Portland Cement Association

Research & Development Information

PCA R&D SN3142

The Durability of Concrete Produced with Portland-Limestone Cement: Canadian Studies

by Michael D.A. Thomas and R. Doug Hooton

5420 Old Orchard Road
Skokie, Illinois 60077-1083
847.966.6200 Fax 847.966.9481

www.cement.org

KEYWORDS

Alkali-silica reactivity (ASR), chloride diffusion, concrete testing, deicer scaling, fineness, freeze-thaw durability, strength, portland-limestone cement (PLC).

ABSTRACT

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 cements containing up to 15% limestone. This new class of cements was then adopted in CSA A23.1, *Concrete Materials and Methods of Concrete Construction*, in 2009. In 2010, the revised A23.1 standard is being adopted in the National Building Code of Canada. Beginning in 2007, in anticipation of the adoption of portland-limestone 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. This report presents and summarizes the findings of many of these research programs.

REFERENCE

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

The Durability of Concrete Produced with Portland-Limestone Cement: Canadian Studies

Michael D.A. Thomas[1] and R. Doug Hooton[2]

INTRODUCTION

Portland-limestone cements (PLC) have been allowed by the European Standard, EN197-1, since its adoption in 2000, although a number of European countries allowed their use through national standards for a decade or more prior to this date. Specification EN197-1 allows up to 20% limestone in CEM II/A-L (and CEM II/A-LL) cements and up to 35% in CEM II/B-L (and CEM II/B-LL) cements. In Canada, the incorporation of up to 5% limestone has been permitted in portland cements since 1983. ASTM allowed the addition of the same amount of limestone in ASTM C150 portland cements in 2004 with AASHTO M85 following suit in 2007. In 2005, in response to growing pressures to reduce the environmental impact of cement production, a proposal was made to the Canadian Standards Association to create a new class of portland-limestone cements (PLC) containing up to 15% limestone. In response to this proposal, a state-of-the-art report was prepared (Hooton et al. 2007) to determine whether sufficient published data existed regarding the performance of concrete produced with PLC to support its inclusion in CSA specifications for cement and concrete. The conclusions of the report were that while there was an abundance of publications on the production and properties of PLC, more data regarding the performance of PLC together with usual levels of supplementary cementitious materials (SCM) in concrete was desirable, as well as data on the performance of PLC concrete in certain aggressive environments. The report recommended further research in three main areas before PLC could be adopted by CSA:

- Testing to determine the effects of PLC together with SCM on the fresh and hardened properties of concrete.
- Testing to determine the sulfate resistance of PLC with up to 15% limestone and to evaluate whether existing preventive measures, such as the use of supplementary cementitious materials (SCM), remained effective when used with PLC as compared with portland cement (PC).
- Testing to determine the durability of concrete containing blends of PLC and SCM in aggressive environments, particularly freezing and thawing in the presence of de-icing salts, as such conditions are prevalent in Canada.

[1] Department of Civil Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada.
[2] Department of Civil Engineering, University of Toronto, Toronto, Ontario, Canada.

In response to these recommendations, cement companies and a number of universities in Canada initiated a series of research studies. Industrial trials were conducted at several cement plants to produce portland-limestone cements containing up to 15% limestone. These cements were tested in mortar and concrete containing a wide range of SCMs and the performance was compared with equivalent mortars and concretes produced with portland cement from the same plant.

As a result of these studies a new class of cement, portland-limestone cement containing up to 15% limestone, was introduced in the cement standard (CSA A3001-08) in 2008 and the concrete standard (CSA A23.1-09) in 2009. Limestone can be used up to this level in all types of cement except for sulfate-resisting cements and PLC can be used in all classes of concrete except for sulfate-exposure classes. Testing to determine the long-term performance of PLC-SCM blends in sulfate exposure is ongoing and the restrictions regarding the use of PLC in sulfate exposure conditions will be reviewed when the long-term testing has been completed. Current data indicates that PLC, when used as the sole cementitious material, is more susceptible to the thaumasite form of sulfate attack when tested according to a modified version of ASTM C1012 conducted at 5°C (41°F); however, based on all current results, thaumasite sulfate attack appears to be prevented when levels of SCM normally associated with providing sulfate resistance are used. As a result, balloting is currently in progress (2010) on a revision to A3001 to allow use of PLC in sulfate exposures provided it contains minimum levels of specific SCM and also meets expansion limits in sulfate resistance tests similar to ASTM C1012 conducted at both 23°C and 5°C (73°F and 41°F).

The performance requirements for PLC in CSA A3001-08 are identical to those for PC of the same type. For example, Type GUL cement (general use PLC) has to meet the same setting-time and mortar-strength requirements as Type GU cement (general use PC). This is a different approach to EN197-1 as CEM II cements may be produced to meet a lower strength class than typical CEM I portland cements. The equivalent performance is achieved by optimizing the PLC with regards to composition and particle-size distribution, and this typically requires that the Blaine fineness has to be increased by approximately 100 m2/kg for PLC to achieve equivalent performance to PC from the same plant in terms of set time and strength at 1 day to 28 days. It should be noted that up to 5% limestone is permitted in ordinary portland cements (PC) in Canada and that typically PC will contain approximately 3% to 4% interground limestone.

This report summarizes the results from various PLC studies conducted by cement companies and universities in Canada between 2007 and 2009. Findings from studies on sulfate resistance are not reported here; these results will be reported when long-term data are available.

STUDY 1

In 2007 three trial grinds were made at a single plant, by intergrinding limestone with portland cement clinker and gypsum to produce PLC with Blaine fineness values from 460 m^2/kg to 560 m^2/kg. The performance of the PLC was compared with that of PC from the same plant having a Blaine fineness of 371 m^2/kg and containing 3.5% limestone. Chemical and physical characteristics of the cements are given in Table 1. A series of 12 concrete mixtures were produced with the four cements (1 PC + 3 PLC) each with no supplementary cementitious material (SCM), 35% slag and 20% fly ash. The properties of the SCMs are also given in

Table 1. The total cementitious material content of all 12 mixtures was in the range from 356 kg/m^3 to 358 kg/m^3 (600 lb/yd^3 to 603 lb/yd^3). The concrete mixtures were not air-entrained.

Test results for the concrete mixtures are presented in Table 2. The data indicate that at a given level of SCM there is little consistent difference between the fresh and hardened properties of concrete produced with the PC as compared with the PLC with Blaine fineness values of 462 m^2/kg or 515 m^2/kg. The concrete produced with the PLC with the highest Blaine (560 m^2/kg) showed faster setting, reduced bleeding and higher strengths at all ages compared with the other concrete mixtures.

Table 1. Chemical Composition of Cementitious Materials in Study 1, % by mass

	PC	PLC-1	PLC-2	PLC-3	Fly ash	Slag
SiO_2	20.56	18.70	18.73	19.06	45.60	35.33
Al_2O_3	4.66	4.46	4.43	4.40	21.04	9.77
Fe_2O_3	2.94	2.70	2.65	2.67	4.33	0.58
CaO	62.16	60.66	59.98	60.68	15.20	35.90
MgO	2.48	2.41	2.38	2.34	2.69	12.38
Na_2O	0.17	0.16	0.16	0.16	0.58	0.29
K_2O	0.76	0.72	0.72	0.75	6.43	0.50
SO_3	3.28	3.45	3.24	3.36	1.05	3.33
LOI	1.97	5.75	6.76	5.50	–	–
Blaine, m^2/kg	371	462	515	560	–	–
Passing 45 µm	97	97.3	98.7	99.3	–	–
Limestone	3.43	13.02	15.80	12.59	–	–

