3rd Specialty Conference on Material Engineering & Applied Mechanics
3e Conférence spécialisée sur le génie des matériaux et mécanique appliquée

Montréal, Québec
May 29 to June 1, 2013 / *29 mai au 1 juin 2013*

Durability of Concrete Produced with Portland Limestone Cement

A. M. Hossack[1], M.D.A. Thomas[1]
[1]Department of Civil Engineering, University of New Brunswick

Abstract: This paper presents data from laboratory and field studies on the durability of concrete containing Portland limestone cement (PLC) containing up to 15% interground limestone together with, in most cases, supplementary cementing materials (SCM) at replacement levels of up to 50%. The data indicate that, provided the PLC is ground sufficiently fine to achieve the same strength as normal Portland cement (PC) produced from the same clinker, the durability of concrete produced with PLC is equivalent to that produced using PC. Concrete produced with PLC-SCM combinations, with up to 50% SCM, also has equivalent durability to that produced with the same PC-SCM combinations. Trial concrete pavements produced with PLC and SCM that have been in service for up to 5 years also show the same performance as control sections produced with PC and SCM. The substitution of PC for PLC allows for reductions of approximately 10% in the CO_2 associated with the production of the cement, further reductions being achieved by partial replacement of the cement with SCM in the concrete.

1 Introduction

1.1 Portland Limestone Cement Production and Popularity

In Canada, Portland limestone cement (PLC) is produced by intergrinding raw limestone with Portland cement clinker and various forms of calcium sulfate (e.g. gypsum); note in some other countries it is permissible to blend limestone and cement without intergrinding. The production of PLC results in reduced CO_2 emissions because the interground limestone does not have to pass through the kiln and this reduces the carbon footprint of the cement significantly. Approximately one tonne of CO_2 is released per tonne of Portland cement clinker produced[1] due to a combination of two causes: the energy required to heat the kiln, usually produced by burning coal or natural gas; and the CO_2 released from the limestone during calcination (equation 1):

[1] $CaCO_3 \rightarrow CaO + CO_2$

[1] Note: although the "1 tonne of CO_2 per 1 tonne of clinker" is an oft-quoted statistic and a reasonable average for cement production worldwide, modern plants produce significantly less CO_2 per tonne of clinker due to improved thermal efficiency.

Therefore, the reduction of the amount of clinkered material results in an almost equal reduction (by mass) of the amount of CO_2 released. Replacement of 15% of Portland cement with interground raw limestone reduces the CO_2 by almost 15% or 0.15 tonne per tonne cement produced.

Currently CSA allows the replacement of up to 15% of Portland cement with raw limestone. However, replacement levels are generally lower than this (typically 10 to 12% limestone) to ensure that tolerances are met and that equivalent strength performance can be readily achieved. Note that Portland cements produced in Canada today are permitted to contain up to 5% interground limestone replacement. Presently much higher replacement levels, up to 35%, are commonly used in Europe. The European standard EN 197-1 includes cements CEM II/A (-L or –LL) and CEM II/B (-L or –LL), which include 6%-20% and 21%-35% limestone, respectively. Portland limestone cement (CEM II) is the most widely produced cement in Europe. The following table (Table 1) reveals how, by adjusting grinding time and Blaine fineness the European cements have achieved equivalent 28-day compressive strength with 15% replacement with different SCMs. Experience in Canada has shown that a Blaine increase of approximately 10 m^2/kg per 1% limestone replacement is, typically, necessary to achieve equivalent compressive strength (Thomas et al. 2010b).

Table 1 CEM II with 15% ”Additions”

Characteristic properties of the cements

Cement	Grinding time (min)	Specific surface (Blaine) (m^2/kg)	28d Compressive strength (MPa)
Portland cement	41	303	40.3
Portland limestone cement	60	511	40.5
Portland cement (pozzolana)	52	418	41.2
Portland cement (fly ash)	40	388	41.0

(Voglis, Kakali, Chaniotakis, & Tsivilis, 2005)

1.2 Barriers to the use of Higher Replacement Levels of Limestone

In laboratory testing samples with high limestone replacement level have exhibited inferior resistance to external sulfate attack, both conventional external sulfate attack (ESA) and, especially, thaumasite sulfate attack (TSA). In a review of the research that has been conducted on sulfate resistance of Portland limestone cements (Irassar, 2009) it was concluded that the predominant manner in which limestone affects sulfate resistance is increased permeability. If the fineness of the cement is not altered to account for the limestone content this will result in increased permeability, thus allowing sulfates to penetrate deeper into the cement matrix.

