LITERATURE REVIEW
PORTLAND-LIMESTONE CEMENT

Prepared by:

MCC Research Committee
August 2013

Purpose

The purpose of this literature review is to assist the members of the Minnesota Concrete Council (MCC) better understand the state-of-the-art of the use of portland-limestone-cement (PLC). In order to appreciate the environmental benefits of the product, our review was to distill, capture, and summarize the performance characteristics when PLC is used in cast-in-place concrete.

Literature Review

We reviewed hundreds of articles and research papers and prioritized the following nine papers as the most informative and therefore, applicable.

1. Concrete International/January 2010
"Field Trials of Concretes Produced with Portland Limestone Cement," Michael D.A. Thomas, Doug Hooton, Kevin Call, Brenton A. Smith, John Dewal, and Kenneth Kazani1.

2. Roads and Bridges/November 2010 "Performance-Enhancing," research shows ways of reducing concrete's footprint, Thomas VanDam, Brooke Smartz, and Todd Laker.

3. "Use of Performance Cements in Colorado and Utah Laboratory Durability Testing and Case Studies."

4. "Portland-Limestone Cement: An Option to Improve Sustainability, John Melander.

5. "Environmental Benefits and Performance of Portland-Limestone Blended Cements," Manuscript of the TRB 2012 Annual Meeting.

6. 55th Annual Transportation Conference, February 23-24, 2013, Montgomery, AL, "Portland-Limestone Cement for Sustainable and Durable Construction," Tim Cost.

7. ASTM Committee C01 and Subcommittee C01.10, September 8, 2011.

8. PCA R & D SN3142, 2010, "Durability of Concrete Produced with Portland-Limestone Cement: Canadian Studies."

9. PCA R & D Serial No. SN3148, 2011, "State-of-the-Art Report on Use of Limestone in Cements at Levels of up to 15%," P.D. Tennis, M.D.A. Thomas, and W.I. Weiss.

What is portland-limestone cement (PLC)?

Let's start by focusing on one of the primary reactions that occurs when portland cement is made:

The primary ingredient, limestone ($CaCO_3$), is heated to around 2,700º F which liberates CO_2 in a process called calcination, and converts it to lime (CaO). The lime then combines with silica and alumina products to form the final clinker components. The production of cement involves the transfer of substantial amount of embodied heat.

Essentially, ($CaCO_3$) (calcium carbonate) - CO_2 = CaO (calcium Oxide). The calcination process, combined with the gas generation to provide the high heat, are the sources of CO_2 generation in the production of portland cement clinker. Clinker, a small dark nodule, is the final product which is produced from the kiln, which is then combined with other ingredients such as gypsum and limestone (<5%) at the finish mill to produce portland cement.

Limestone ($CaCO_3$) had been used as an ingredient at additions of less than 5% in portland cement for around10 years in the US including Minnesota. It should be noted that generic term limestone refers to material greater than 50% $CaCo_3$. The common substitute for Ca in limestone is magnesium (Mg).

More recently, ASTM C595 and AASHTO M 240 for blended cement, such as Type IS or IP, has been modified to allow portland-limestone cement, IL, as well as ternary blended cement, IT.

The amount of limestone addition allowed in this specification is 5-15% target addition, and the limestone must be a minimum of 70% $CaCO_3$.

Physical Advantages of PLC

- In the finishing mill, the limestone portion is generally more finely ground than clinker since it is softer. This results in a higher overall Blaine for the product, a typical broadening of the gradation, and a uniform distribution of the limestone particles, resulting in better particle packing. Note that even though the Blaine is typically higher, this does not mean that the water demand is increased.

- Early hydration products nucleate on the limestone particles.

- Additional hydration products beyond the calcium-silicates, carbo-aluminates, form due to reactions between limestone and aluminates, and can provide a synergistic effect when used with supplementary cementitious materials such as fly ash and slag cement.

- Due to the improvement in the overall particle packing, the finishability of concretes made with PLC may be improved.

Environmental Advantages of PLC

Concrete is the most commonly used construction material on the planet. Although portland cement is a relatively minor constituent by volume, its presence is responsible for the vast majority of CO_2 associated with concrete. In the U.S., the production of portland cement is responsible for 1.5 to 2.0 percent of the nation's CO_2 emissions; globally, cement production is responsible for 5 to 8% percent of world-wide CO_2 emissions.