Table 2. Properties of Concrete Produced with PC and PLC in Study 1

	No SCM				35% Slag				20% Fly ash			
	PC	PLC-1	PLC-2	PLC-3	PC	PLC-1	PLC-2	PLC-3	PC	PLC-1	PLC-2	PLC-3
Limestone, %	3.43	13.02	15.80	12.59	3.43	13.02	15.80	12.59	3.43	13.02	15.80	12.59
Blaine, m^2/kg	371	462	515	560	371	462	515	560	371	462	515	560
W/CM	0.482	0.482	0.482	0.482	0.482	0.482	0.482	0.482	0.453	0.453	0.453	0.453
Air, %	1.3	1.3	1.2	1.3	1.2	1.3	1.2	1.1	1.4	1.4	1.3	1.3
Slump, mm	115	115	105	110	115	120	110	120	125	115	110	110
Slump, in.	4.5	4.5	4.1	4.3	4.5	4.7	4.3	4.7	4.9	4.5	4.3	4.3
Set time, min	345	395	355	300	415	435	390	395	405	440	405	385
Bleed water,* mL/kg	3.2	3.6	1.7	2.2	4.4	4.6	2.8	2.8	2.9	3.4	1.6	1.2
Strength, MPa												
1 day	19.0	17.9	18.9	22.7	10.3	10.3	9.8	12.0	16.2	15.7	16.5	20.0
7 days	36.8	36.6	36.4	39.5	34.3	34.4	34.5	35.2	36.7	36.2	36.7	39.0
28 days	47.0	45.7	45.1	49.1	50.2	47.6	48.9	50.8	49.8	47.4	47.8	51.5
56 days	50.7	50.2	48.5	53.1	55.4	53.9	55.3	57.5	55.2	54.3	55.6	57.3
Strength, psi												
1 day	2755	2596	2741	3292	1494	1494	1421	1740	2349	2277	2393	2900
7 days	5336	5307	5278	5728	4974	4988	5003	5104	5322	5249	5322	5655
28 days	6815	6627	6540	7120	7279	6902	7091	7366	7221	6873	6931	7468
56 days	7352	7279	7033	7700	8033	7816	8019	8338	8004	7874	8062	8309

*Bleed water that accumulated during setting.

STUDY 2

In 2007 trials were conducted at a second plant to determine the effect of limestone quality and fineness on the performance of PLC. Portland cements and portland-limestone cements were produced with two different limestones (92% and 80% $CaCO_3$) and a range of Blaine fineness values; a total of six cements were produced for this trial. Details of the cements are given in Table 3.

Tables 4 and 5 present details of 20 different concrete mixtures that were produced with these cements using 0% SCM, 35% slag and 20% fly ash. The chemical composition of the SCMs is given in Table 3. The total cementitious material content of all 20 mixtures was in the range from 351 kg/m^3 to 355 kg/m^3 (592 lb/yd^3 to 598 lb/yd^3). The concrete mixtures were not air-entrained.

Table 4 shows the results for mixtures without SCM. Four of these concrete mixtures were produced without any admixtures and had W/CM in the range from 0.505 to 0.518. A normal-range water-reducing admixture (WRA) was used in the other six mixtures without SCM and the W/CM was in the range from 0.491 to 0.508. Table 5 shows the results for mixtures with either 35% slag or 20% fly ash. These mixtures all contained WRA.

Collectively the data indicate a very small increase in the water demand and a slight reduction in the setting time and amount of bleed water for the mixes with PLC compared to comparable mixes with PC, especially for the PLC mixes with the highest Blaine fineness. In terms of strength, mixes produced with the PLC with a Blaine fineness of 500 m^2/kg are generally similar to the equivalent mixes produced with PC with a Blaine of 380 m^2/kg. The strengths are slightly lower for the PLC with the lowest Blaine fineness (450 m^2/kg) and slightly higher for the PLC with the highest Blaine fineness (550 m^2/kg). It is also apparent from these data that the purity of the limestone has little impact on the performance of the PLC in the range studied (80% to 92% $CaCO_3$). CSA A3001-08 imposes a minimum $CaCO_3$ content of 75% for limestone used in the production of limestone cement. The impact of fineness and limestone content are illustrated in Fig. 1.

Table 3. Chemical Composition of Cementitious Materials in Study 2, % by mass

	PC-1	PLC-1	PLC-2	PLC-3	PC-2	PLC-4	Fly ash	Slag
SiO_2	19.78	18.76	18.74	19.04	20.53	19.90	53.98	36.84
Al_2O_3	5.09	4.61	4.82	4.77	5.14	5.00	23.52	10.15
Fe_2O_3	1.86	1.72	1.78	1.76	1.89	1.84	3.82	0.53
CaO	62.21	61.70	61.71	61.82	61.83	60.37	11.66	36.41
MgO	2.25	2.07	2.13	2.07	2.30	2.29	1.27	12.92
Na_2O	0.09	0.08	0.09	0.09	0.10	0.10	3.08	0.42
K_2O	1.14	1.08	1.04	1.05	1.20	1.17	0.69	0.62
SO_3	4.19	3.86	3.70	3.68	4.10	4.02	0.22	3.63
LOI	2.94	5.86	5.59	5.50	2.57	4.99	0.89	-1.27
Blaine, m^2/kg	380	450	500	580	380	500	–	–
Passing 45 μm	92.9	97.0	98.3	99.5	93.2	97.4	–	–
Limestone	4.8	12	12	12	4.8	12	–	–
$CaCO_3$*	92	92	92	92	80	80	–	–

*Calcium carbonate content of the limestone.

Table 4. Properties of Concrete Produced with PC and PLC without SCM in Study 2

	No WRA				With WRA					
	PC-1	PLC-2	PC-2	PLC-4	PC-1	PLC-1	PLC-2	PLC-3	PC-2	PLC-4
Limestone, %	4.8	12	4.8	12	4.8	12	12	12	4.8	12
$CaCO_3$, %*	92	92	80	80	92	92	92	92	80	80
Blaine, m^2/kg	380	500	380	500	380	450	500	580	380	500
W/CM	0.505	0.512	0.505	0.518	0.491	0.498	0.498	0.508	0.495	0.502
Air, %	1.1	1.1	1.1	1.0	1.2	1.2	1.3	1.2	1.2	1.3
Slump, mm	115	110	115	110	110	110	110	80	105	105
Slump, in.	4.5	4.3	4.5	4.3	4.3	4.3	4.3	3.1	4.1	4.1
Set time, min	230	220	235	230	290	285	270	265	290	270
Bleed water, mL/kg†	1.6	0.5	1.3	0.5	1.4	1.2	0.3	0.1	1.5	0.3
Strength, MPa										
1 day	19.2	21.4	18.5	18.9	21.8	21.9	23.6	24.6	21.0	22.0
7 days	33.5	32.7	32.3	31.6	35.3	34.4	35.2	36.7	35.6	35.0
28 days	41.1	39.8	39.3	39.9	42.2	40.3	41.9	42.5	42.3	41.5
56 days	43.8	43.3	44.0	43.0	45.2	43.6	44.7	46.6	45.2	45.8
Strength, psi										
1 day	2784	3103	2683	2741	3161	3176	3422	3567	3045	3190
7 days	4858	4742	4684	4582	5119	4988	5104	5322	5162	5075
28 days	5960	5771	5699	5786	6119	5844	6076	6163	6134	6018
56 days	6351	6279	6380	6235	6554	6322	6482	6757	6554	6641

*Calcium carbonate content of the limestone.
†Bleed water that accumulated during setting.