Extensive research, both laboratory and field research, has been conducted on the performance of Portland limestone cement in sulfate environments including studying the effect of C_3A content (Irassar et al. 2005), effect of calcium to silicon ratio (Bellmann & Stark, 2007), the effect of SCMs and aggregate type (Crammond & Collett, 2003), the effect of varying limestone content and sulfate exposure (Hartshorn et al. 1999), and many others. Despite the extensive research in this area, and two decades of using 5% interground limestone in cements in Canada, there has yet to be a documented case of thaumasite in Canada involving Portland limestone cement in field trials (Hooton & Thomas, 2002). Nonetheless, a significant amount of laboratory research has demonstrated inferior performance in sulfate environments, preventing the use of greater than 5% limestone replacement in cements exposed to sulfate environments in Canada.

The replacement of Portland cement with raw limestone effectively reduces the amount of Portland cement in concrete and increases the water-to-Portland cement ratio. The decreased cement content would be expected to reduce the performance of the concrete; however, as demonstrated in Table 1, equal compressive strength, and equivalent performance in other parameters can be achieved with PLC. There are two theories as to how limestone affects Portland cement hydration: the fineness of the limestone particles creates nucleation sites for the formation of hydration products; and limestone particles react chemically in the cement paste, creating more hydration products. In addition, the increased grinding required for PLC results in an increased fineness of the Portland cement clinker particles which, in turn, accelerates the hydration of the cement.

2 Field Trials

2.1 Three Outdoor Field Trials with PLC

Recent field trials were conducted with PLC produced at three different cement plants in combination with varying levels of fly ashes and slag. The field trials are in Gatineau, Quebec (Bath, Ontario cement), constructed in 2008; Exshaw, Alberta (Exshaw cement) constructed in 2009; and Brookfield, Nova Scotia (Brookfield cement) constructed in 2009. See Figure 1 for the locations of the field trials.