Forty percent of the CO_2 generated in making cement is the burning of fossil fuels to acquire and process raw materials to make clinker.

Sixty percent of the CO_2 is from the calcination of the limestone or calcium carbonate ($CaCO_3$) itself, a necessary reaction in the production of portland cement.

- Reducing concrete's CO_2 footprint generally relates to reducing portland cement clinker content, which addresses both the CO_2 from the calcination process and the overall heating process.

- The greatest and most immediate potential of any available tool for reducing CO_2 footprint and embodied energy is the use of PLC.

- The use of 10% crushed limestone results in an around 10% carbon-dioxide reduction and less embodied energy as well.

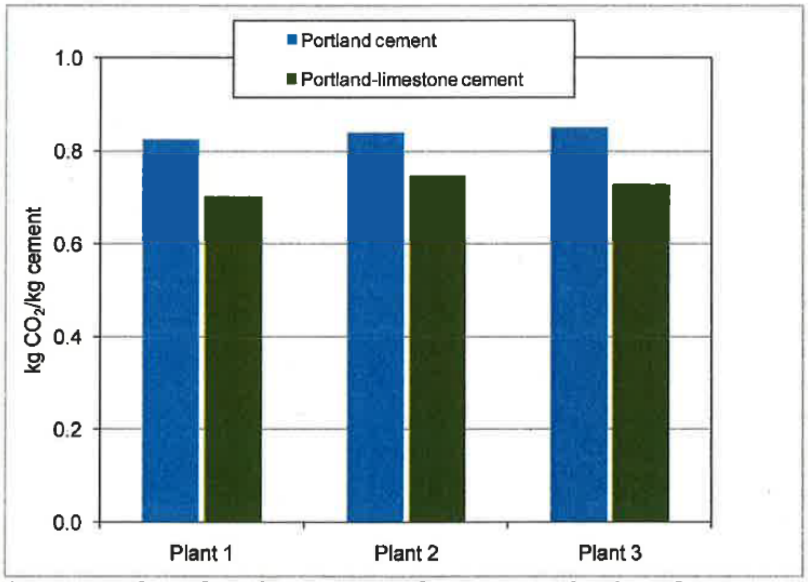


Figure 1.2 Specific CO_2 emissions from the production of portland cement or portland-limestone cement for 3 German cement plants (adapted from Schmidt 1992).

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

	10% limestone (per million tons of cement)	15% limestone (per million tons of cement)
Energy Reduction		
Fuel (million BTU)	443,000	664,000
Electricity (kWh)	6,970,000	10,440,000
Emissions Reduction		
SO_2 (lbs)	581,000	870,000
NO_X (lbs)	580,000	870,000
CO (lbs)	104,000	155,000
CO_2 (tons)	189,000	283,000
Total Hydrocarbon, THC (lbs)	14,300	21,400

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

History of PLC

- Experiences with PLC span several decades in other countries
  - Since the 1970's in Europe, PLC predominates specification categories for up to 35% LS
  - Up to 5% LS allowed in Canada since early 1980's
  - New CSA A23.1 classification created for up to 15% LS in 2008 and was adopted by Canadian building code in 2010

- US Experiences: Up to 5% LS allowed in portland cement for around 10 years.
  - ASTM C150 in 2004
  - AASHTO M85 in 2007
  - ASTM and AASHTO cement specifications became "harmonized" in 2009
  - Practical limitations mean common LS% content usually ~ 3.5% or less

- Only US specification option for LS > 5% up to now has been ASTM C1157 (performance spec); there is no AASHTO equivalent
  - Several US producers have made 10% or more LS under C1157 since around 2004 to 2005 including Minnesota market.

- Portland blended cement specifications now allow portland-limestone-cements between 5-15% addition and has gained acceptance for use by many state DOTs.
  - ASTM C595 and AASHTO M 240 Type IL or IT if used in a ternary blend.
  - MNDOT has used and currently allows PLC by request and is planning on full acceptance in 2014.
  - PLC was first used in MNDOT work in 2008 and is still performing well.