Table 5. Properties of Concrete Produced with Slag and Fly Ash in Study 2

	35% Slag						20% Fly ash			
	PC-1	PLC-1	PLC-2	PLC-3	PC-2	PLC-4	PC-1	PLC-2	PC-2	PLC-4
Limestone, %	4.8	12	12	12	4.8	12	4.8	12	4.8	12
$CaCO_3$, %*	92	92	92	92	80	80	92	92	80	80
Blaine, m^2/kg	380	450	500	580	380	500	380	500	380	500
W/CM	0.485	0.492	0.492	0.495	0.485	0.495	0.459	0.459	0.459	0.462
Air, %	1.1	1.0	1.1	1.2	1.2	1.2	1.2	1.3	1.3	1.4
Slump, mm	120	115	120	100	115	110	120	120	110	110
Slump, in.	4.7	4.5	4.7	3.9	4.5	4.3	4.7	4.7	4.3	4.3
Set time, min	320	330	310	300	325	310	305	285	305	285
Bleed water, mL/kg†	1.0	1.3	0.6	0.6	1.4	0.8	0.3	0.0	0.2	0.2
Strength, MPa										
1 day	12.2	12.4	13.2	13.5	12.2	12.8	20.0	20.8	18.5	18.8
7 days	32.3	32.1	33.1	33.0	32.6	31.7	34.9	35.1	34.7	33.2
28 days	41.7	40.8	41.3	42.7	41.9	42.0	43.3	44.3	43.8	43.6
56 days	44.6	43.9	45.0	46.8	44.7	46.7	49.1	48.2	48.8	49.1
Strength, psi										
1 day	1769	1798	1914	1958	1769	1856	2900	3016	2683	2726
7 days	4684	4655	4800	4785	4727	4597	5061	5090	5032	4814
28 days	6047	5916	5989	6192	6076	6090	6279	6424	6351	6322
56 days	6467	6366	6525	6786	6482	6772	7120	6989	7076	7120

*Calcium carbonate content of the limestone.
†Bleed water that accumulated during setting.

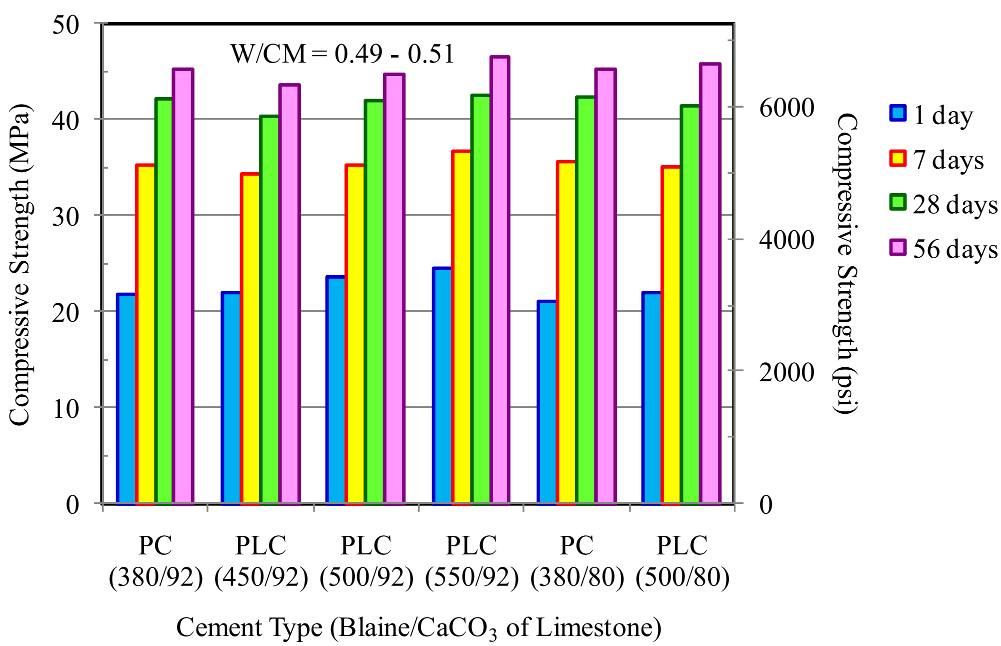

Figure 1. Effect of Surface Area (Blaine) and Purity of Limestone on the Strength of Concrete.

Concrete mixtures for durability testing were produced with PC-2 and PLC-4, using the limestone containing 80% $CaCO_3$. Details of the concrete mixtures are given in Table 6. Air-entraining admixture (AEA) was added to mix Series B and C to achieve a target air content of 5% to 7%. Mixes with PLC required slightly more AEA than mixtures with PC. A normal range water-reducing admixture (ASTM C494 Type B) was added to all mixtures at a dosage of 180 mL/100kg (3 fl. oz/cwt). A high-range water-reducing admixture (sulfonated naphthalene-formaldehyde) was added where required to raise the slump to the target level of 100 mm to 125 mm (4 in. to 5 in.). There was no noticeable difference between PC and PLC concretes in terms of workability, placing or finishing characteristics. However, the mixtures without SCM in mix Series A and B did show reduced bleeding with PLC compared with PC. No bleed water was observed for mixes with SCM and mixes in Series C. Concrete mixtures with PLC set more quickly (by about 30 to 45 minutes) than similar mixes with PC (see Table 6).

Figures 2 and 3 show the results of compressive strength tests for all ten concrete mixtures. In all cases a higher strength is observed at early ages (1 day or 7 days) for concretes with PLC compared with the equivalent concrete with PC. At later ages (28 days or 56 days) the differences are smaller but the strength of PLC mixes is generally slightly higher or similar to the equivalent PC mixtures.

None of the concretes tested (W/CM = 0.40 or 0.45) exhibited any deterioration after 300 cycles in the ASTM C666 (Procedure A) test, the lowest durability factor recorded being DF = 98%. All concretes showed satisfactory salt scaling resistance in the ASTM C672 test (Fig. 4) with scaling mass losses being less than 600 g/m^2 (17.6 oz/yd^2). Mixes with 35% slag and 20% fly ash showed increased scaling compared to the mixes without SCM, but values were still below typically specified performance limits in Canada (800 g/m^2 to 1000 g/m^2 or 23.4 oz/yd^2 to 29.3 oz/yd^2). No consistent trend was observed between the behavior of PLC versus PC concrete. Results from the "Rapid Chloride Permeability Test" (ASTM C1202) are shown in Fig. 5. As expected, the incorporation of SCM resulted in a significant reduction in "permeability" (electrical conductivity), but it is evident that the use of PLC or PC has no significant impact on the results.

Table 6. Concrete Mix Proportions and Test Results – Study 2 – Durability Tests

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

*Durability factor after 300 freeze-thaw cycles - ASTM C666 Procedure A.

†Mass loss after 50 freeze-thaw cycles ponded with salt solution - ASTM C672 "Salt Scaling Test."

‡Charged passed after 6 hours - ASTM C1202 "Rapid Chloride Permeability Test."

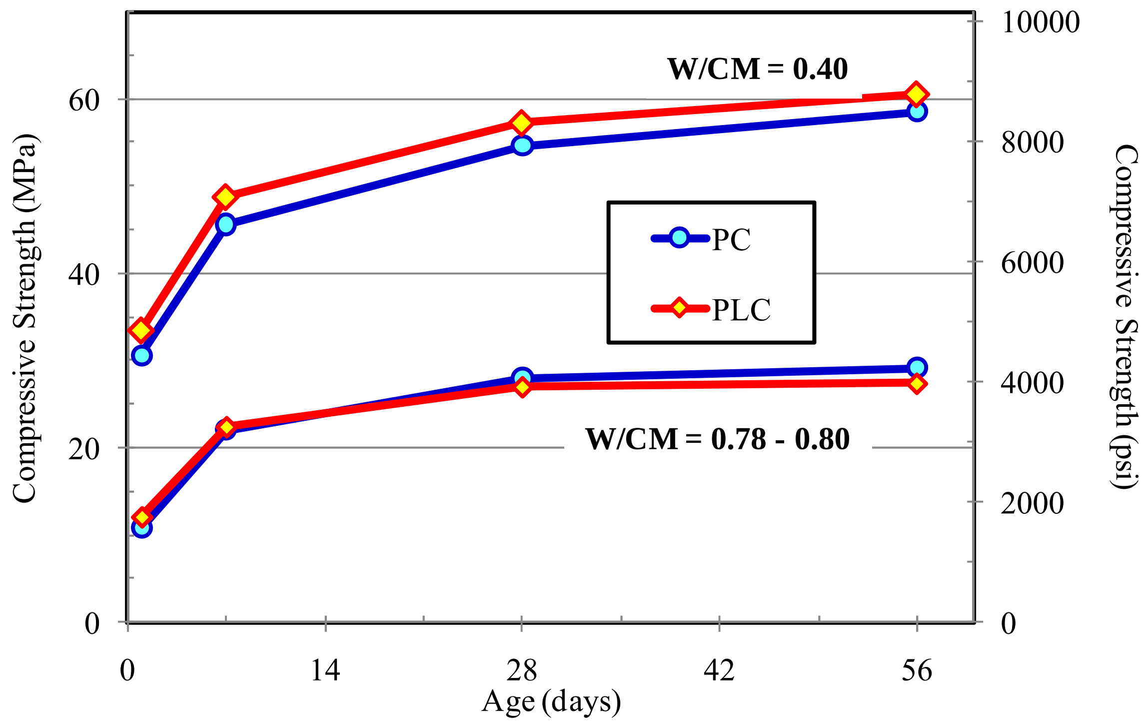

Figure 2. Strength Development of PC and PLC Mixes without SCM at W/CM = 0.78 to 0.80 and 0.40.

