typical limits used in Canada (e.g. maximum allowable losses from 800 g/m^2 to 1000 g/m^2).

6.1.4 Follow up Studies in 2012

Hossack et al. (2014) present the results of follow-up studies of each of the three Canadian field trials described in 6.1.1 – 6.1.3, after three to four years in service. Pavements at each location were subject to heavy truck traffic along with winter sand and salt applications. Visual inspection during site visits revealed only minor surface damage attributed to snowplows and abrasion from heavy truck loading on curves at both the Quebec and Nova Scotia sites. The most severe damage was observed on a portland cement section in Quebec without SCMs; the use of PLCs or SCMs did not correlate with any increase in damage relative to PC sections. Core samples were also extracted for laboratory testing of compressive strength, carbonation depth, chloride permeability and diffusion characteristics.

Compressive strengths of cores from each site were similar for portland cement vs. PLC mixtures. Cores from both portland cement and PLC sections containing fly ash from the Alberta site had higher strengths than those using straight cement mixtures.

Carbonation depth was most strongly influenced by the location of the field trial. The Nova Scotia site has the highest annual precipitation and all concrete mixtures exhibited minimal carbonation. The Alberta site has the lowest annual precipitation and cores from this site had the greatest carbonation depths, although none exceeded 6 mm. The use of PLC did not cause increased carbonation relative to mixtures using portland cement, nor was the use of high doses of SCMs associated with increased carbonation.

Rapid chloride permeability tests (ASTM C1202) on concrete without SCMs indicated an average increase in charge passed of 38% for PLC mixtures compared to portland cement mixtures. However, with SCMs, both portland cement and PLC mixtures achieved similarly low values (generally <500 Coulombs). Similar trends were observed in bulk diffusion testing (ASTM C1556) in both the chloride penetration profiles and the calculated apparent chloride diffusion coefficients. Concretes containing PLC exhibited excellent chloride resistance in all mixtures containing SCMs.

6.2 U.S. STUDIES

In 2008, the Colorado DOT became the first state DOT in the U.S. to permit PLC, allowing up to 10% limestone in ASTM C1157 cement and allowing those cements to be used in concrete with fly ash (Innis 2018). Van Dam and Smartz (2010) reported results of three pilot paving projects in Colorado using ASTM C1157 cements with 10% limestone. Included were a section of an interstate highway, a rural highway, and a local road. After noting the environmental advantages of using limestone, the report concludes that in each case, "…slip form paving concrete made with ASTM C1157 cement are readily constructible and can easily achieve specified strength requirements." It was further noted that the concretes also contained 20% fly ash (added at the batch plant), which further improved the carbon footprint of the concrete. Van Dam et al. (2010) also report on pilot projects in Utah and refers to laboratory durability testing on ASTM C1157 Type GU and ASTM C150 Type I/II cements. The laboratory testing included ASTM C1012 (sulfate resistance), ASTM C1567 (ASR mitigation—using Class F fly ash), ASTM C666 (freeze-thaw testing), ASTM C672 (deicer scaling resistance), ASTM C157 (shrinkage), and ASTM C1202 (rapid chloride permeability), and the Type GU cement demonstrated acceptable performance in these tests. Tables 6.6 and 6.7 summarize some of the concrete parameters of these pilot projects. In 2014 Colorado accepted PLC with up to 15% limestone by 2018 was reported to have constructed more than 800 lane-miles of pavement containing PLC, considerably more than any other state to that point. Colorado DOT engineers have stated that their use has not affected the quality and performance of these pavements (Innis 2018).

Table 6.6 Concrete in Colorado and Utah Pilot Programs

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

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

Table 6.7 Laboratory Strength Results on Portland Cements and Portland-Limestone Cements from Two Plants

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

Source: Adapted from Van Dam et al. 2010.

