

**1916-2016**  
Celebrating 100 Years of Excellence



*Research & Development Information*

PCA R&D SN3285a

# **Sulfate Resistance of Mortar and Concrete Produced with Portland- Limestone Cement and Supplementary Cementing Materials: Recommendation for ASTM C595/AASHTO M 240**

by R. D. Hooton and M. D. A. Thomas

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

[www.cement.org](http://www.cement.org)

©Portland Cement Association 2016  
All rights reserved

## KEYWORDS

Blended cement, ettringite, fly ash, portland-limestone cement, slag cement, sulfate resistance, supplementary cementing materials, thaumasite, concrete, portland cement

## ABSTRACT

This report summarizes extensive sulfate resistance testing of mortar bars (laboratory) and concrete (both in the laboratory and under simulated field conditions), with a focus on the performance of cements with between 5% and 15% limestone as an ingredient. The majority of the tests were conducted with portland-limestone cements produced from higher- $C_3A$  content clinkers (11% to 12%  $C_3A$ ) with some of the mortar tests using cements made with clinkers with more moderate- $C_3A$  content (8% to 9%  $C_3A$ ). The data show that when mitigated with appropriate levels of SCMs, there is no influence of limestone on sulfate resistance. Concretes made with ASTM C595 Type IL and IT cements blended with appropriate levels of SCMs are performing as well or better than ASTM C150 Type V cements in both mortar bars and in concrete in very severe sulfate exposure for up to 5 years. Modified (5°C) ASTM C1012 test results indicate that non-sulfate resistant mixtures are initially damaged by ettringite-based sulfate attack and thaumasite is only observed after significant deterioration. (This finding is supported by thermodynamic modeling.) As a result of the findings from these research projects, at this time, it is recommended that the *standard* ASTM C1012 test method (*not* modified to be conducted at 5°C) be used, as it is appropriate and sufficient for determining the sulfate resistance of ASTM C595 Type IL and IT cements, and for mixtures with supplementary cementing materials.

## REFERENCE

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.

**TABLE OF CONTENTS**

	<u>Page</u>
Keywords .....	i
Abstract .....	i
Reference .....	i
Table of Contents .....	ii
Executive Summary .....	1
1. Introduction.....	1
2. University of Toronto Studies.....	3
2.1 Introduction.....	3
2.2 Mortar Bar Studies at University of Toronto.....	4
2.3 Concrete Studies at University of Toronto .....	9
2.4 Discussion of Concrete Performance.....	15
2.5 Conclusions from the University of Toronto Concrete Studies.....	15
3. University of New Brunswick Studies.....	16
3.1 Introduction.....	16
3.2 Mortar Studies at University of New Brunswick.....	16
3.3 Concrete Studies at University of New Brunswick .....	16
3.4 Discussion of University of New Brunswick Results.....	18
4. Discussion of All Data .....	22
5. Conclusions and Recommendations .....	23
6. Acknowledgements.....	23
7. References.....	24

# Sulfate Resistance of Mortar and Concrete Produced with Portland-Limestone Cement and Supplementary Cementing Materials: Recommendation for ASTM C595/AASHTO M 240

by R. D. Hooton\* and M. D. A. Thomas\*\*

## EXECUTIVE SUMMARY

When Type IL and IT cements with up to 15% interground limestone were introduced in ASTM C595, it was decided to not allow their use in sulfate exposures until more data was collected and analysed due to concerns with possible increased risk of thaumasite sulfate attack. This restriction followed the approach initially taken in CSA A3001 when similar Type GUL cements were introduced in 2008. Since then, literature reviews as well as extensive mortar bar testing, and concrete testing, both in the lab and under simulated field conditions, were conducted. The data have shown that when mitigated with appropriate levels of supplementary cementing materials (SCMs), there was no influence of limestone on performance. Concretes made with Type IL and IT cements blended with appropriate levels of SCMs are performing as well or better than currently allowed ASTM C150 Type V cements in both mortar bars and in concrete in very severe sulfate exposures for 5 years. When modified to be performed at 5°C (40°F), ASTM C1012 test results indicated that non-sulfate resistant mixtures were initially damaged by ettringite-based sulfate attack and thaumasite was only observed after significant deterioration. Moreover, the 5°C (40°F), modified ASTM C1012 test accelerates deterioration whether or not limestone is present and does not provide a reliable indication of how cements or blends of cementing materials are going to perform in concrete exposed to sulfate at cold temperature in laboratory or field exposure. As a result it is concluded that the current ASTM C1012 test method is sufficient for determining the sulfate resistance of Type IL and IT cements, and for mixtures with additional supplementary cementing materials.