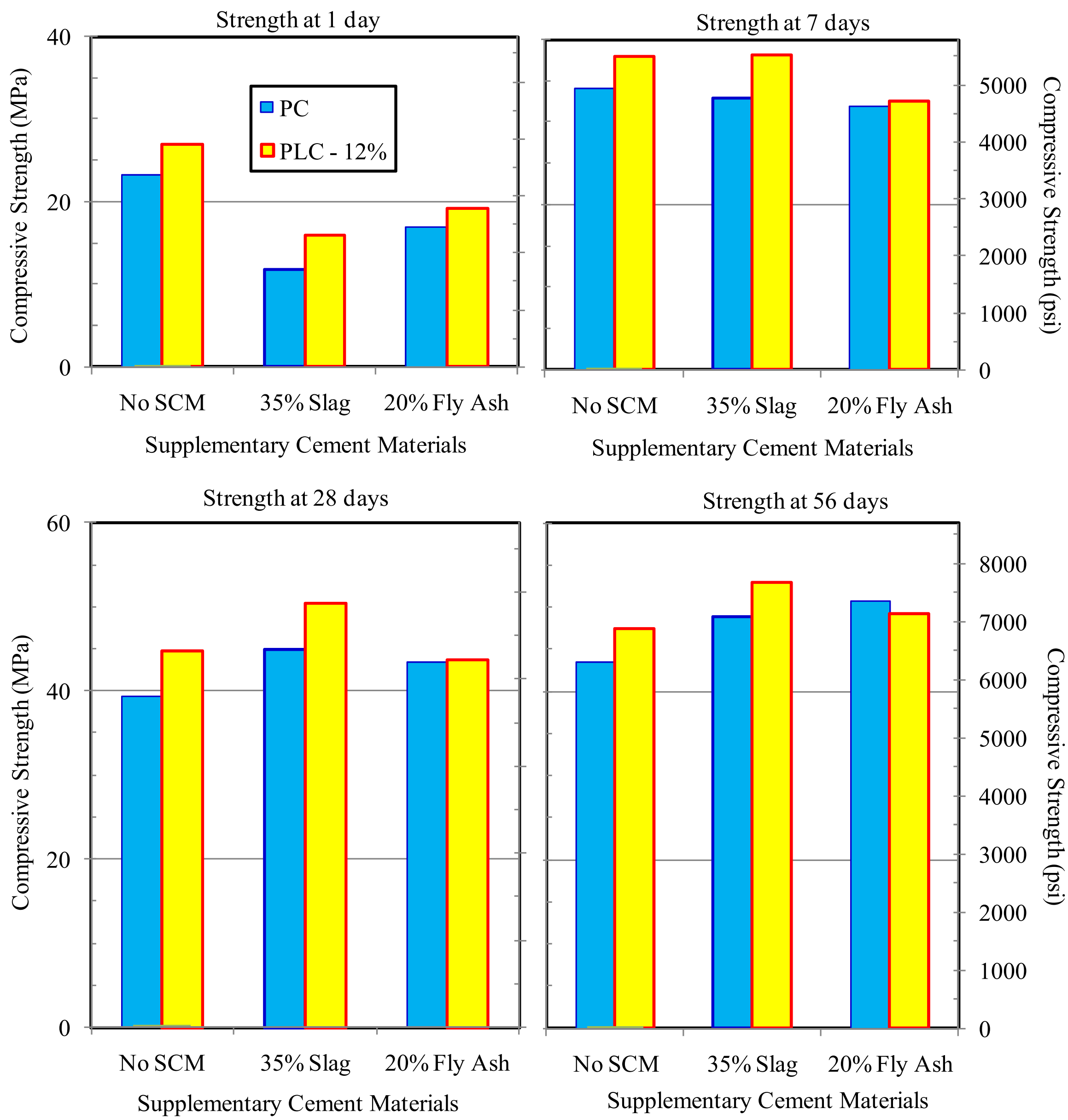

Figure 3. Strength Development of PC and PLC Mixes with and without SCM at W/CM = 0.45.

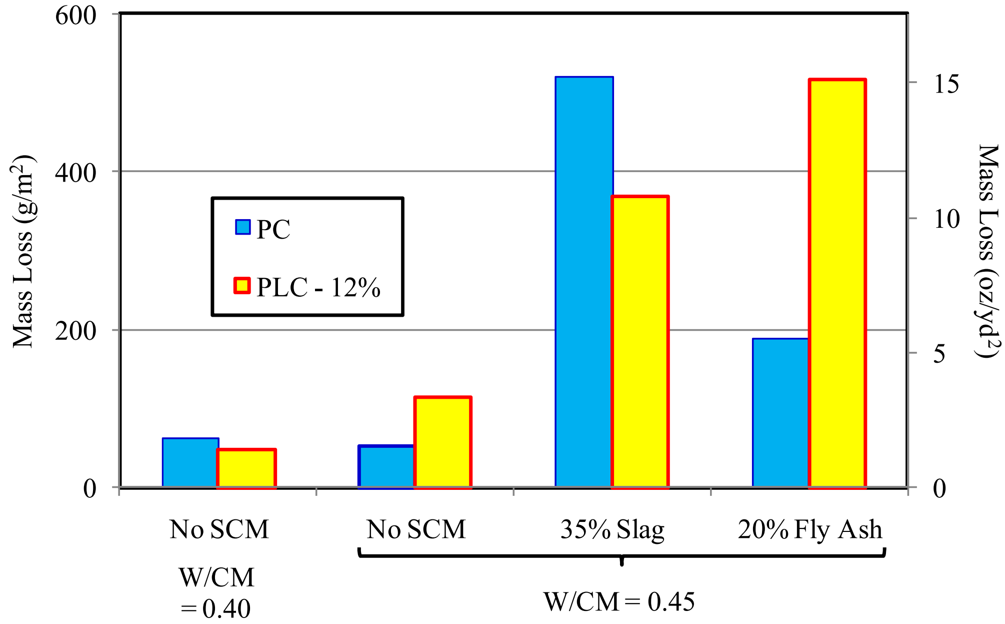

Figure 4. Scaling Mass Loss after 50 Cycles of Freeze-Thaw – ASTM C672.

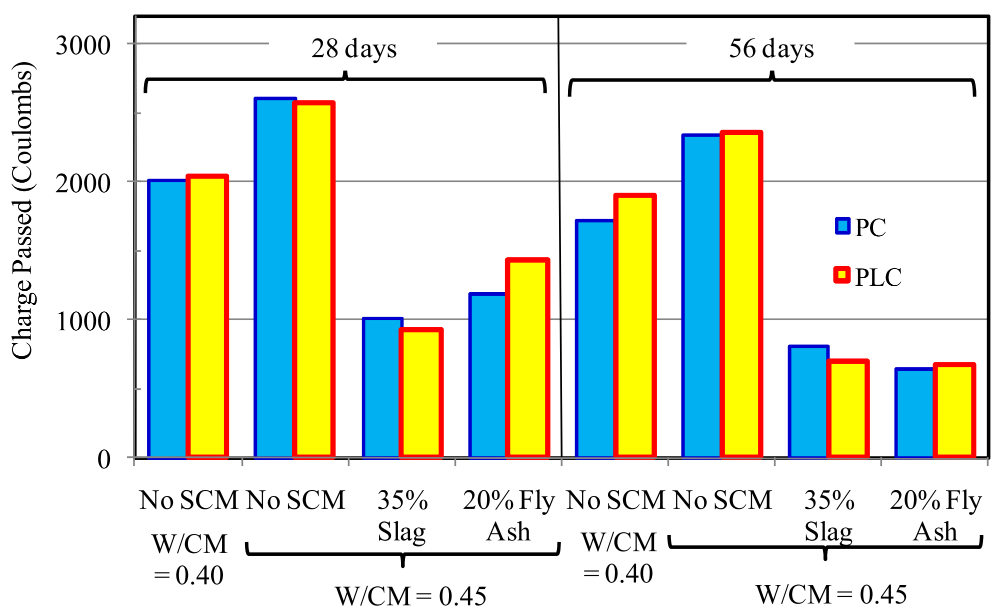

Figure 5. "Rapid Chloride Permeability" – ASTM C1202.