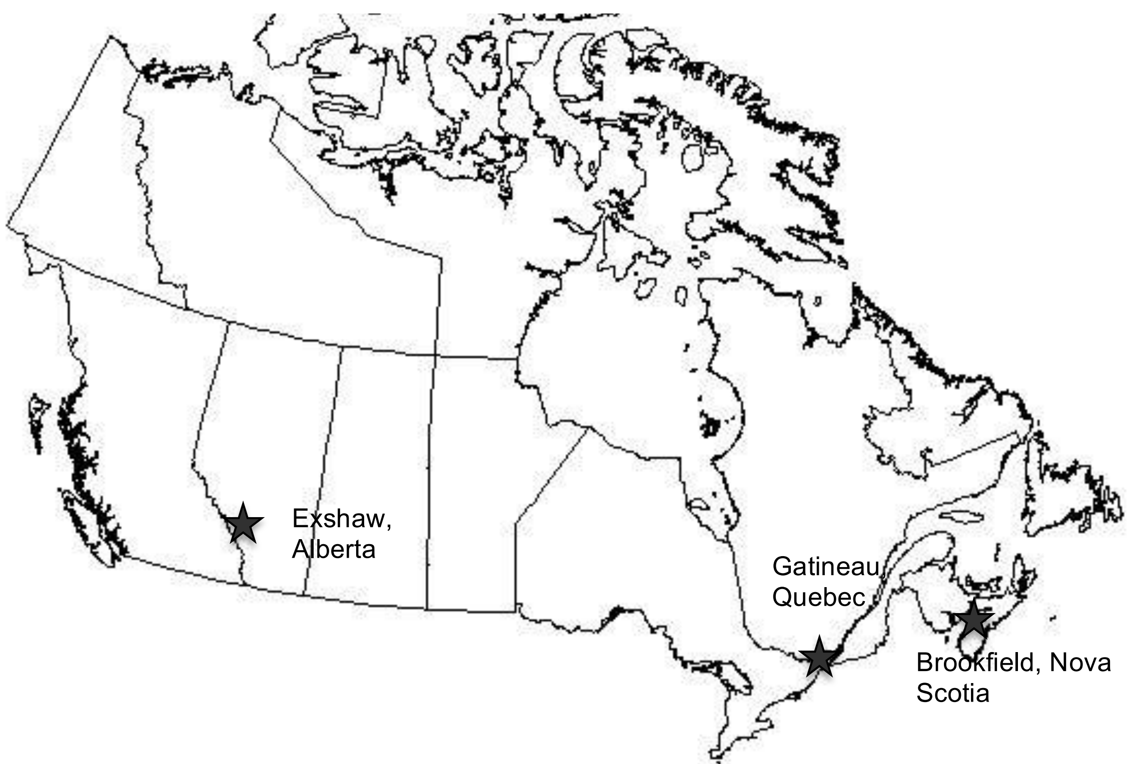

Figure 1 Locations of PLC field trials conducted in 2008 and 2009

The Gatineau field trial included two different cements (PC, 3.5% limestone; and PLC, 12% limestone) and SCM replacement levels of 0%, 25%, 40%, and 50%. The SCM used was a combination of 2/3 slag and 1/3 fly ash. The Exshaw field trial also included two cements (4% and 12% limestone) and fly ash replacement levels of 0%, 15%, 25%, and 30%. Lastly, the Brookfield trial, which was the only trial to include a blended cement (with 15% slag), incorporated three cements: PC-slag (0 limestone, 15% interground slag), PLC-slag (12% limestone, 15% interground slag), and PC (4% limestone, lab trial only). These cements were used in combination with fly ash replacements of 0%, 15%, and 20%. Class F fly ashes were used in all three field trials.

After three to four years in the field cores were taken from each of the pavements and tested for compressive strength, chloride penetrability (rapid chloride permeability test), and depth of carbonation. Furthermore, photos were taken of each pavement for a visual comparison of performance. Significant differences were observed as a function of varying SCM replacement levels; however, little variation existed in the performance of different limestone replacement levels despite the clinker content varying from 92% to 42% (Figure 2). The clinker contents and complete compositions of all mixes used in these projects are shown in the figure below; Exshaw cements (AB), Brookfield cements (NS) and the Gatineau cements (QC), The variations in performance will be discussed in greater detail throughout the paper.

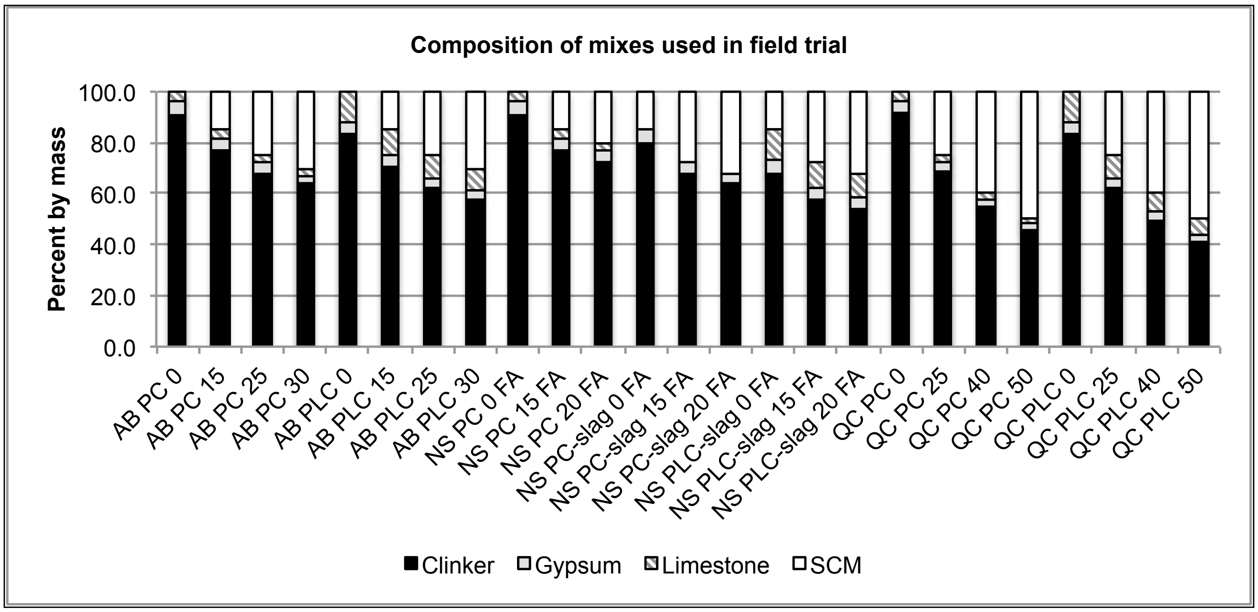

Figure 2 Clinker, gypsum, limestone, SCM content of mixes used in field trials

3 Results and Discussion

3.1 Fresh Properties of Concrete in Field Trials

Table 2 shows the properties of the fresh concrete. For the trials in Nova Scotia and Quebec, the concretes were batched with equal cementitious materials content and water-to-cementitious-materials (W/CM) ratio. In Alberta, advantage was taken of the reduced water demand imparted by the fly ash and the W/CM decreases with increasing fly ash content; however, each PLC mix (4% limestone) had the same W/CM as the companion PLC (12% limestone) mix. In all three trials the workability (slump) and air contents were controlled within a fairly small range by the judicious use of admixtures. Generally, the use of PC versus PLC had no significant impact on the fresh concrete properties.