## 1. INTRODUCTION

The beneficial effect of SCMs and blended cements on sulfate resistance of concrete has been known for almost 100 years. With the exception of some Class C fly ashes that contain CaO contents in excess of 18% to 20% and possibly C<sub>3</sub>A, SCMs improve sulfate resistance by (Thomas 2013):

---

\* Professor and NSERC/CAC Chair in Concrete Durability & Sustainability, Department of Civil Engineering, University of Toronto, 35 St. George St., Toronto, ON, M5S 1A4, Canada; [hooton@civ.utoronto.ca](mailto:hooton@civ.utoronto.ca).

\*\* Chair and Professor of Civil Engineering, University of New Brunswick, Fredericton, NB, E3B 5A3, Canada; [mdat@unb.ca](mailto:mdat@unb.ca).

- (a) Reducing the rate of ingress of sulfate ions due to increased resistance to fluid penetration;
- (b) Diluting and, through pozzolanic reactions, reducing the content of calcium hydroxide in the paste (needed for gypsum and ettringite formation);
- (c) Diluting the amount of  $C_3A$  in the total cementitious binder; and
- (d) Possibly altering hydrated aluminate phases to ones less susceptible to sulfate attack, e.g. strätlingite.

The ASTM C1012 test method was developed to evaluate the beneficial effect of SCMs and blended cements on sulfate resistance. Limits on ASTM C1012 expansion have been adopted in ASTM C595, C1157, and the ACI 318 Building Code as well as in the appendices of ASTM C618, C989, and C1240. In Canada, limits for the CSA version of the ASTM C1012 test (CSA A3004-C8) have been adopted in CSA A3000 and in CSA A23.1.

In 2005, in response to growing pressures to reduce the environmental impact of cement, a proposal was made to the Canadian Standards Association Committee for Cementitious Materials (CSA A3001) to define portland-limestone cement (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 that report were that while there was an abundance of publications on the production and properties of PLC, there were insufficient data regarding the performance of PLC concrete in sulfate exposures.

One of the recommendations was that testing be initiated 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 cementing materials (SCM), remained efficacious when used with PLC as compared with portland cement (PC).

In 2006 when the review was conducted, the available literature indicated that 5% limestone was not a concern. Data for 10% limestone was limited and the data for 15% was mixed. It was also noted that most of the cited studies evaluated the performance of cements with relatively high  $C_3A$  contents (ranging from 8.2% to 13.1%  $C_3A$ ) with limestone additions in sulfate exposure, and one has to consider whether this is relevant information, as these cements would not be allowed by Canadian or ACI building codes to be used in sulfate exposures without use of sufficient SCMs. It was concluded that more work was needed on the performance, at both 5°C (40°F) and 23°C (73°F), of portland-limestone cements in combination with levels of SCMs currently known to provide good sulfate resistance, as well as on CSA Type MS and HS cements (ASTM Type II and V cements).

Since from the literature, and from experimental work conducted by universities and Canadian industry, concrete properties and performance of PLC in other exposures appeared to be satisfactory, portland-limestone cement containing up to 15% limestone, was introduced in the cement standard (CSA A3001) in 2008 and in the concrete standard (CSA A23.1) in 2009. At the time of introduction, it was decided that up to 15% interground limestone would be allowed 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 was ongoing and the restrictions regarding the use of PLC in sulfate exposure conditions were to be reviewed after longer-term testing had been completed.

The main concern was that introducing higher levels of ground limestone might increase the risk of thaumasite sulfate attack, especially at cool temperatures, where it tends to be favored.