Tests were also conducted on PC and PLC mortars and concretes containing an alkali-silica reactive aggregate (siliceous limestone from the Spratt quarry in Ontario). Figure 6 shows the expansion of mortar bars and concretes at the age typically used for evaluation. All tests indicated deleterious expansion (no preventive measures were included) and there is no significant difference attributed to the use of PLC compared with PC.

PLC has to be ground to higher fineness to achieve equivalent performance and this is demonstrated in Fig. 7a which shows results from laser particle analysis for the PLC and PC used in the durability testing discussed above. Figure 7b shows the particle size distribution of the clinker and limestone in the PLC cement. This distribution was calculated using the results from laser particle analysis and chemical analysis to determine the limestone content of different size fractions. It can be seen that the softer limestone is ground to a significantly finer particle size than the harder clinker particles when the two materials are interground. It can also be observed by comparison of the curve for the PLC clinker in Fig. 7b with the curve for the PC in Fig. 7a that the clinker in the PLC is finer than the clinker in the PC.

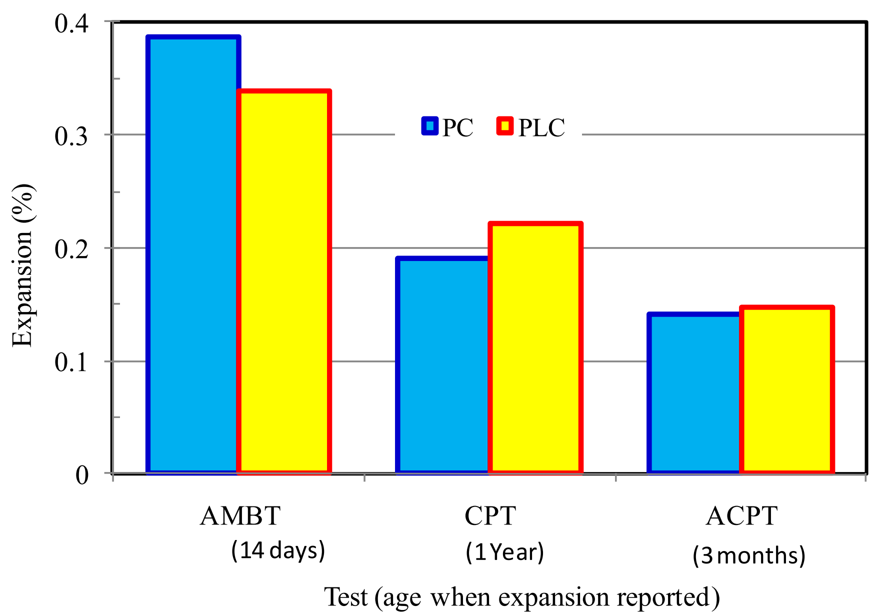

Figure 6. Expansion of Mortar Bars and Concrete Prisms Containing Alkali-Silica Reactive Aggregate. AMBT – ASTM C1260 Accelerated Mortar Bar Test; CPT – ASTM C1293 Concrete Prism Test; ACPT – Accelerated Concrete Prism Test at 60°C (140ºF).

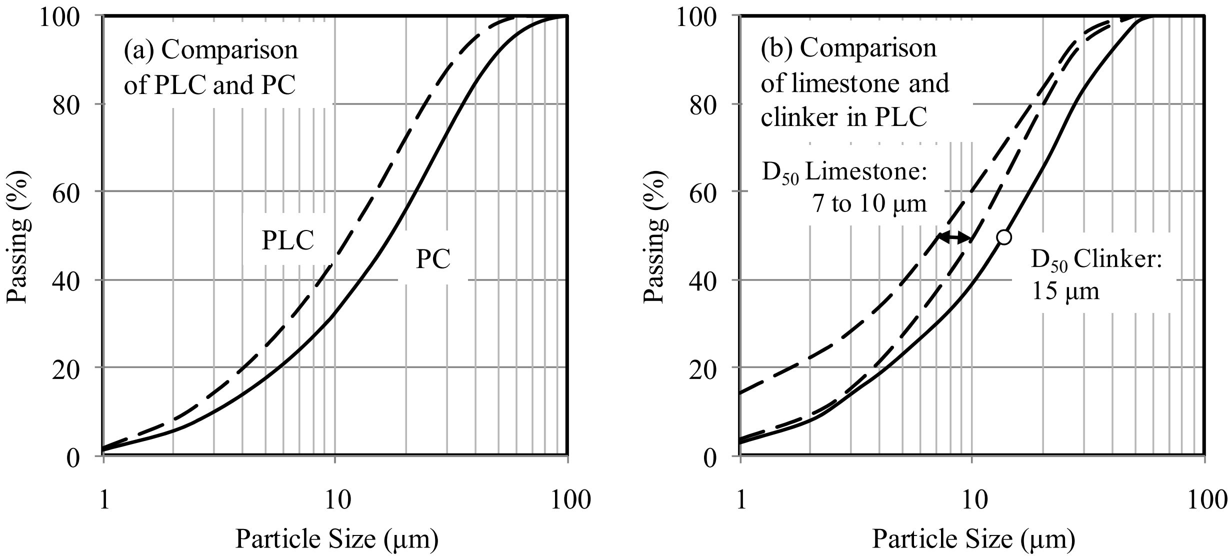

Figure 7. Particle Size Distribution of (a) PC and PLC, and (b) Clinker and Limestone in PLC.

STUDY 3

In 2008 a second industrial trial was conducted at Plant 1. The performance of PC with 3.5% limestone was compared with PLC with 12% limestone in concrete mixtures with and without SCM. The SCM used comprises two parts slag cement and one part fly ash, by mass; this blended SCM is currently marketed commercially. The chemical composition of the cements and SCM are given in Table 7.

Table 7. Chemical Composition of Cementitious Materials in Study 3, % by mass

	PC	PLC	Fly Ash	Slag
SiO_2	20.53	16.23	36.53	35.75
Al_2O_3	4.63	4.4	19.39	9.72
Fe_2O_3	2.77	2.64	5.27	0.50
CaO	62.7	61.45	18.62	35.66
MgO	2.48	2.41	4.92	13.05
Na_2O	0.21	0.20	5.69	0.33
K_2O	0.71	0.68	0.85	0.52
SO_3	3.23	3.4	2.06	2.93
LOI	2.26	5.25	0.30	–
Blaine, m^2/kg	373	453	–	–
Limestone, %	3.5	12	–	–

A total of eight concrete mixtures were batched at a ready-mixed concrete plant and mixed in a truck mixer. Details of the eight mixtures are given in Table 8. The total cementitious materials content of all mixtures was 355 kg/m^3 and the materials consisted of either PC or PLC together with 0%, 25%, 40%, or 50% SCM. The target air content was 6% and the target slump was 100 mm. All mixes contained a normal-range water-reducing admixture.