Table 2 W/CM, Slump and Air Content of Concretes

Fresh Properties			
Location	W/CM	Slump (mm)	Air (%)
Brookfield, NS	0.42-0.44	60-80	5.8-6.6
Gatineau, QC	0.44-0.45	75-100	6.0-6.8
Exshaw, AB	0.37-0.42	95-135	6.0-7.8

3.2 Hardened Properties of Concrete in Field Trials

An understanding of the hardened properties of concrete is essential for evaluating the differences and similarities among different cementing materials; and therefore, selecting the appropriate materials. Throughout the field trials several key hardened properties were studied: compressive strength, chloride penetrability, depth of carbonation, salt scaling and a visual assessment of the performance of the pavements. The environmental differences that exist between the three different sites have lead to some variation in these properties.

Concrete cylinders were cast at the same time as the pavements to test the hardened properties. Furthermore, cores were taken after 35 days and 3 or 4 years to test the in-place concrete. The results of the hardened concrete tests are explained in detail below.

3.3 Compressive Strength

The compressive strengths of the cylinders were tested after 3, 7, 28, and 56 or 90 days. The graphs below (figures 3-5) include these values along with the compressive strengths of the cores taken after 3 or 4 years.

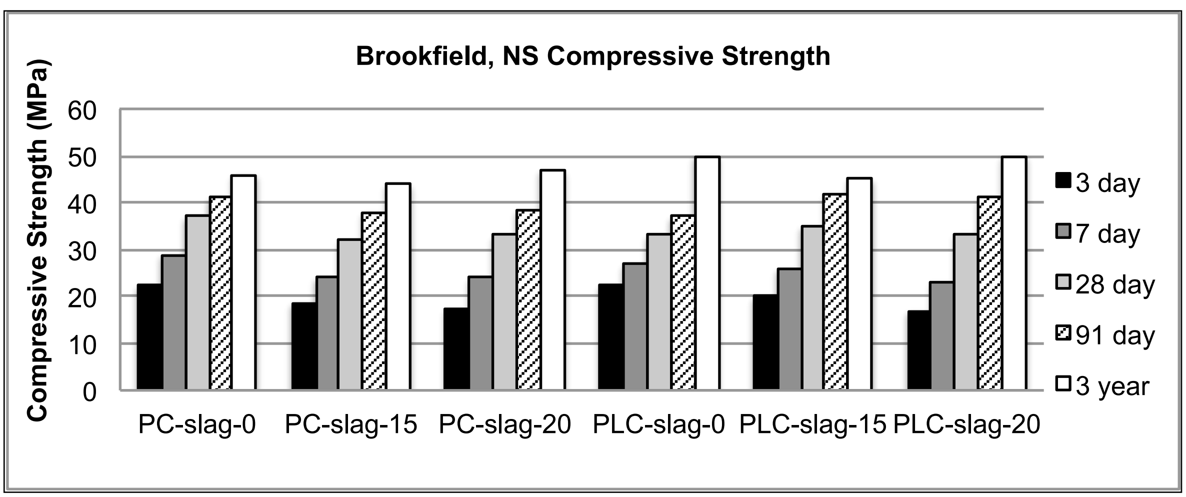

Figure 3 Brookfield, NS Compressive Strength

In the Nova Scotia trial the highest compressive strengths at early ages (3 and 7 days) were achieved with the concretes without fly ash. However, at later ages the concretes all reached similar compressive strengths (within 15% after 3 years). The presence of fly ash and limestone did not have a consistent effect on compressive strength.