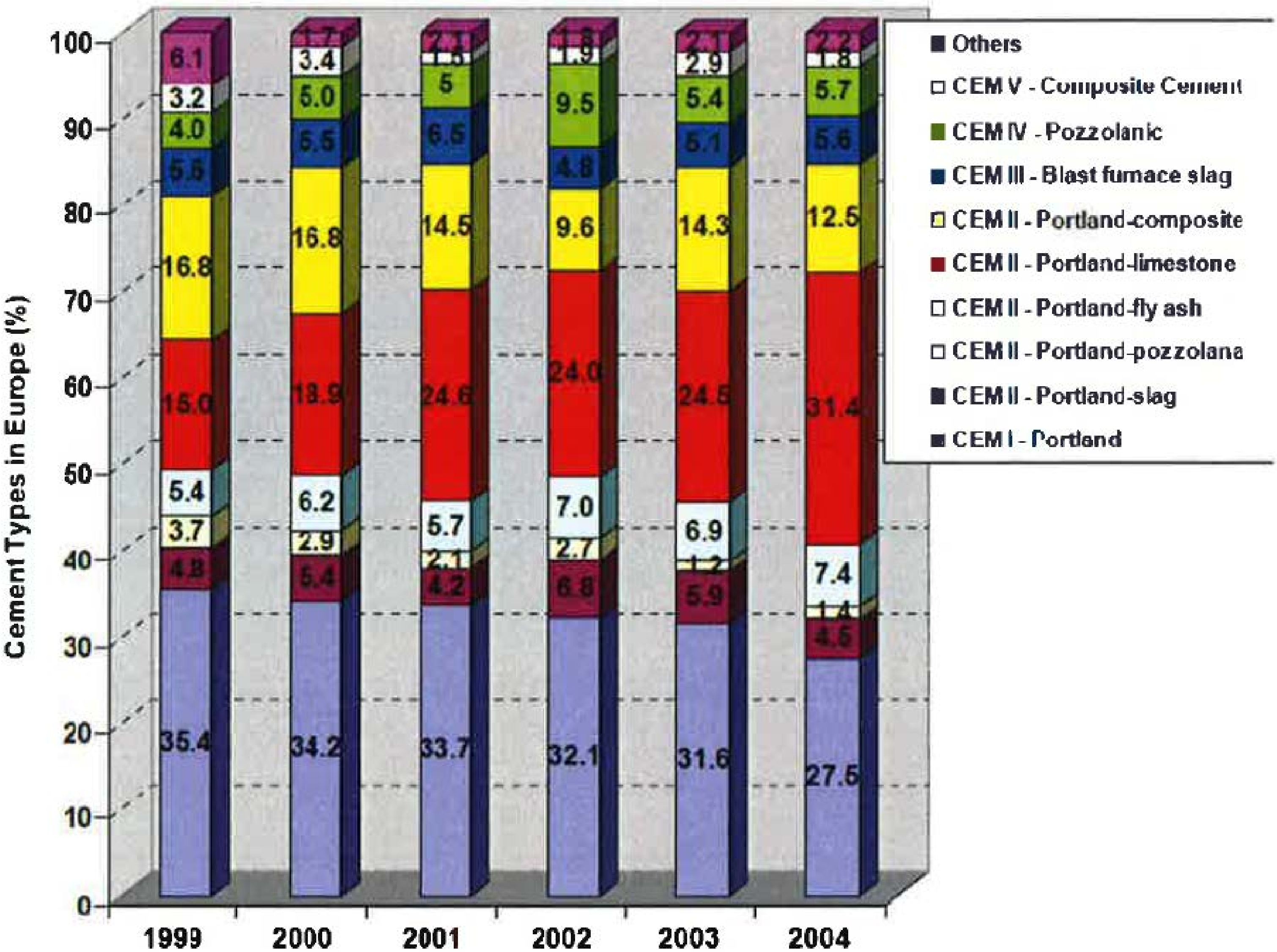


Figure 1.1 Percentage of various EN197-1 cement types used in Europe between 1999 and 2004 (Hooton et al., 2007, quoting Cembureau data.).

Table 1.6 Limestone contents permitted in Central and South America

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

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

Canadian Research Studies

After a literature review was completed in 2006, the Canadian standard, Cementitious Materials for Use in Concrete (CSA A3001), was revised in 2008 to include a new class of Portland-Limestone blended cements containing up to 15% limestone.