Table 8. Concrete Mix Proportions and Test Results – Study 3

	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, %	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, %	5.3	5.6	4.9	5.4	5.6	5.3	5.6	6.6
Spacing factor, µm	173	187	148	149	164	165	150	147
Spacing factor, in.	0.068	0.074	0.058	0.059	0.065	0.065	0.059	0.058
Strength, MPa								
1 day	24.2	25.2	21.7	20.7	18.9	19.2	15.3	15.6
7 days	30.2	30.5	29.8	29.6	30.3	31.1	29.4	28.8
28 days	37.7	38.2	41.3	39.8	43.5	43.5	43.0	42.5
56 days	41.3	40.9	45.4	44.7	48.6	48.3	48.7	46.5
Cores at 35 days	39.7	35.3	35.7	35.5	42.3	43.2	37.6	39.4
Strength, psi								
1 day	3509	3654	3147	3002	2741	2784	2219	2262
7 days	4379	4423	4321	4292	4394	4510	4263	4176
28 days	5467	5539	5989	5771	6308	6308	6235	6163
56 days	5989	5931	6583	6482	7047	7004	7062	6743
Cores at 35 days	5757	5119	5177	5148	6134	6264	5452	5713
Durability factor, %*	101	100	101	104	101	103	102	100
Scaling mass C 672, g/m^2†	40	10	30	50	80	230	400	320
Scaling mass C 672, oz/yd^2 †	1.17	0.29	0.88	1.46	2.34	6.73	11.71	9.36
Scaling mass BNQ, g/m^2 ‡	39	114	273	127	106	142	380	497
Scaling mass BNQ, oz/yd^2‡	1.14	3.34	7.99	3.72	3.10	4.16	11.12	14.54
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
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

*Durability factor after 300 freeze-thaw cycles - ASTM C666 Procedure A

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

‡Mass loss after 56 freeze-thaw cycles ponded with salt solution - BNQ "Salt Scaling Test"

§Charged passed after 6 hours - ASTM C1202 "Rapid Chloride Permeability Test"

‖Chloride diffusion coefficient, D_a, determined on 35-day-old cores using ASTM C1556 "Bulk Diffusion Test"

The concrete mixtures were used to construct a parking slab, approximately 450 m^2 (540 yd^2) and approximately 150 mm to 200 mm (6 in. to 8 in.) thick, at a ready-mixed concrete plant at Gatineau, Quebec (see Fig. 8). The concrete was placed by direct chute discharge, consolidated with a hand-held vibrating screed, bullfloated, broom finished and cured under insulated tarps for one day. All mixes were placed in one day on October 6, 2008; the ambient temperature ranged from -2°C to +5°C and the relative humidity from 44% to 93%. No problems were encountered with placing or finishing the slabs, and no differences were observed between the fresh properties of mixes with PC or PLC at the same SCM content. Figure 9 shows the appearance of the slab after one winter.

Figure 8. Completed Slab at Ready-Mixed Concrete Plant (Study 3).

During placing a number of specimens were cast for laboratory testing to determine the strength and durability properties of the concrete. The results of these tests are presented in Table 8. Cores 100 mm (4 in.) in diameter were also cut from the slabs at 35 days to determine the in-situ strength, rapid chloride permeability (ASTM C1202), and the bulk chloride diffusion coefficient (ASTM C1556).

A detailed discussion of these results has been published elsewhere (Thomas et al. 2010a). Essentially the test data indicate that there is no significant difference between the performance of concrete with PLC compared with PC at the same level of SCM.

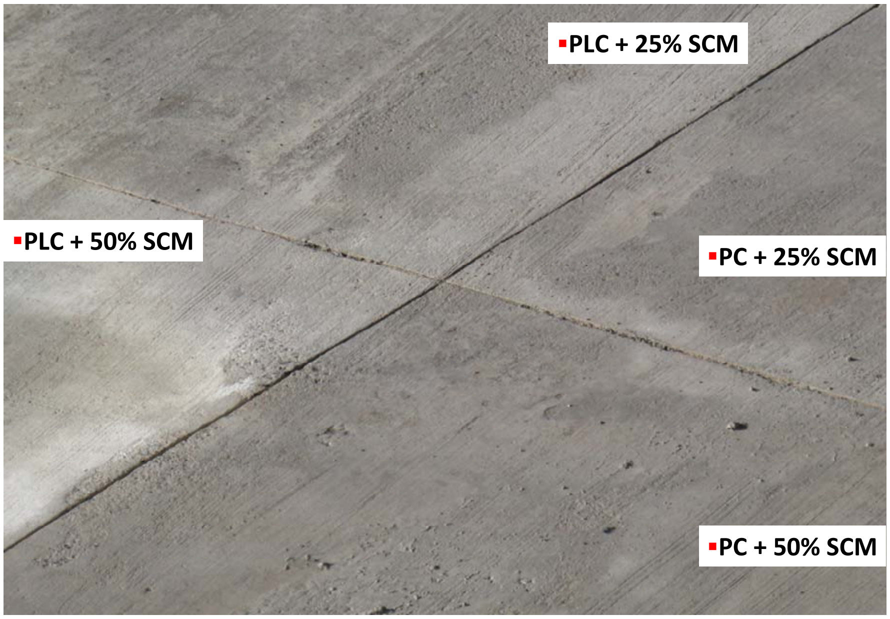

Figure 9. Appearance of Slabs in Study 3 after 1 Winter.

STUDY 4

In 2008 the performance of PC with 3.5% limestone was compared with PLC with 10% and 15% interground limestone in concrete mixtures with and without 15% and 30% slag cement. The chemical composition of the cements and SCM are given in Table 9.

Table 9. Chemical Composition of Cementitious Materials in Study 4, % by mass

	PC	PLC10	PLC15	Slag
SiO_2	19.6	19.3	18.6	38.14
Al_2O_3	5.4	5.2	5.1	7.18
Fe_2O_3	2.36	2.3	2.2	0.74
CaO	62.4	61.7	60.0	39.95
MgO	2.4	2.3	2.3	10.57
Na_2O	0,2	0.19	0.18	0.33
K_2O	1.16	1.15	1.14	0.46
SO_3	4.5	4.3	4.2	2.71*
LOI	1.8	3.6	5.9	0.27
Blaine, m^2/kg	391	442	507	–
Passing 45 μm	6.5	7	8.1	–
Limestone	3.5	10	15	–

* Sulfide sulfur expressed as SO_3

Four types of concrete were cast with each of the nine cementitious materials combinations for a total of 36 concrete mixtures: (a) air-entrained concrete with W/CM = 0.70 and 225 kg/m^3 (375 lb/yd^3) cementitious materials meeting the CSA A23.1 residential class R-1, (b) non-air entrained concrete with W/CM = 0.65 and 257 kg/m^3 (428 lb/yd^3) meeting the CSA A23.1 residential class R-3, (c) air-entrained concrete with W/CM = 0.40 and 360 kg/m^3 (600 lb/yd^3) meeting the CSA A23.1 exposure class C-1, and (d) air-entrained concrete with W/CM = 0.37 and 420 kg/m^3 (700 lb/yd^3) meeting the CSA A23.1 residential class C-XL except that silica fume was not used and the 56-day 1000-coulomb limit was not met. All of the mixtures contained a water-reducing admixture and a high-range water reducer.

Results for fresh concrete properties are shown in Tables 10a and 10b, and strength development is shown in Tables 11a and 11b.

For the 0.40 W/CM concretes, chloride bulk diffusion (ASTM C1556) test results, ASTM C1202 “rapid chloride permeability” results, and ASTM C157 drying shrinkage (7-day wet cure followed by 28 days of drying) are shown in Table 12. It can be seen that the limestone had little impact on these properties, but 30% slag significantly reduced chloride diffusion, coulomb values and drying shrinkage.

Alkali-silica reactivity was assessed using the accelerated mortar bar test (ASTM C1567) and the concrete prism test (ASTM C1293) using a siliceous limestone (Spratt) as the reactive aggregate. The results of these tests are presented in Fig. 10. The clinker for these PC and PLC was high alkali (0.96% Na_2O_{eq}) and deleterious expansions were observed in both tests when no slag was present. The expansions were reduced significantly with 30% slag and mitigation (expansion < 0.10% at 14 days for mortar bars and expansion < 0.040% at 2 years) was achieved with 50% slag regardless of limestone content.