When portland-limestone cements were adopted in ASTM C595/AASHTO M 240 in 2013, this same restriction was also included as the testing was still ongoing (for example, Thomas and Hooton 2010).

As the result of extensive testing of sulfate resistance at low-temperatures at Universities of Calgary, New Brunswick and Toronto, as well by several cement companies, a new version of the CSA A3004-C8 (essentially the same as ASTM C1012) was adopted where the mortar bars are exposed to 5% sodium sulfate solution at 5°C (40°F): CSA A3004-C8 Procedure B. After much discussion, and to be on the conservative side, it was agreed to set an expansion limit in the low temperature test at 0.10% after 18 months of sulfate exposure and limit the increase in expansion from 12 to 18 months to 0.03% (to be more conservative than the standard 12-month test). Also to provide an additional factor of safety based on evaluation of the available test data, it was agreed to also require minimum levels of specific SCMs in sulfate exposures. As a result, in 2010, CSA A3001 was revised 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. At the same time, sulfate resistance test programs for concrete at low temperatures were initiated at Universities of New Brunswick and Toronto. Based on the satisfactory interim concrete test data, in 2014 the CSA A23.1 concrete standard was also revised to allow use of portland-limestone cements in sulfate exposures, provided that concrete containing PLC also used the minimum levels of particular SCMs required to pass the tests according to CSA A3001, and the maximum w/cm of concrete in all levels of sulfate exposure is limited to 0.40.

As summarised in this report, there are now 5-year test data from these concrete test programs, and the results from those, as well as the wider scale mortar bar tests programs, now indicate that the numerous safeguards in CSA standards regarding PLC in sulfate exposures are overly excessive.

## **2. UNIVERSITY OF TORONTO STUDIES**

### **2.1 Introduction**

Studies at the University of Toronto (U of T) have included testing of mortars and concrete with a range of cementing materials at both laboratory and cool temperatures. The results of two of the three the mortar studies have been published in journal articles (Ramezani pour and Hooton 2013a and 2013b) and are only discussed briefly here. The concrete studies have included exposure of concrete samples in the laboratory at 5°C (40°F) and buried outdoors in tanks of sulfate solutions to simulate field conditions. Only preliminary data have been published in

conference proceedings and in oral presentations. This report will summarize the mortars studies, but focus on the concrete data.

## 2.2 Mortar Bar Studies at University of Toronto

**2.2.1. Effects of Portland-limestone cement on thaumasite sulfate attack in mortar bars.** In this study, the resistance of a portland cement and a portland cement with 21.8% interground limestone (higher than allowed in CSA, ASTM and AASHTO standards), both made using the same 12% C<sub>3</sub>A clinker, to sulfate attack at 5°C were evaluated. It should be noted that to obtain equal strength performance, the Blaine fineness of the 21.8% limestone blend was 562 m<sup>2</sup>/kg versus 402 m<sup>2</sup>/kg for the portland cement. Detailed results can be found in Ramezani-pour and Hooton (2013b). A modified version of ASTM C1012 was used where, after the mortar mixtures achieved 20 MPa (2850 psi) strength, the bars were placed in sodium sulfate solution cooled to 5°C (40°F). This test method has been standardized in CSA A3000 as A3004-C8 Procedure B. All length change measurements were taken at 5°C. The expansion of mortar bars exposed to sodium sulfate solution was measured over time and different chemical phases formed at various stages of the sulfate attack were identified using XRD. Although both sets of mortar bars expanded and failed, the mortar bars made with 21.8% interground limestone expanded more than 0.10% much sooner than the same cement without limestone. However, in both cases, results show that any deteriorating mortar bars stored at 5°C initially formed ettringite and gypsum causing some expansion, but expanded much more and ultimately, after significant deterioration, eventually started forming thaumasite. Damage due to ettringite formation opened up the microstructure, by extensively cracking of the samples at the early stages: the formation of thaumasite only occurred after initial damage due to ettringite formation. This is of significance since it demonstrates that thaumasite sulfate attack, separate from minor thaumasite formation in air voids, etc., does not initiate the deterioration; it only occurs in non-sulfate resistant systems after ettringite causes the primary degradation. This has been confirmed by thermodynamic modelling as detailed in Barcelo et al. (2014).