In anticipation of the adoption of Portland-Limestone blended cements, several Canadian cement producers initiated plant trial grinds and research was conducted by the cement companies and by several universities on properties of these cements as well as their performance and durability in concrete.

ASTM C150 allowed the addition of 5% limestone in 2004 in the United States, while Canada allowed the addition of 5% limestone in 1983.

Type GUL Cement (general use PLC)
Type GU (general use PC)

Study 1

Study 1 dealt with the resultant Blaine fineness values of various intergrinding limestones with portland clinker and gypsum to produce PL.

The concrete with highest Blaine showed faster setting, reduced bleeding, and higher strengths at all ages compared with other concrete mixtures.

Study 2

In 2007, trials were conducted to determine the effect of limestone quality and fineness on the performance of PLC. Two different percent of carbonate were used (80% and 92% $CaCO_3$).

The result of Study 2 was that the purity of the limestone has little impact on the performance of the PLC when the CaCo3 content is in the range of 80% and 92%.

The study also looked at freeze-thaw durability and found that use of PLC has no significant impact on the durability.

Study 3

PC with 3.5% versus PLC with 12% limestone   Gatineau, Quebec

Results, no significant difference between the performance of concrete with PLC compared with PC at the same level of SCM.

Study 4

2008   3.5% PC compared with PLC 10% and 15% interground limestone with and without 15% and 30% slag cement.

The results indicated that limestone content can be increased from that typically used in PC (about 3.5%) to 15% while maintaining equivalent performance.

One of the conclusions reached in this study was that additional research was needed in long-term performance of PLC in sulfate environments.

As a result of these Canadian studies, the following requirements were adopted by CSA.

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

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

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

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

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

The Story of Three ASTM Specifications

ASTM C150/AASHTO M 85 allows up to 5% limestone to be added in portland cement production, though the practical limit is 3-3.5% due to Loss of Ignition (LOI) restrictions.

ASTM C595/AASHTO M 240 for blended cements currently allows blending/intergrinding portland cement with fly ash and other pozzolans (IP), slag cement (IS), limestone (>70% $CaCO_3$) (IL), and ternary blends (IT).

ASTM C1157 is a performance base standard for hydraulic cement which allows a wide range of cement based on the performance requirements. The first version appeared in 1992 and there is no AASHTO equivalent.

GU (general use)
LH (low heat of hydration)
MH (moderate heat of hydration)
HE (high early strength)
MS (moderate sulfate-resistance)
HS (high sulfate-resistance)

The majority of states allow ASTM C1157 cements in their building and residential codes, but only a limited number of state Departments of Transportation (DOT) accept their use for transportation projects.

TABLE 1—Summary of Cement Classifications (Adopted with Permission from Ref 2)

Specification	General purpose	Moderate heat of hydration	High early strength	Low heat of hydration	Moderate sulfate resistance	High sulfate resistance	Resistance to alkali-silica reactivity
C 150	I	II	III	IV	II	V	Low alkali option
C 595	I IP I(PM) I(SM) S,P	IS(MH) IP(MH) I(PM)(MH) I(SM)(MH)		P(LH)	IS(MS) IP(MS) P(MS) I(PM)(MS) I(SM)(MS)		Low reactivity option
C 1157	GU	MH	HE	LH	MS	HS	Option R

TABLE 2—Summary of Physical Properties Specified for Hydraulic Cements

Physical Property	Portland Cement (C 150)	Blended Hydraulic Cement (C 595)	Hydraulic Cement (C 1157)
Fineness	s	r,m	r
Density	...	...	...
Activity index	...	m	...
Water requirement	...	s	...
Set			
Time of set	s	s	s
False set	o	...	o
Heat of hydration	o	s	s
Volume change			
Drying shrinkage	...	s	...
Expansion	c	...	s
Autoclave expansion	s	s	s
Strength			
Minimum	s	s	s
Maximum	o	...	s
Durability			
Air Content	s	s	r
Alkali reactivity	...	o,m	o
Sulfate expansion	o	s	s

KEY:

s = specified for one or more types.
m = specified for constituent materials.
c = specified under certain conditions.
o = specified optionally.
r = report required but no limit specified.