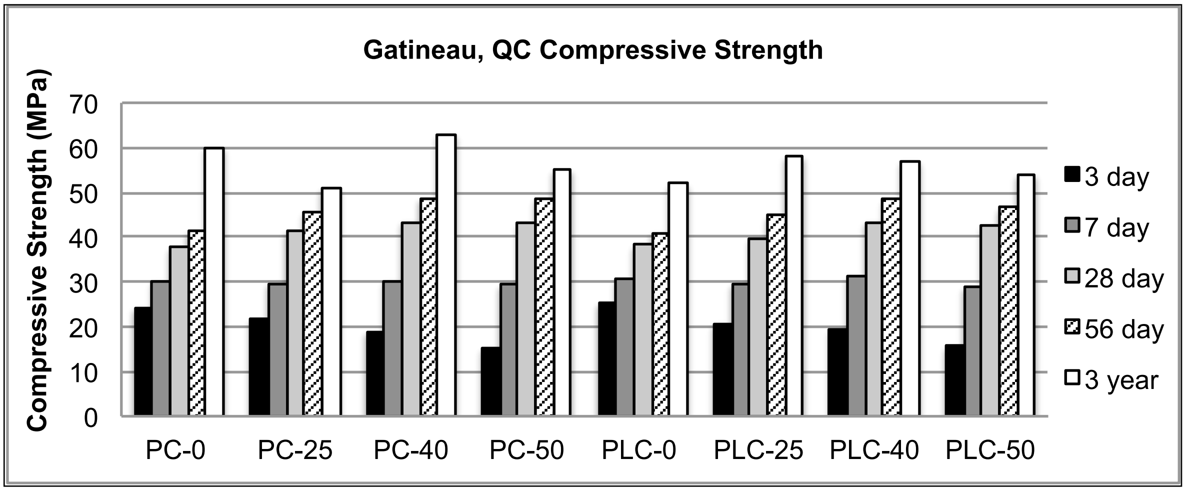

Figure 4 Gatineau, QC Compressive Strength

The 3-day strength in the Quebec trial exhibited a similar trend to that noted in the Nova Scotia trial; compressive strength decreased with increasing fly ash content. After 7 days the compressive strengths levelled off and, after 28 and 56 days the fly ash mixes surpassed the strength achieved with the control mixes. There was not a consistent trend in the 3-year data; the limestone and fly ash have not affected the long-term strength.

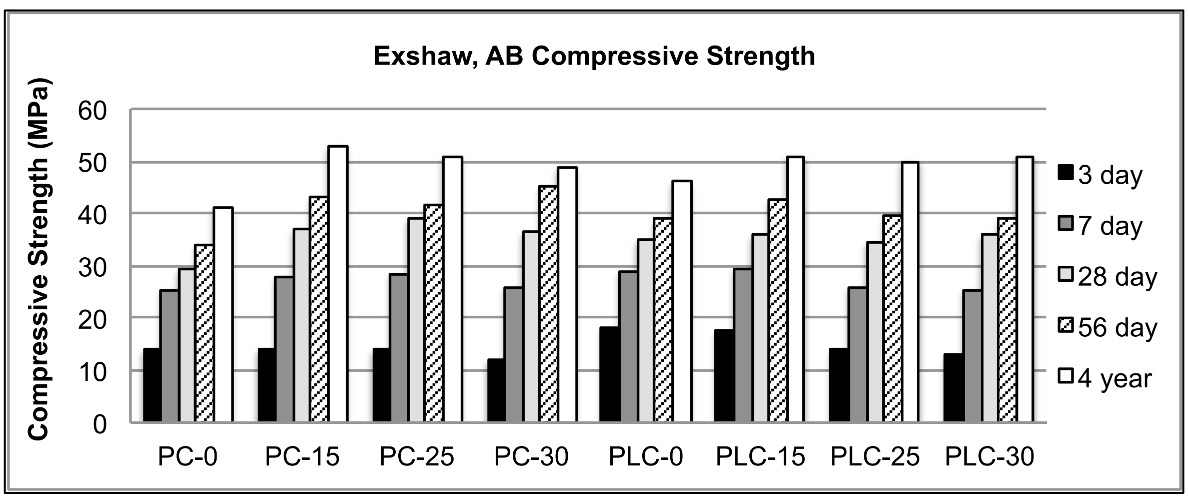

Figure 5 Exshaw, AB Compressive Strength

In the Exshaw trial similar compressive strengths were achieved among all mixes at early ages. This is likely due to the decreasing w/cm with increasing fly ash content as noted in *Fresh Properties* above. At later ages the control mixes had the lowest compressive strengths. Minimal variation exists in the PC versus PLC mixes; the limestone content has not affected the compressive strength.