While the XRD analyses also confirmed that the ultimate disintegration of the samples stored at 5°C was due to thaumasite sulfate attack, it was interesting that both sets of samples including the Type I, which had no limestone, were destroyed. This shows that there must be sufficient minor amounts of carbonate in the cement or dissolved in the storage solutions during the period of test to allow thaumasite sulfate attack to occur. Therefore, the CSA standard test appears to be far more severe than field exposures where thaumasite sulfate attack is relatively rare.

**2.2.2 The effects of SCMs in mitigating sulfate attack at low-temperatures.** In this study a modified version of ASTM C1012 (CSA A3004-C8, Procedure B), conducted at 5°C (40°F), was used. All length change measurements were taken at 5°C. A portland cement clinker with 12% C<sub>3</sub>A content was interground at a cement plant with 0%, 2.4%, 10.6%, 12.7%, and 21.8% limestone and combinations with 0%, 30%, and 50% slag were examined after sulfate exposure at both 5 and 23°C. It was found that in 23°C exposure, while 100% cement mixes deteriorated due to conventional ettringite-based sulfate attack, partially replacing the cements with 30% or 50% slag was effective in making the mixes highly sulfate-resistant. At 5°C, all of the 100% cement mortar bars expanded more than the test limits due to initial ettringite formation, and eventually completely disintegrated due to the formation of thaumasite. Partially replacing the

high-C<sub>3</sub>A cement with 30% slag was only effective in controlling the deterioration for portland cements but not portland-limestone cements. However, all the portland-limestone cements with 50% slag were resistant to sulfate attack after 2 years exposure. Note that the 5°C expansion limit adopted in CSA A3001 is 0.10% at 18 months. Detailed results can be found in Ramezani-pour and Hooton (2013a).

**2.2.3 Effects of increased initial curing on sulfate resistance in C1012 at 5°C and 23°C.** A mortar bar study was undertaken in 2013-2015 to evaluate the impact of increasing curing of blended cements or PC-SCM mixtures prior to exposure to the ASTM C1012 sulfate resistance test. This was undertaken since the ASTM C1012 test method only requires that mortars reach 20 MPa (2850 psi) with initial curing at 35°C for 24 hours in a moist closet prior to demolding, and prior to sulfate exposure. This is often attained at 24 h or 48 h when high SCM replacement levels are used. This is of concern since the mortar microstructure has not fully developed due to insufficient hydration, since SCM's such as slag and fly ash will have not yet reacted to any great extent prior to sulfate exposure. The original reason for developing the ASTM C1012 test method was to allow SCMs to react prior to sulfate exposure (unlike the ASTM C452 test), and the original draft method required the mortar mixtures to attain 27.6 MPa (4000 psi) prior to sulfate exposure. Unfortunately, prior to its adoption in 1984, it was decided to reduce this strength to 20 MPa to shorten the time of test by 1 or 2 days. Since then it has been found, especially with some Class F fly ashes, that it is difficult to meet the ASTM C1012 expansion criteria adopted in the ASTM C595 and C1157 specifications as well as in the ACI 318 Building Code as shown in Table 2.1.

**Table 2.1. Test Limits for cementitious materials in different classes of sulfate exposure**

Exposure class	Maximum exposure strain if tested using ASTM C1012		
	At 6 months	At 12 months	At 18 months
S1	0.10 %	No requirement	No requirement
S2	0.05 %	0.10 %*	No requirement
S3	No requirement	No requirement	0.10 %

Source: ACI 318-14 Table 26.4.2.2(c).

\*The 12-month expansion limit applies only if the measured expansion exceeds the 6-month expansion limit.

As a result, and independent of the limestone issue, in 2015 ASTM Subcommittee C01.29 initiated an interlaboratory evaluation where a series of cementitious systems are being tested using the standard curing as per ASTM C1012 and alternately after curing in limewater for 7 days at 38°C. Preliminary tests had shown that bulk resistivity (an indirect indicator of resistance to fluid ingress) of mortars containing SCMs was significantly increased after the alternative 7-day curing.