Summary of Research Data

The overall results of the reviewed research studies indicate that the testing showed no significant or consistent difference between concrete produced with PC or PLC for fresh concrete characteristics, compressive strength, rapid chloride permeability, freeze-thaw resistance or hardened air void system.

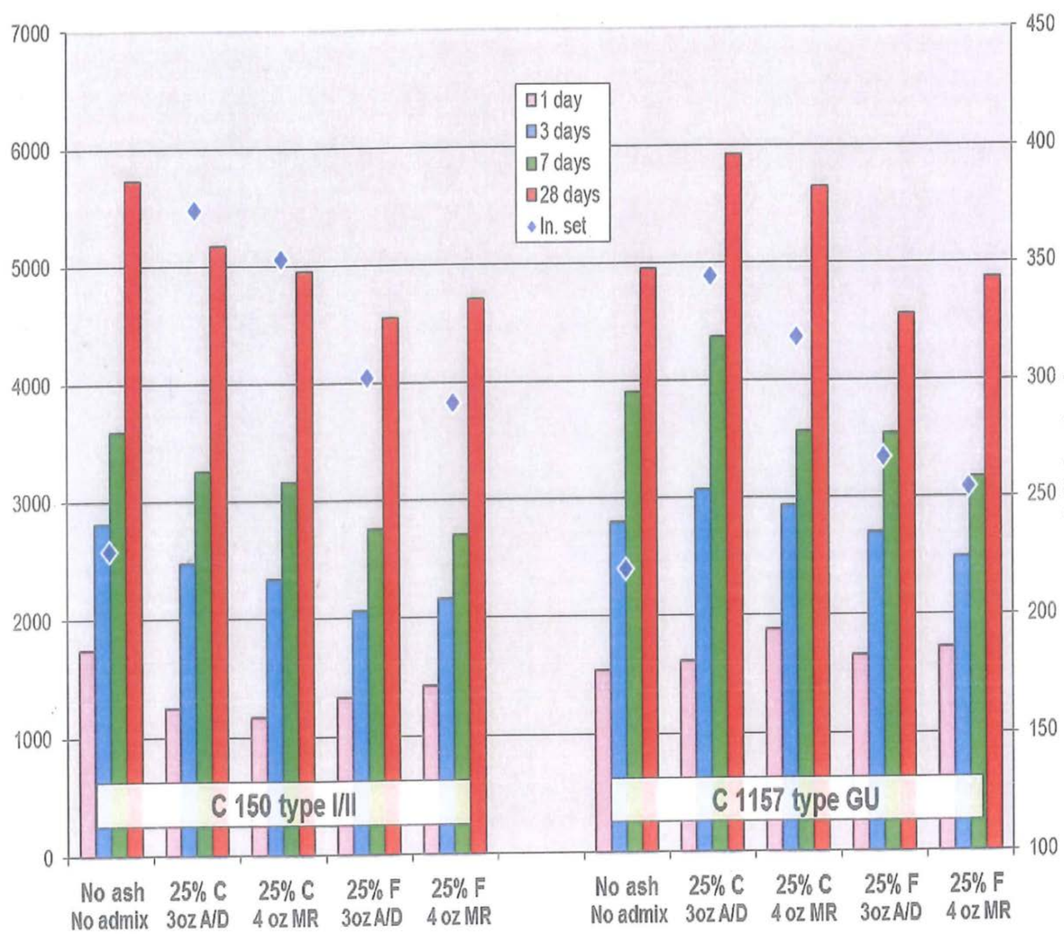
Laboratory research indicates that sulfate resistance and scaling resistance of Portland-Limestone cement showed mixed results from the same to somewhat reduced. Preliminary laboratory research indicates that use of supplementary cementitious materials (SCMs), in conjunction with PLC, can mitigate this effect and provide sulfate resistant concrete.

The following graphs are typical of the research results.

Compressive Strength and Set Time

- Type I/II and 10% LS Type GU cements (Theodore, 2008) compared, concrete mixes with gravel CA, 517 pcy total cementitious, 5 inch slump.