3.4 Chloride Penetrability

Chloride penetrability of hardened concrete can be tested using the standard RCPT (Rapid Chloride Permeability Test, ASTM C1202), which measures the amount of electrical charge passing through a standard 50mm thick sample in a 6-hr period. The chloride penetrability of the pavements was tested at several ages. Only the 3- or 4-year results are discussed in this paper; RCPT data for cylinders and cores tested at earlier ages have been reported elsewhere (Thomas et al. 2010a; 2010b). The RCPT values for each of the 3- and 4-year cores are presented in the figure below, figure 6. Chloride penetrability is also being tested with the bulk diffusion test (ASTM C1556). Samples of the concrete cores not previously exposed to chlorides are submerged in sodium chloride solution (165 g/L) for 70 days; the depth of penetration and the concentration profile of the chlorides are measured and the diffusion coefficient calculated.

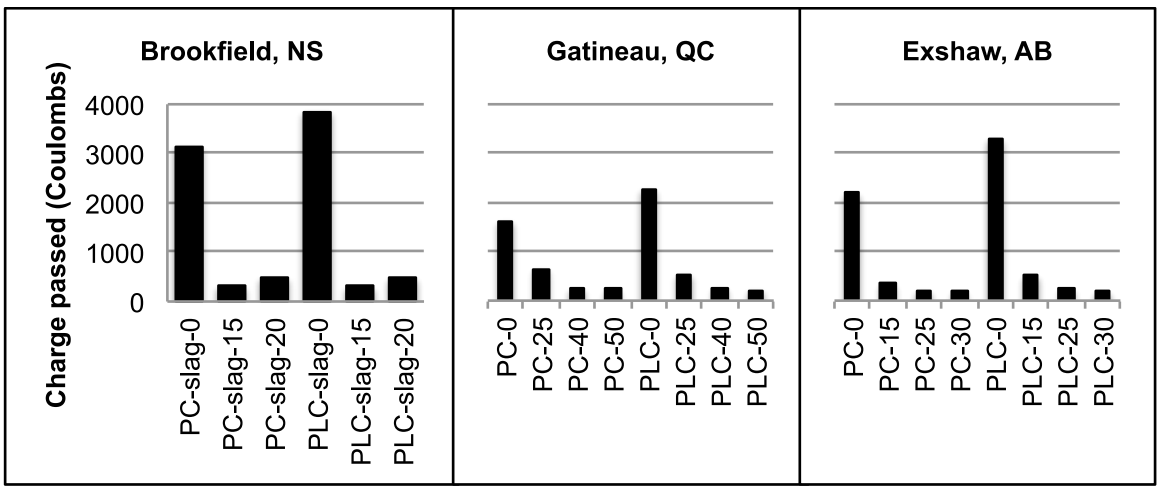

Figure 6 RCPT Chloride Penetrability of Concrete Cores

Based on the amount of charge passed through the sample the concrete will belong to one of five categories of permeability (negligible, very low, low, moderate, or high), see table 3. All of the concretes with SCMs exhibited negligible or very low permeability; the concretes without SCMs had moderate or high permeability. The concretes made with limestone cement had slightly greater permeability than the same mixes without limestone at later ages. No significant consistent differences in the RCPT were observed between companion PC and PLC concrete mixes for cylinders tested at earlier ages (28 to 91 days).

Table 3 Chloride Penetrability Ratings (from ASTM C 1202)

RCPT Permeability Rating

Charge passed (Coulombs)	Chloride ion penetrability
>4,000	High
2,000–4,000	Moderate
1,000–2,000	Low
100–1,000	Very Low
<100	Negligible

The diffusion coefficients of the concrete cores from all of the pavements will be measured; presently, only the data for the Exshaw pavements is complete (Table 4 and Figure 7 below).

Table 4 Diffusion Coefficients

Cement	SCM	Diffusion Coefficient (m^2/s)
PC	0 FA	7.6E-12
PLC	0 FA	2.1E-11
PC	15% FA	6.0E-13
PLC	15% FA	1.5E-12
PC	25% FA	9.9E-13
PLC	25% FA	5.5E-13
PC	30% FA	8.7E-13
PLC	30% FA	3.9E-13