Innis (2018) reported on additional projects using PLC in Utah and Oklahoma. From 2014 to 2015, a section of Interstate 80 in Utah was reconstructed using portland cement with 25% fly ash in the eastbound lanes and PLC with 25% fly ash in the westbound lanes. Both mixtures performed similarly during construction. The Utah DOT's pavement management system ratings also show that the sections constructed with PLC in this project and the earlier pilot project described by Van Dam et al. (2010) are performing similarly to, or slightly better than, the sections constructed with portland cement, as of 2018. PLC with 10% limestone was used in the reconstruction of a section of Interstate 40 in Oklahoma City that was completed in 2012. Although this project did not include a comparative study of PLC against portland cement, the contractor stated that the PLC provided "identical" performance to a typical Type I/II cement and both the contractor and ODOT reported positive feedback regarding the finishing characteristics of the concrete during construction.

6.3 ADDITIONAL EXAMPLES OF PROJECTS MADE WITH PLC

PCA has also begun to maintain a list of producer-submitted case studies on its website dedicated to PLC-related resources (https://www.greenercement.com/casestudies). While less detailed than the case studies documented in this chapter and generally not intended as comparative studies against portland cements, these do cover a wider variety of applications and structures, including marine concrete, high-rise residential, and bridges. They help to further illustrate that PLC is an all-purpose cement like the portland cement upon which it is based. Figure 6.6 shows examples of the types of projects described in these case studies.