- 100% cement mixes without admix compared to 25% Class C ash and 25% Class F ash mixtures with mild dosages of 2 different WR's



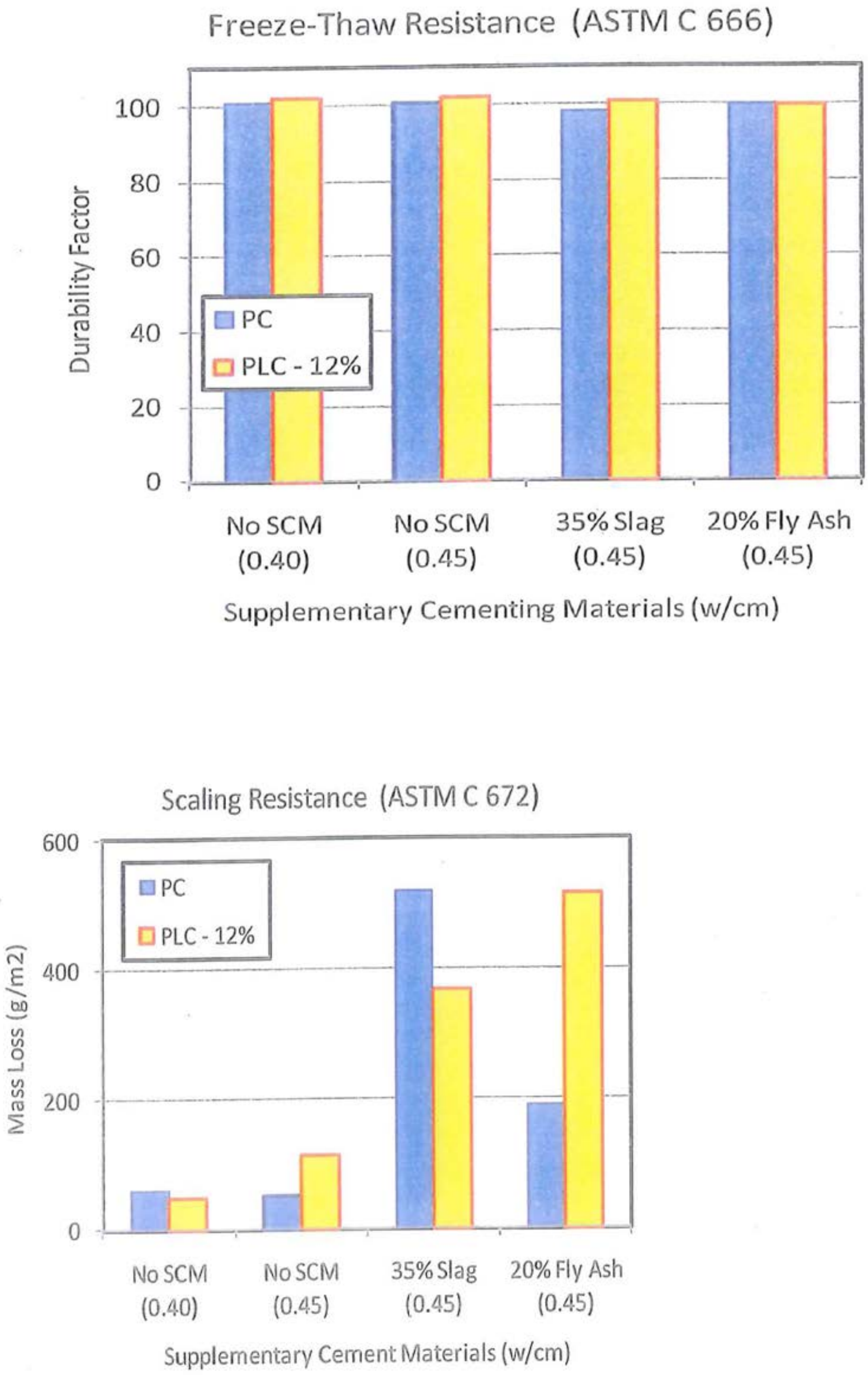


Figure 4.9 Results of freeze-thaw (top) and deicer-salt scaling tests for PC and PLC concretes with and without SCM (Thomas et al. 2010b).