With the modified low-temperature expansion test, adopted as CSA A3004-C8, Procedure B, this problem of early-age exposure is even worse. At 5°C, SCMs, and especially Class F fly ashes, hydrate far more slowly than when stored at 23°C.

In this study, 23 mixtures were made with different portland cements and portland-limestone cements, with and without different SCM replacements, and tested both after curing until 20 MPa and after 7-day curing at 38°C. The Bogue-estimated C<sub>3</sub>A content of the Type GU cement used with different levels of interground limestone to create PLC was 9.9%. The Type II/V cement had a C<sub>3</sub>A of 4.7%. The C<sub>3</sub>A of HS-A was 2.0% and in HS-B was 4.2%. In 2015, an additional 18 mixtures were cast. Strengths at initial sulfate exposure ranged from 20.6 MPa to 27.7 MPa for the standard curing and 37.3 MPa to 49.5 MPa after the alternative 7-day curing.

For the 23 mixtures cast in 2013-2014, the expansions when stored at 23°C are shown in Table 2.2. The legends for cement types are as per CSA A3001 (e.g. CSA Type GU, which is equivalent to ASTM C150 Type I). Values in red have exceeded 0.10% expansion. For the standard ASTM C1012 curing, mixes 1, 12, 19, 20, 21, and 22 exceeded the 12-month, 0.10% expansion limit in ASTM C595. It should be noted that Mixes 21 and 22 are ASTM Type V (CSA Type HS) cements that have a long history of satisfactory use in very severe sulfate exposures in western Canada. The two Class F fly ashes (A and B) are widely used in western Canada in sulfate exposures.

After 7 days of curing at 38°C, there was very little change in the mixtures that passed or failed the 12-month expansion limit, the only additional failure was for mix #6 with 15% metakaolin. However, the expansions of the Class F fly ash mixtures were lower with the 7-day curing. It was also found that, with 7 days of curing, if the 6-month 0.05% expansion limit was met, the same mixtures expanded less than 0.10% at 18 months.

The low-temperature mortar bar expansions at 5°C for the same two curing regimes are shown in Table 2.3. With mortar specimens cured to 20 MPa, only 4 of the 23 mortar mixtures met the CSA A3001 18-month expansion limit of 0.10%. When given 7 days of curing, 8 mixtures passed this expansion limit, notably those with slag and/or silica fume. The fly ash mixtures were unable to pass the 18-month limit.