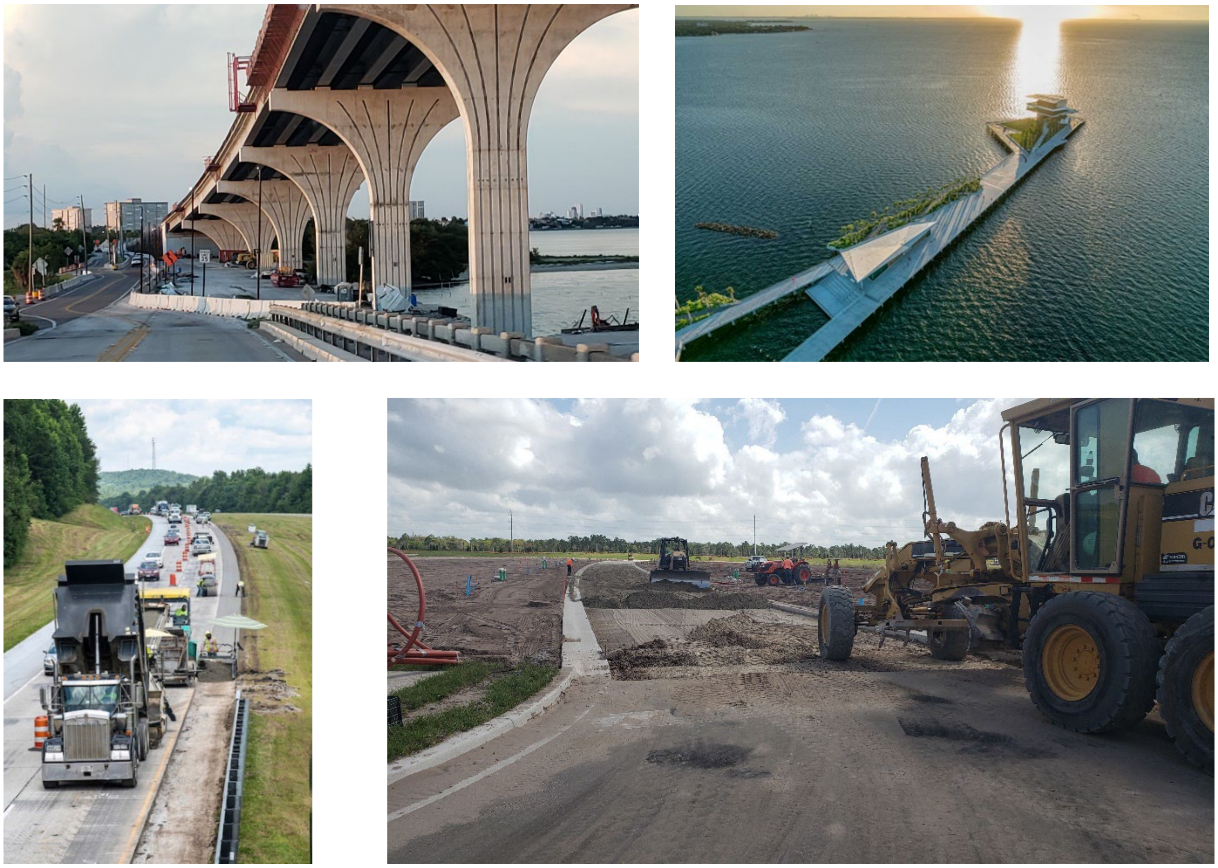


Figure 6.6 Examples of projects using PLC. Clockwise from top left: high-rise residential building, vertically slip-formed cement storage silo, marine pier, geotechnical improvements for soil stabilization, roller-compacted concrete highway shoulders, and cast-in-place bridge components.

6.4 SUMMARY

The data from the three Canadian field trials show that concrete can be produced using PLC containing 12% interground limestone to give comparable performance to concrete using portland cement provided that the PLC is ground to a higher fineness. The performance of concrete with PLC-SCM blends is comparable to that of concrete with a corresponding blend of PC-SCM. In some of the concrete mixtures used in these studies, the clinker content was less than 50% of the total cementitious material content. In-service performance of the pavements in the Canadian studies was verified with site visits and laboratory testing of cores three to four years after construction.

As of 2018, over 900 lane-miles of concrete pavement containing PLC have been constructed in the U.S. (Innis 2018). Data from U.S. projects also indicates good performance with cements with limestone as a significant ingredient, with generally slightly higher strengths compared to pavements made with portland cements. This includes ratings of in-service performance as measured by Utah's state pavement management system.

6.5 REFERENCES AND FURTHER READING

Barcelo, L.; Blair, B.; Delagrave, A.; Innis, F. A.; Knight, G.; Thomas, M. D. A.; and Weiss, J., "The Five W's and One H of Portland Limestone Cement (PLC)," *Concrete International*, Vol. 35, No. 11, November 2013, pages 37 to 40.

Barcelo, L.; Thomas, M. D. A.; Cail, K.; Delagrave, A.; Blair, B., "Portland Limestone Cement Equivalent Strength Explained," *Concrete International*, Vol. 35, No. 11, November 2013, pages 41 to 47.

Barrett, T.; Sun, H.; Villani, C.; Barcelo, L.; and Weiss, J., "Early-Age Shrinkage Behavior of Portland Limestone Cement," *Concrete International*, Vol. 36, No. 2, February 2014, pages 51 to 57.

Bentz, D.; Tanesi, J.; and Ardani, A., "Ternary Blends for Controlling Cost and Carbon Content," *Concrete International*, Vol. 35, No. 8, August 2013, pages 51 to 59.

Hossack, A.; Thomas, M. D. A.; Barcelo, L.; Blair, B.; and Delagrave, A., "Performance of Portland Limestone Cement Concrete Pavements," *Concrete International*, Vol. 36, No. 1, January 2014, pages 40 to 45.

Innis, F. A., "Portland-Limestone Cement after 10 Years in the Field," MAP Brief, October 2018, 7 pages, https://intrans.iastate.edu/app/uploads/2019/10/MAPbriefOctober2018.pdf.

PCA, https://www.greenercement.com/casestudies, July 2023.

Smartz, B. W.; Laker, T. S.; and Van Dam, T., "Performance and Sustainability," *Concrete International,* Vol. 35, No. 9, September 2013, pages 39 to 43.

Tennis, P. D., *U.S. Production of Portland-Limestone Cements—2012 through 2018*, R&D SN3313b, Portland Cement Association, Skokie, Illinois, USA, 2019, 10 pages. www.cement.org/pdf_files/SN3313b.pdf.