Alkali-Silica Reaction

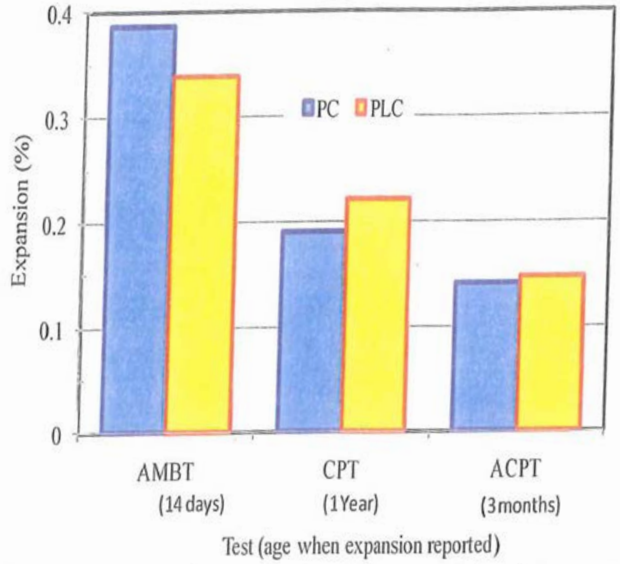


Figure 4.14 Expansion of mortar and concrete containing an alkali-silica reactive aggregate (Thomas et al. 2010b).

Scaling

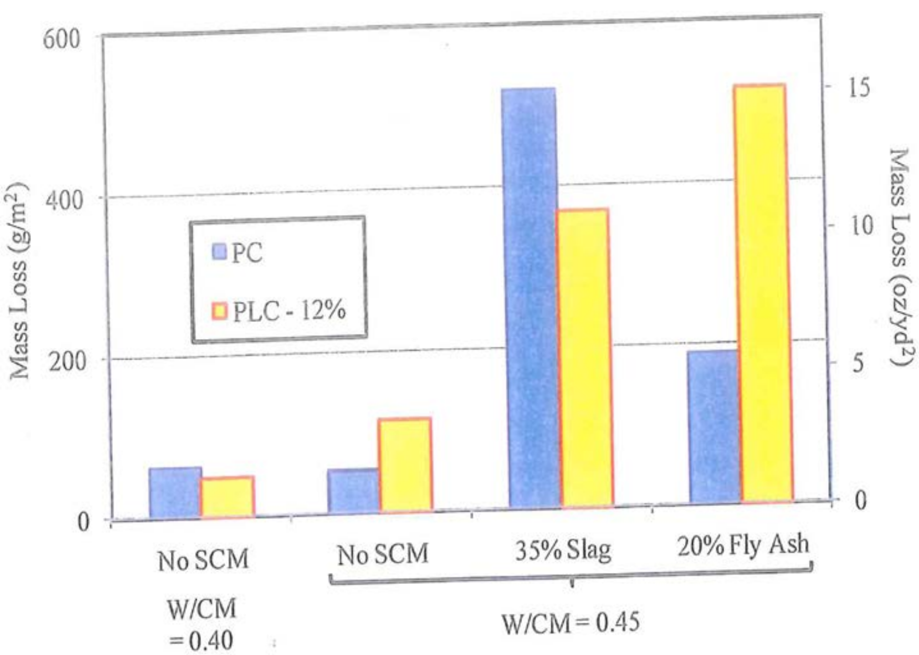


Figure 4. Scaling Mass Loss after 50 Cycles of Freeze-Thaw – ASTM C672.