Table 10a. Concrete Mix Proportions and Fresh Concrete Properties—Study 4
CSA A23.1 Class R-1 and R-3 Residential Mixtures

	Mix ID	Total CM kg/m^3	Limestone %	Slag %	w/cm	Slump, mm			Air, %		
						10 min.	60 min.	90 min.	10 min.	60 min.	90 min.
NR (Wall Mix)	NR - 1	225	3.5	0	0.70	230	210	190	4.2	4.5	4.6
	NR - 2	225	3.5	15	0.70	225	140	90	4.4	4.9	5.1
	NR - 3	225	3.5	30	0.70	240	205	165	3.5	3.2	3.9
	NR - 5	225	10	0	0.70	220	160	90	3.9	3.6	3.8
	NR - 6	225	10	15	0.70	220	195	170	3.0	3.4	3.8
	NR - 7	225	10	30	0.70	220	180	165	5.5	4.9	5.1
	NR - 9	225	15	0	0.70	225	160	110	4.7	3.8	4.0
	NR - 10	225	15	15	0.70	230	180	150	4.7	4.2	4.5
	NR - 11	225	15	30	0.70	220	155	120	5.4	4.5	5.2
NS	NS - 1	257	3.5	0	0.65	190	170	145	*		
	NS - 2	257	3.5	15	0.65	200	130	115			
	NS - 3	257	3.5	30	0.65	175	155	115			
	NS - 5	257	10	0	0.65	185	165	120			
	NS - 6	257	10	15	0.65	190	170	135			
	NS - 7	257	10	30	0.65	190	145	115			
	NS - 9	257	15	0	0.65	185	150	120			
	NS - 10	257	15	15	0.65	190	170	140			
	NS - 11	257	15	30	0.65	170	140	115			

* No air data available for NS mixtures

Table 10b. Concrete Mix Proportions and Fresh Concrete Properties—Study 4
CSA A23.1 Class C-1 and Class C-XL Mixtures

	Mix ID	Total CM kg/m^3	Limestone %	Slag %	w/cm	Slump, mm			Air, %		
						10 min.	60 min.	90 min.	10 min.	60 min.	90 min.
N Class C1	NC1 - 1	360	3.5	0	0.40	230	215	205	5.0	5.8	5.3
	NC1 - 2	360	3.5	15	0.40	220	195	180	5.8	4.8	6.2
	NC1 - 3	360	3.5	30	0.40	240	210	195	6.0	7.0	6.5
	NC1 - 5	360	10	0	0.40	225	180	160	5.0	4.6	4.8
	NC1 - 6	360	10	15	0.40	225	180	145	5.1	4.0	4.5
	NC1 - 7	360	10	30	0.40	225	220	205	5.3	4.1	6.3
	NC1 - 9	360	15	0	0.40	220	160	120	5.0	3.7	4.0
	NC1 - 11	360	15	30	0.40	225	205	180	6.0	4.9	5.5
N Class CXL	NCXL - 1	420	3.5	0	0.37	230	*	*	5.0	*	*
	NCXL - 2	420	3.5	15	0.37	230			8.0		
	NCXL - 3	420	3.5	30	0.37	240			6.3		
	NCXL - 5	420	10	0	0.37	230			6.4		
	NCXL - 6	420	10	15	0.37	230			6.6		
	NCXL - 7	420	10	30	0.37	235			6.6		
	NCXL - 9	420	15	0	0.37	220			5.3		
	NCXL - 10	420	15	15	0.37	225			5.3		
	NCXL - 11	420	15	30	0.37	225			5.2		

* No slump and air measurements taken at 60 min or 90 min.

Table 11a. Concrete Strengths and RCPT Values –Study 4
CSA A23.1 Class R-1 and R-3 Residential Mixtures

	Mix ID	Total CM	Limestone	Slag	w/cm	Strength, MPa						RCP, coulombs		
		kg/m^3	%	%		1 d	3 d	7 d	28 d	56 d	91 d	28-day	56-day	85-day
NR (Wall Mix)	NR - 1	225	3.5	0	0.7	8.4	15.3	19	23.7	25.6		7070		
	NR - 2	225	3.5	15	0.7	8.6	14.4	19.7	26.4	30.4		3640	2820	
	NR - 3	225	3.5	30	0.7	5.1	9.3	13.4	23.4	24.8		2540	2030	
	NR - 5	225	10	0	0.7	11.9	18.8	20.2	25.1	26.9				
	NR - 6	225	10	15	0.7	7.9	14.7	19.7	27	30.3		4940	3040	
	NR - 7	225	10	30	0.7	7.4	12.8	17.1	26.2	27.8			1480	1360
	NR - 9	225	15	0	0.7	9.9	17.6	20.2	24.4	25				
	NR - 10	225	15	15	0.7	5.6	13.4	16.1	23.7	26.7			2820	2650
	NR - 11	225	15	30	0.7	5.7	9.6	13.9	23.9	26.7			1630	1330
NS	NS - 1	257	3.5	0	0.65	14.8	25.3	28.6	35.4	45.3		7410		
	NS - 2	257	3.5	15	0.65	12.3	21.7	26.7	34.6	40.3		3470		2340
	NS - 3	257	3.5	30	0.65	7.7	15.8	21.3	32.2	35		1870	1590	
	NS - 5	257	10	0	0.65	14.8	23.2	26.9	30.6	33.6				
	NS - 6	257	10	15	0.65	10.1	19.5	23.1	32.9	37.8		3470	2620	
	NS - 7	257	10	30	0.65	6.4	17.4	19.9	35.3	35.7		2270	1630	
	NS - 9	257	15	0	0.65	12.6	21.2	23.7	29.3	31.2				
	NS - 10	257	15	15	0.65	9.1	16.3	22.5	28.7	34.8			3150	2530
	NS - 11	257	15	30	0.65	5.8	12.4	20.9	30.8	34.7			1570	1160

Table 11b. Concrete Strengths and RCPT Values –Study 4
CSA A23.1 Class C-1 and Class C-XL Mixtures

	Mix ID	Total CM	Limestone	Slag	w/cm	Strength, MPa						RCP, coulombs		
		kg/m^3	%	%		1 d	3 d	7 d	28 d	56 d	91 d	28-day	56-day	85-day
N Class C1	NC1 - 1	360	3.5	0	0.4	20.8	31.1	39.3	47.3	50.2	58.5		3130	2370
	NC1 - 2	360	3.5	15	0.4	15.6	27.2	33.4	38.6	43.5	49.6		700	1370
	NC1 - 3	360	3.5	30	0.4	6.9	12.9	19.4	29.7	33	33.6		1070	910
	NC1 - 5	360	10	0	0.4	25.4	38	42.6	50.7	56.8	60.2		3060	2510
	NC1 - 6	360	10	15	0.4	23.2	35.4	42.3	51.7	59.1	68.5		1790	670
	NC1 - 7	360	10	30	0.4	13	22.9	30	42.6	46.2	53.4		1060	970
	NC1 - 9	360	15	0	0.4	25.9	36.1	40.4	49.4	55.9	56.1		3130	2800
	NC1 - 11	360	15	30	0.4	12.6	21.2	31.5	43	46.8	53.9		1310	940
N Class CXL	NCXL - 1	420	3.5	0	0.37	22	41.1	45.2	53.8	62.8	66.3	3970		2120
	NCXL - 2	420	3.5	15	0.37	19.1	34.8	41.8	52.5	58.2	63.3	3040		1450
	NCXL - 3	420	3.5	30	0.37	15.6	30.3	40.9	51.6	54.6	55.8	1900		1120
	NCXL - 5	420	10	0	0.37	25.4	38.2	42.7	51.5	54.9	65.1	3720		2220
	NCXL - 6	420	10	15	0.37	20.9	35.5	41.9	53.4	57.9	65.4	2720		1210
	NCXL - 7	420	10	30	0.37	15	29.9	38.3	53	57.4	61.3	1380		1070
	NCXL - 9	420	15	0	0.37	25.7	40.6	47.7	56.2	57.4	64.2	4450		2560
	NCXL - 10	420	15	15	0.37	16.4	33.4	39.6	53.2	56.5	60.9	2550		1490
	NCXL - 11	420	15	30	0.37	12.6	30.4	41.9	55.2	61.2	63.1	1550		970