Thomas, M. D. A. and Hooton, R. D., *The Durability of Concrete Produced with Portland-Limestone Cement: Canadian Studies,* SN3142, Portland Cement Association, Skokie, Illinois, USA, 2010, 28 pages.

Thomas, M. D. A.; Delagrave, A.; Blair, B.; and Barcelo, L., "Equivalent Durability Performance of Portland Limestone Cement," *Concrete International*, Vol. 35, No. 12, December 2013, pages 39 to 45.

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

Van Dam, T. J. and Smartz, B. W., "Use of Performance Specified (ASTM C1157) Cements in Colorado Transportation Projects: Case Studies," *TRB 2010 Annual Meeting CD-ROM*, Transportation Research Board, Washington, D.C., USA, 2010, 9 pages.

Van Dam, T.; Smartz, B.; and Laker, T., "Performance-Enhancing: Research Shows Ways of Reducing Concrete's Footprint," *Roads and Bridges*, November 2010, pages 52 to 59.

CHAPTER 7 SUMMARY

This report reviewed published literature related to the use of limestone as an ingredient in portland-limestone cements (PLCs). Special emphasis was placed on limestone in amounts of up to 15%, although in some instances the effects of higher amounts were reviewed to provide additional information. Case studies of several concrete field trials in the U.S. and Canada were also summarized. The following general statements are supported by the literature and case studies:

- Limestone has been commonly used in European and other countries for several decades. Canadian specifications in the CSA A3000 compendium have permitted limestone as an ingredient in portland cements since 1983 and contained provisions for PLCs since 2008. Portland cements with limestone as an ingredient in amounts up to 5% have been in common use in the U.S. since 2004 and cements meeting ASTM C1157 with 10% limestone were introduced several years later and have been successfully used as well. Portland-limestone blended cements with up to 15% limestone were defined in ASTM C595 and AASHTO M 240 in 2012 as Type IL cements and these have seen increasing availability and acceptance in recent years. Experience with these cements has demonstrated that they can be used to produce strong, durable concretes and mortars.

- The environmental benefits of cements with limestone are appreciable. Although more grinding energy can be required compared to portland cements, the energy saved by reducing clinker in the finished cement clearly outweighs the extra grinding energy. Because less limestone is calcined to produce the clinker for a given amount of PLC, both calcination and fuel combustion CO_2 emissions are reduced compared to portland cement.

- Control of limestone particle size distribution and overall fineness of the cement, along with sulfate content optimization can yield comparable behavior or even slight benefits when limestone is used in amounts up to 15%.

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

    1) Particle packing effects: softer limestone grinds preferentially finer in finish milling, producing a broader particle size distribution, which can lead to denser concrete;
    2) Nucleation effects: products of traditional cement hydration reactions are accelerated slightly and more broadly distributed due to the additional limestone surfaces; and
    3) Chemical reactions: although only minor in extent, carboaluminate phases are produced, reducing porosity, benefitting strength and permeability.

  These effects will vary based on characteristics of the materials involved, those of other concrete mixture ingredients, and external factors like temperature. Water demand, for example, has been observed to increase or decrease in different concrete mixtures.

- Laboratory research indicates that sulfate resistance of PLCs is strongly dependent on the chemistry of the base cement. Laboratory and simulated field exposure research results also indicate that use of supplementary cementitious materials (SCMs) in combination with PLCs can permit production of highly sulfateresistant concrete suitable for even severe exposures. Performance testing of PLCs and PLC-SCM combinations based on ASTM C1012 testing is required to qualify the sulfate-resistance characteristics of the cementitious materials.

- Field studies in the U.S. and Canada, in addition to decades of experience in Europe and other countries, demonstrate that PLCs with up to 15% limestone can be effectively used in concretes and that SCMs can be used with PLC as a component of ternary blended cements or ternary concrete mixtures.