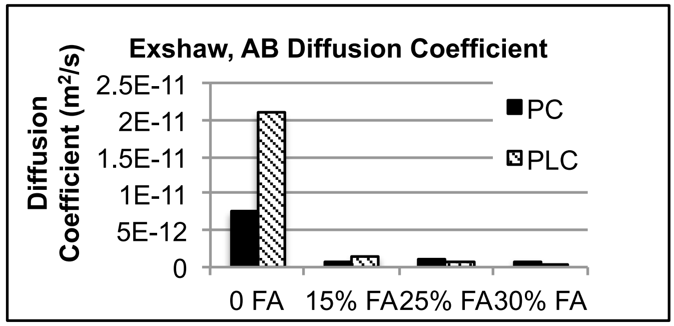

Figure 7 Diffusion Coefficients

The control pavement (0 fly ash content) cast with PLC had a considerably higher diffusion coefficient than the control pavement without limestone. However, the addition of fly ash reduced the diffusion coefficients of both the PC and PLC concretes. These results agree with the results of the rapid chloride permeability tests. The chloride profiles for the concrete cores from the Exshaw pavements with 0 fly ash, 15% fly ash, and 30% fly ashes are shown below (figure 8). For the control concrete without fly ash, the chloride concentrations at depths below 15 to 10 mm are increased for the concrete produced with PLC compared with PC. All of the concretes with fly ash have reached near-background chloride content within 7mm-8mm of depth in the concrete regardless of whether the concrete contained PC or PLC.

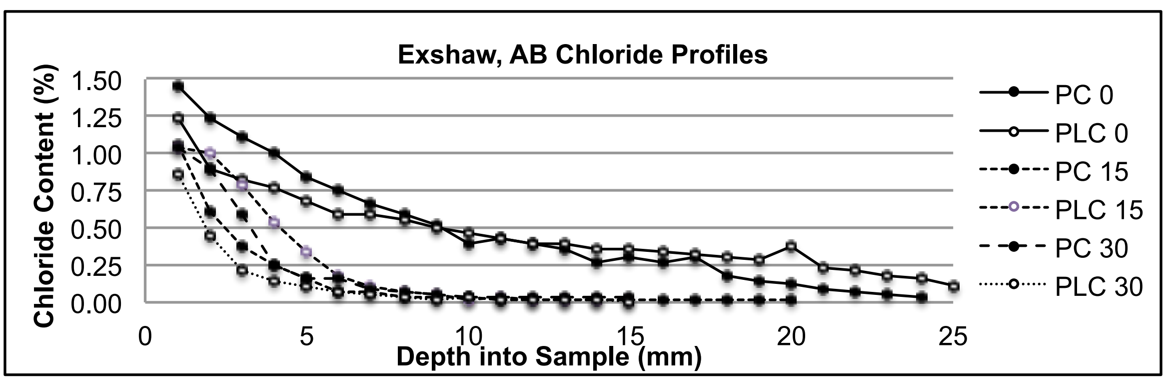

Figure 8 Chloride Profiles for Cores from the Exshaw Pavement after Ponding for 70 days in NaCl Solution (ASTM C 1556)

3.5 Depth of Carbonation

The depth of carbonation into the concrete was measured for each of the concretes. In the Brookfield, NS cores minimal (< 2 mm) carbonation was observed in all of the concretes. Very little carbonation was observed in the Gatineau, QC cores also; an average of 2.5 mm in the PC cores and an average of 1.1 mm in the PLC cores. The depth of carbonation was slightly greater in the Exshaw cores. The PC cores had on average 4.5 mm of carbonation; the PLC cores had 4.0 mm of carbonation. Among these results, the presence of SCMs did not have a consistent effect on the depth of carbonation.

3.6 Deicer Salt Scaling and Visual Assessment

The deicer salt scaling mass loss was evaluated with ASTM C672 for slabs cast at the time of placing the field trials. The resulting mass loss after 50 cycles is reported in figure 9.