Table 12. Chloride Bulk Diffusion and Drying Shrinkage of 0.40 W/CM Concretes – Study 4

w/cm = 0.40		ASTM C1556		C157 drying shrinkage	ASTM C1202
% Limestone	% Slag	C_s, %	D_a, m^2/s	28d, %	56 d, coulombs
3.5	0	0.73	1.59E-11	0.036	3130
3.5	30	1.1	8.07E-12	0.026	1070
10	0	0.84	1.56E-11	0.037	3060
10	30	1.07	6.11E-12	0.027	1060
15	0	0.8	2.25E-11	0.037	3130
15	30	0.98	8.25E-12	0.025	1310

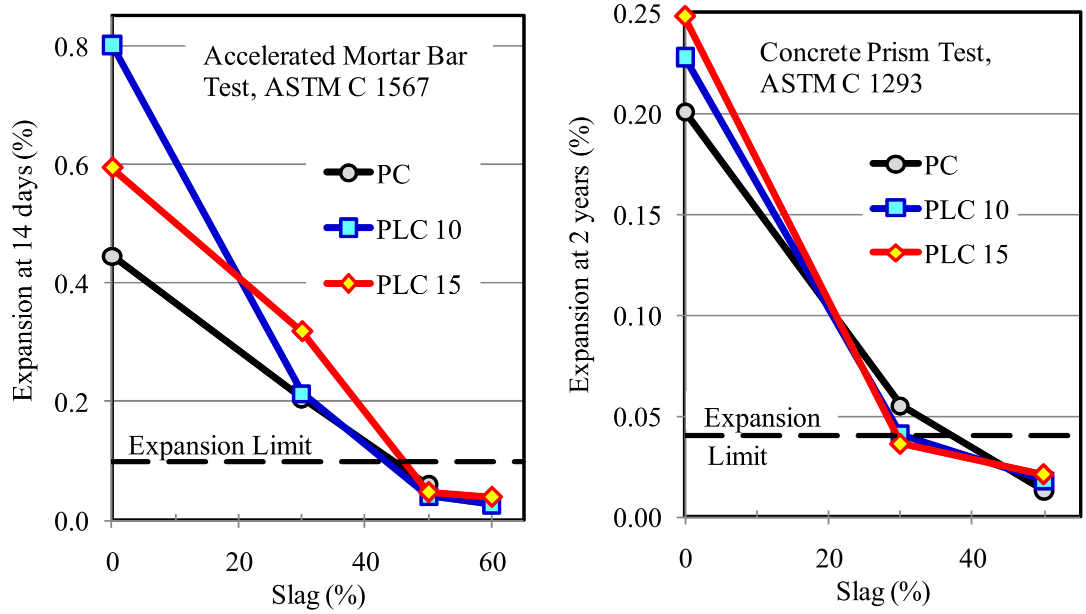

Figure 10. Expansion results from accelerated mortar bar test (left) and concrete prism test (right) from Study 4 using alkali-silica reactive siliceous limestone (Spratt).

DISCUSSION

The data shown here indicate that the limestone content of cement can be increased from the level typically used in PC (about 3.5%) to 15% while maintaining equivalent performance. Intergrinding clinker and limestone produces an improved (broadened) particle size distribution with the softer limestone grinding finer than the harder clinker. In these studies, equivalent performance was obtained by increasing the Blaine fineness of PLC with 10% to 15% limestone by roughly 100 m^2/kg compared with PC from the same plant.

In addition to improving particle packing, the fine limestone particles also act as nucleation sites thereby increasing the rate of hydration of the calcium silicates at early ages and, possibly, improving the distribution of the hydrates. Furthermore it has been demonstrated that $CaCO_3$ will react chemically (although to a small extent, depending on the C_3A content of the clinker) with the aluminate phases to form carboaluminate phases (for example, Bonavetti et al. 2001), which may contribute to reducing the porosity and increasing the strength of the paste (Matschei et al. 2007). The additional aluminates supplied by pozzolans and slag may increase the formation of carboaluminates. Further studies are required to quantify how these various mechanisms contribute to the performance of PLC concrete.

Based on the results of these studies, PLC with up to 15% limestone is now permitted for use in cement and concrete in Canada. However, PLC cannot currently be used to produce sulfate-resisting cement and cannot be used in concrete exposed to sulfate environments. Several test programs are currently underway in Canada to examine the long-term performance of PLC in sulfate environments.

Since adoption of PLC by CSA A3001, there have been a number of successful field trials in addition to the field application described in Study 3 above. Four trials were conducted in Fall 2009. One trial involved highway barrier walls cast with PC and PLC with 11% interground limestone along with 25% slag added at the ready-mixed concrete plant (Hooton et al. 2010). A paving project was carried out in Toronto using PC and PLC with 10% interground limestone, and with and without 25% slag cement added at the ready mix plant. Another paving project was carried out in Alberta using PC and PLC produced at that plant with various levels of fly ash added at the concrete plant. At another site, plant-blended cements were produced with 15% slag and either 4% or 12% limestone; the clinker, gypsum, slag granules, and limestone were interground (Thomas et al. 2010b; 2010c). Concrete mixes were produced with these two cements and various levels of fly ash added at the ready-mixed concrete plant and these mixes were used to pave the road outside the entrance to the plant (Thomas et al. 2010d). In all four trials, concrete samples were cast on-site for laboratory testing which included strength, chloride permeability and diffusion, scaling resistance, and drying shrinkage. The results indicate that while the level of SCM significantly impacts performance, at a given level of SCM there is no significant consistent difference between the performance of the concrete with different levels of limestone in the cement (Hooton et al. 2010; Thomas et al. 2010b; 2010c; 2010d).

It is anticipated that PLC produced in Canada will contain approximately 8% to 9% more limestone than PC currently produced from the same plant, which means that the clinker content of the cement is reduced by the same amount (assuming the gypsum content remains unaltered). This translates to a similar reduction in the CO_2 NO_x, SO_x, and particulate emissions associated with the manufacture of the clinker.

CONCLUSIONS

1. Portland limestone cement (PLC) containing up to 15% by mass limestone can be produced to provide equivalent performance as portland cement containing approximately 3.5% limestone.
2. The equivalent performance is achieved by producing a PLC with a Blaine fineness that is approximately 100 m^2/kg higher than the PC. This provides a particle size of the clinker fraction that is is slightly finer to that in a PC.
3. Performance in this study was evaluated based on the following concrete properties: strength, resistance to freeze-thaw and de-icer salt scaling, chloride permeability and chloride diffusion. Studies also showed that the expansion of concrete containing alkali-silica reactive aggregate was unaffected by using PLC instead of PC.

REFERENCES

Bonavetti, V.L.; Rahhhal, V.F.; and Irassar, E.F., "Studies on Carboaluminate Formation in Limestone Filler-Blended Cements," *Cement and Concrete Research*, Vol. 31, pages 853 to 859, 2001.

Hooton, R.D.; Nokken, M.R.; 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, June 17, 2007, 59 pages.

Hooton, R.D.; Ramezanianpour, A.; and Schutz, U., "Decreasing the Clinker Component in Cementing Materials: Performance of Portland-Limestone Cements in Concrete in Combination with Supplementary Cementing Materials," *Proceedings of the 2010 International Concrete Sustainability Conference*, National Ready Mixed Concrete Association, Tempe, Arizona, USA, April 12-15, 2010, 15 pages.

Matschei, T.; Lothenbach, B.; and Glasser, F.P., "The Role of Calcium Carbonate in Cement Hydration," *Cement and Concrete Research*, Volume 37, pages 118 to 130, 2007.

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," *Proceedings of the 2010 International Concrete Sustainability Conference*, National Ready Mixed Concrete Association, Arizona State University, Tempe, Arizona, USA, April 12-15, 2010b.

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, California, USA, 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, Nova Scotia, Canada, September 2010d.