Rapid Chloride Permeability

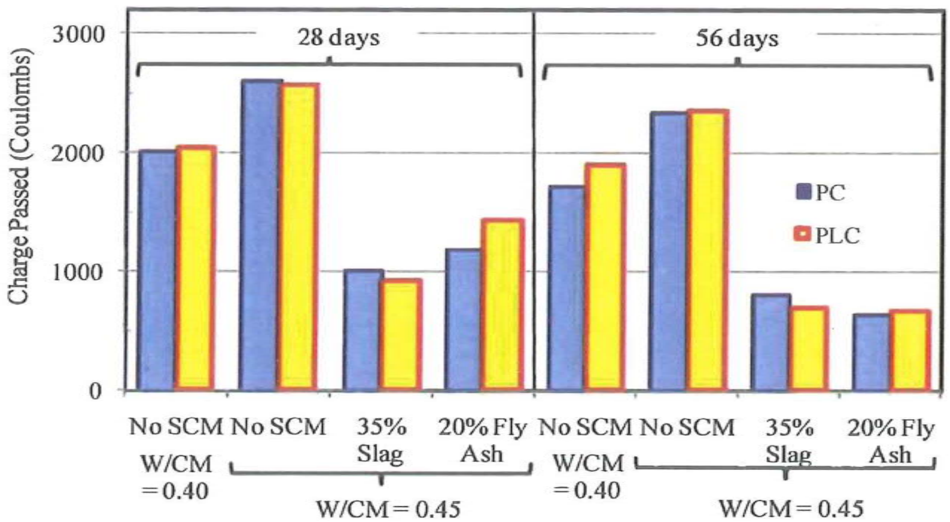


Figure 4.6 "Rapid Chloride Permeability Test" (ASTM C1202) data for PC and PLC concrete with and without SCM (Thomas et al. 2010b).

Why 15%?

Of all the data we consumed during this review, the following was the most revealing.

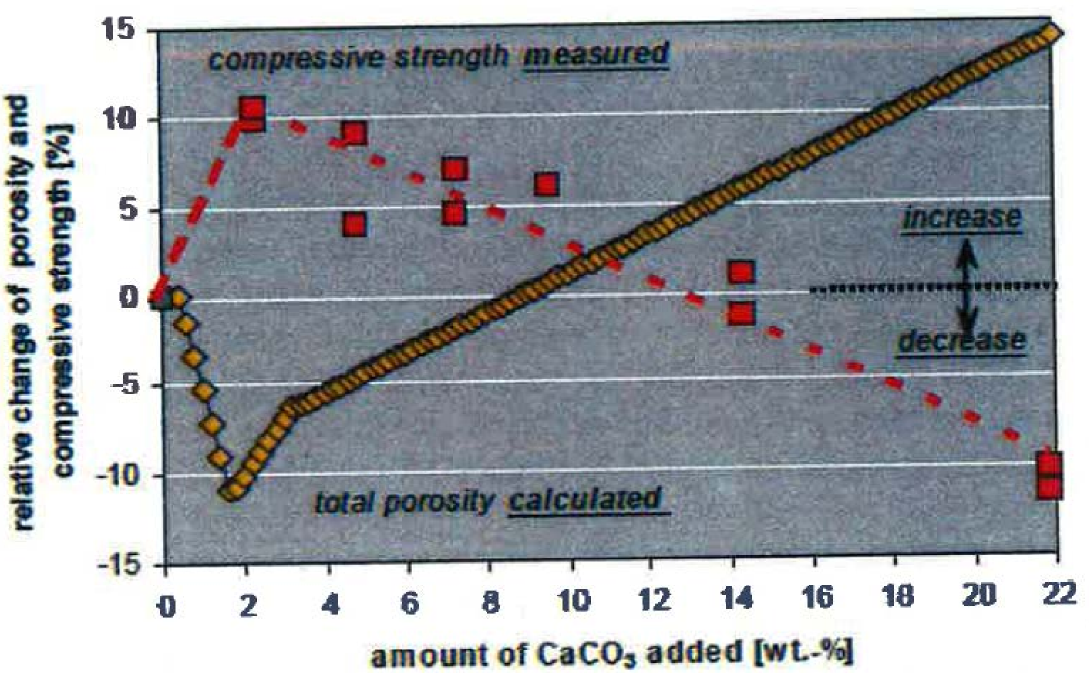


Figure 2.4 A correlation between porosity and strength development with limestone (Matschei et al. 2007b).

When adding limestone, the porosity decreases up to 2% replacement, after 2% the porosity gradually increases until approximately 10% replacement when the porosity is back to 0% change.

The compressive strength increases as the porosity decreases at the lowest porosity (2%); the compressive strength is 10% higher than 0% replacement. At about 15% $CaCO_3$ replacement, the compressive strength is about the same as a 0% replacement concrete.

Action Plan

The two areas of needed research with regard to limestone cement is sulfate and scaling resistance. The industry is currently continuing to evaluate the use of PLC in high sulfate environments including the use of the ASTM C1202 test as an evaluation. For our members, a scaling resistance study may be valuable.

Another option is to prepare a presentation based on the information contained in this review. The scaling resistance study would require funding. The presentation option would require an investment of time.