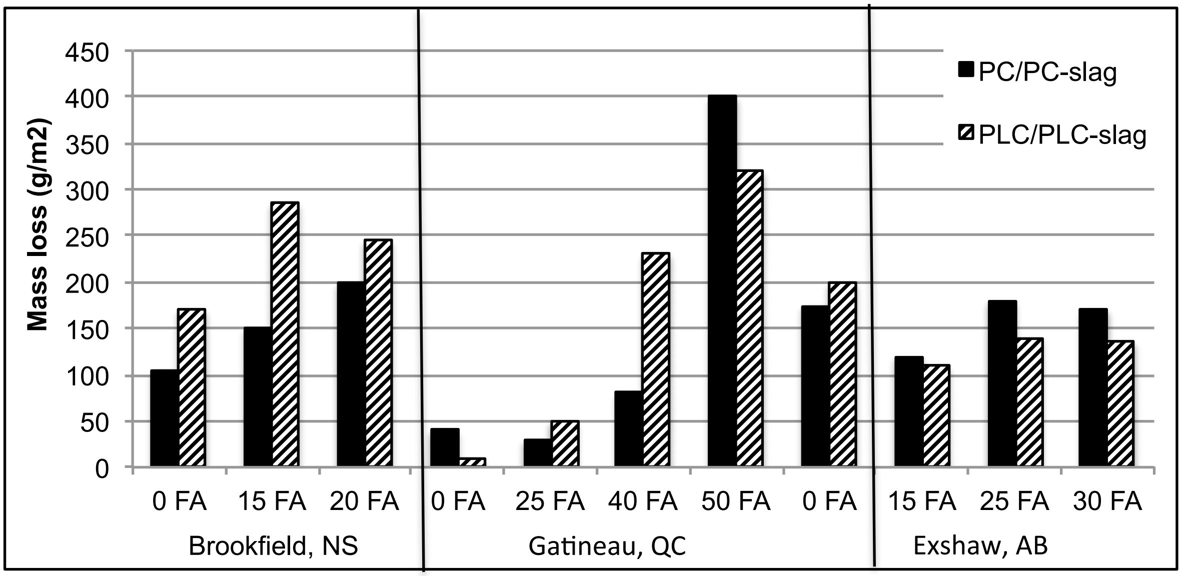

Figure 9 Deicer Salt Scaling Mass Loss

All of the results are well below the typical maximum limits of 800-1000 g/m^2. The concretes cast with limestone cement at the Brookfield, NS site (PLC-slag) appear to have slightly greater mass losses than their PC-slag counterparts. However, the same trend is not observed at the other sites. Mixes containing fly ash did, in general, exhibit higher amounts of scaling.

The visual inspections after 3 and 4 years of heavy wear indicate that all of the pavements are performing very well. Abrasion from heavy truck traffic and snow removal has caused some mass loss on the surfaces of all of the pavements. Given the harsh environments at the ready-mix and cement plants where these pavements are located, it's likely that very little of the observed mass loss is attributed to scaling. No significant or consistent differences were observed between concretes produced with different cements (PC versus PLC) or different amounts of fly ash. The performance of the pavements will continue to be monitored.

4 Conclusions

The replacement of Portland cement with SCM resulted in lower early age strengths; however, at later ages the SCM content did not affect the compressive strengths achieved. The limestone content did not affect the compressive strength at any age.

The permeability of the concretes was decreased significantly with as little as 15% SCM replacement. Both the PC and PLC concretes achieved very low permeability with the addition of fly ash.

All of the concretes had salt scaling results that were well within the acceptable limit. In the Nova Scotia trial the concretes with higher limestone content had greater mass losses than the same mixes without limestone. In the Quebec trial the mass loss increased with increasing SCM replacement.

After 3 and 4 years all of the concretes have performed very well; minimal surface abrasion or scaling has been observed.

Equal performance can be achieved with as little as 42% clinker. The increased Blaine fineness of the Portland limestone cement allows equal performance to be achieved despite the reduced clinker content.

5 References

Bellmann, F., & Stark, J. (2007). Prevention of thaumasite formation in concrete exposed to sulphate attack. *Cement and Concrete Research , 37*, 1215-1222.

Crammond, N., & Collett, G. L. (2003). Thaumasite field trial at Shipston on Stour: three-year preliminary assessment of buried concretes. *Cement and Concrete Composites , 25*, 1035-1043.

Hartshorn, S., Sharp, J., & Swamy, R. (1999). Thaumasite formation in Portland-limestone cement pastes. *Cement and Concrete Research , 29*, 1331-1340.

Hooton, R., & Thomas, M. (2002). *The Use of Limestone in Portland Cements: Effect on Thaumasite Form of Sulfate Attack.* Portland Cement Association, Research and Development Information.

Irassar, E. (2009). Sulfate attack on cementitious materials containing limestone filler - A review. *Cement and Concrete Research* , 241-254.

Irassar, E., Bonavetti, V., Trezza, M., & Gonzalez, M. (2005). Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20C. *Cement and Concrete Composites* , 77-84.

Thomas, M. D., Hooton, D., Cail, K., Smith, B. A., De Wal, J., & Kazanis, K. J. (2010a). Field Trials of Concretes Produced with Portland Limestone Cement. *Concrete International* , January, 35-41.

Thomas, M.D.A., Cail, K., Blair, B., Delagrave, A., Masson, P. and Kazanis, K. (2010b). “Use of low-CO2 Portland limestone cement for pavement construction in Canada.” *International Journal of Pavement Research and Technology*, 3 (5), pp. 228-233.

Voglis, N., Kakali, G., Chaniotakis, E., & Tsivilis, S. (2005). Portland-limestone cements. Their properties and hydration compared to those of other composite cements. *Cement and Concrete Composites*, 191-196.