**Table 2.2. ASTM C1012 expansion after standard curing to 20 MPa and after 7 days of curing at 38°C**

Mix #	Binder	A						E						concrete condition at 4 years
		Curing as per C1012 then exposed at 23C						Curing 7d at 38C, then exposed at 23C						
		3 months	6 months	9 months	12 months	15 months	18 months	3 months	6 months	9 months	12 months	15 months	18 months	
1	GU (Type I)	0.036	0.110	0.280	0.773	x	x	0.035	0.258	0.66	x	x	x	poor
13	GU+25FA (A)	0.029	0.047	0.053	0.079	0.110	0.128	0.018	0.029	0.033	0.050	0.057	0.070	no test
11	GU+30FA (A)	0.032	0.063	0.077	0.115	0.159	0.189	0.031	0.061	0.076	0.115	0.153	0.178	no test
12	GU+35FA (A)	0.031	0.048	0.055	0.076	0.101	0.112	0.018	0.029	0.033	0.052	0.058	0.069	no test
6	GU+15MK	0.023	0.036	0.042	0.045	0.047	0.052	0.021	0.065	0.195	0.391	x	x	good
3	GU+40Slag	0.023	0.038	0.044	0.054	0.057	0.068	0.015	0.032	0.036	0.047	0.058	0.066	excellent
2	GU+50Slag	0.021	0.036	0.040	0.048	0.049	0.056	0.012	0.024	0.028	0.034	0.039	0.042	excellent
5	GU+65F+25Slag	0.017	0.029	0.032	0.040	0.044	0.055	0.012	0.023	0.024	0.033	0.034	0.034	excellent
4	GU+85F	0.017	0.029	0.032	0.043	0.047	0.055	0.014	0.025	0.028	0.037	0.041	0.044	excellent
7	PLC 9 + 40Slag	0.019	0.034	0.038	0.046	0.052	0.058	not tested						good
8	PLC 9 + 50Slag	0.019	0.032	0.035	0.039	0.042	0.046	not tested						excellent
9	PLC 15 + 40Slag	0.018	0.033	0.039	0.044	0.046	0.055	0.014	0.021	0.025	0.036	0.037	0.042	good
10	PLC15 + 50Slag	0.022	0.029	0.034	0.040	0.043	0.047	0.011	0.019	0.023	0.031	0.031	0.036	excellent
17	PLC15 + 65F +25Slag	0.019	0.022	0.027	0.031	0.037	0.038	0.018	0.02	0.028	0.034	0.039	0.044	excellent
14	PLC10.5 + 25FA (B)	0.034	0.042	0.044	0.053	0.059	0.075	0.016	0.021	0.027	0.033	0.052	0.062	excellent
23	PLC10.5 + 35 FA (B)	0.034	0.048	0.059	0.072	0.074	0.075	0.011	0.015	0.022	0.028	0.028	0.028	good
15	PLC10.5 + 40S	0.029	0.037	0.038	0.043	0.046	0.048	0.016	0.022	0.027	0.032	0.038	0.044	excellent
16	PLC10.5 + 50S	0.023	0.03	0.035	0.040	0.046	0.049	0.016	0.02	0.027	0.031	0.037	0.039	excellent
18	PLC12 +30FA(A)	0.024	0.033	0.06	0.071	0.092	0.108	0.009	0.015	0.020	0.027	0.042	0.049	no test
19	II/V-L10	0.041	0.107	0.231	0.375	0.512	x	0.028	0.152	0.302	0.460	0.564	x	poor
20	II/V-L5	0.028	0.065	0.121	0.182	0.261	x	not tested						poor
21	HS-A	0.033	0.062	0.108	x	x	x	0.021	0.08	0.141	x	x	x	good
22	HS-B	0.053	0.214	0.379	x	x	x	0.063	0.235	0.397	x	x	x	good

It was observed that after 7 days of curing, mixtures that had not exceeded 0.04% expansion at 6 months also passed the CSA A3001 expansion limit of 0.10% at 18 months. If this is confirmed by the additional 18 mixtures still in test, then the current 0.10% 18-month limit could be replaced by a 6-month limit of 0.04%.

**2.2.4 Discussion of Mortar Bar Results.** When tested in CSA A3004-C8 Procedure B [modified ASTM C1012 tests where mortar bars are exposed to sodium sulfate solution at 5°C (40°F)], the performance of blends of PC-SCM and PLC-SCM, is variable (poor with class F fly ashes, but better with slag and silica fume) even though most of these blends passed the standard ASTM C1012 (CSA A3004-C8 Procedure A) tests at 23°C. At 5°C, many of the mortar mixtures exceeded the CSA 18-month 0.10% expansion limit, and often failed at early ages. Extending the curing time to 7 days at 38°C (100°F) prior to 5°C (40°F) sulfate exposure improves performance, but not sufficiently for the fly ash mixtures tested and Type V portland cements.

**Table 2.3. CSA A3004-C8 Procedure B expansions at 5°C after standard curing to 20 MPa and after 7 days of curing at 38°C**

Mix #	Binder	B						C						concrete condition at 4 years
		Curing as per C1012 then exposed at 5C						Curing 7d at 38C, then exposed at 5C						
		3 months	6 months	9 months	12 months	15 months	18 months	3 months	6 months	9 months	12 months	15 months	18 months	
1	GU (Type I)	0.034	x	x	x	x	x	0.054	0.234 (4m)	x	x	x	x	poor
13	GU+25FA (A)	0.038	x	x	x	x	x	0.015	0.060	x	x	x	x	no test
11	GU+30FA (A)	0.180	x	x	x	x	x	0.029	0.090 (4m)	x	x	x	x	no test
12	GU+35FA (A)	0.067	x	x	x	x	x	0.016	0.042	x	x	x	x	no test
6	GU+15MK	0.031	0.050	0.074	0.101	x	x	0.031	0.048 (4m)	x	x	x	x	good
3	GU+40Slag	0.028	0.043	0.055	0.066	0.077	0.120	0.014	0.024	0.032	0.041	0.051	0.075	excellent
2	GU+50Slag	0.025	0.040	0.054	0.062	0.074	0.108	0.012	0.024	0.03	0.033	0.042	0.043	excellent
5	GU+65F+25Slag	0.024	0.045	0.051	0.060	0.070	0.075	0.015	0.026	0.035	0.039	0.054	0.059	excellent
4	GU+85F	0.028	0.042	0.068	0.100	0.118	0.141	0.013	0.019	0.027	0.033	0.052	0.080	excellent
7	PLC 9 + 40Slag	0.026	0.112	0.211	0.320	0.481	x	not tested						good
8	PLC 9 + 50Slag	0.029	0.086	0.108	0.125	0.165	0.225	not tested						excellent
9	PLC 15 + 40Slag	0.027	0.064	0.086	0.104	0.123	0.169	0.019	0.044	0.063	0.093	0.135	0.211	good
10	PLC15 + 50Slag	0.032	0.062	0.072	0.085	0.093	0.095	0.010	0.032	0.036	0.048	0.051	0.052	excellent
17	PLC15 + 65F + 25Slag	0.028	0.038	0.051	0.056	0.059	0.059	0.011	0.014	0.028	0.033	0.048	0.052	excellent
14	PLC10.5 + 25FA (B)	x	x	x	x	x	x		0.051	x	x	x	x	excellent
23	PLC10.5 + 35 FA (B)	0.247	x	x	x	x	x	0.008	0.014	x	x	x	x	good
15	PLC10.5 + 40S	0.029	0.057	0.084	0.106	0.138	0.201	0.017	0.026	0.041	0.058	0.072	0.090	excellent
16	PLC10.5 + 50S	0.029	0.039	0.054	0.063	0.067	0.073	0.015	0.02	0.024	0.029	0.044	0.045	excellent
18	PLC12 +30FA(A)	0.079 (2m)	x	x	x	x	x	0.014	0.062	x	x	x	x	no test
19	II/V-L10	0.041	0.105	0.227	0.369	x	x	0.028	0.264	1.339	x	x	x	poor
20	II/V-L5	0.023	0.059	0.127	x	x	x	0.020	0.048	0.167	0.449	x	x	poor
21	HS-A	0.027	0.042	0.053	x	x	x	0.017	0.048	0.089	x	x	x	good
22	HS-B	0.035	0.132	0.470	x	x	x	0.042	0.192	0.597	x	x	x	good

The takeaways from the mortar bar studies are:

1. ASTM C1012 mortars should be cured for 7 days in a moist environment at 38°C prior to sulfate exposure for both the 23°C and 5°C exposure tests to allow SCMs to hydrate.
2. Class F fly ash mixtures are able to pass the ASTM C595 expansion limit when given 7 days of curing prior to exposure; however, they are unable to pass the 5°C test. CSA Type GUL (ASTM Type IL) cements mixed with slag and/or silica fume can pass the CSA A3004-C8, Procedure B, 5°C test with 7 days of extended curing.
3. The 5°C test period can possibly be shortened from the CSA A3001 maximum expansion of 0.10% at 18 months in all sulfate exposures to a maximum expansion of 0.04% at 6 months when modified using extended curing for 7 days at 38°C.

Also, given both the experimental and thermodynamic modelling evidence that degradation of non-sulfate resistant mixtures at low temperatures occurs by initial formation of ettringite, with thaumasite only forming after significant deterioration has occurred, the need for adoption of a 5°C mortar bar test method to demonstrate sulfate resistance is doubtful. In addition, ASTM Type V cements appear to be unable to pass the 5°C test adopted by CSA in spite of over 80 years of good performance in concrete structures in cold climates.

## 2.3 Concrete Studies at University of Toronto

For the concrete studies, mixtures were produced with a water-to-cementing-materials ratio (w/cm) of 0.40, 0.50 or 0.70 and concrete prisms were cast with either a 50 × 50-mm (2 × 2-inch) or 75 × 75-mm (3 × 3-inch) cross-section for laboratory or field exposure, respectively. The mix proportions used are shown in Table 2.4. Cements designated as PC-4, PLC-9 and PLC-15 were the same used in the UNB studies and were produced from a high-C<sub>3</sub>A (12%) clinker with, respectively, 4%, 9% and 15% interground limestone. All cementing materials were obtained from commercially available sources. A CSA A3001 Type HSB blended cement that is being used in sulfate exposures in field concrete in western Canada was included; it is composed of a clinker with less than 8% C<sub>3</sub>A content interground with 30% Class F fly ash. In each case, the fineness of the finished cements was targeted such that the cements produced from each of the two clinkers achieved equivalent 28-day mortar strengths. The exception to this was the PLC-9 cement, which had lower 28-day strengths, but was included prior to this being realized.

The 0.40 w/cm concretes used 400 kg/m<sup>3</sup> (670 lb/yd<sup>3</sup>) cementitious materials, 1070 kg/m<sup>3</sup> (1795 lb/yd<sup>3</sup>) of a 20-mm (¾-in.) crushed dolomitic limestone coarse aggregate, and a glacial sand of mixed origin. The 0.50 w/cm concretes were similar but used 320 kg/m<sup>3</sup> (540 lb/yd<sup>3</sup>) cementitious materials. The 0.70 w/cm concretes used 230 kg/m<sup>3</sup> (388 lb/yd<sup>3</sup>) cementitious materials and 1040 kg/m<sup>3</sup> (1750 lb/yd<sup>3</sup>) coarse aggregate. All mixtures were air-entrained to a target of 6.5 ± 1.5% air, with a standard dose of water reducer, and high-range water reducer added as needed to attain a target slump of 100 mm ± 30 mm (4 in. ± 1.2 in.). A summary of the mix proportions is given in Table 2.4.

Concrete batches were cast, starting in 2010, with additional mixtures added in 2011 and 2012. Concrete prisms were exposed to sulfate solutions after moist curing at 23°C (73°F) for 28 days.

**Table 2.4. Proportions used for U of T control mixtures\***

W/CM	0.40	0.50	0.70
Cementing materials (kg/m <sup>3</sup> )	400	320	230
Water (kg/m <sup>3</sup> )	160	160	161
Coarse aggregate (kg/m <sup>3</sup> )	1070	1070	1040
Fine aggregate (kg/m <sup>3</sup> )	699	767	869
Target air (%)	6.5	6.5	6.5

\*For SCM mixtures adjustments were made to the sand content to compensate for differences in the specific gravity of the SCMs.

Concrete specimens were periodically measured to determine changes in length, mass and resonant frequency. These data are not presented here as, for most mixes, the duration of exposure has not been sufficiently long yet for significant changes in the bulk properties to have occurred. What is most evident after 4 to 5 years is surface damage which ranges from no visible damage, to a loss of corners and edges, to complete loss of the surface concrete, and finally to complete deterioration. Consequently, a visual rating system from 0 to 5 was developed as shown below, and this is used to present the findings for some of the concretes in field exposure.

- 0 = Undamaged:** Excellent Condition. No visible damage
- 1 = Minor damage:** Slight mass loss and/or cracking at some corners and/or some longitudinal edges
- 2 = Minor to Moderate damage:** Slight to moderate mass loss and cracking at some corners and/or longitudinal edges
- 3 = Moderate damage:** Moderate mass loss and/or cracking at some corners and/or some faces. Localized scaling at some faces
- 4 = Moderate to Severe damage:** Moderate to severe mass loss and/or cracking at most of the faces and corners. Widespread scaling at most of the faces
- 5 = Severe damage:** Severe mass loss from all faces and ends. Complete peeling of surface paste from all faces and both ends.

The following sulfate concentrations were used for laboratory exposure at 5°C: 5% Na<sub>2</sub>SO<sub>4</sub> (33,800 ppm SO<sub>4</sub>), 5.0 % MgSO<sub>4</sub> (14,400 ppm SO<sub>4</sub>), and saturated limewater. All solutions were maintained at 5°C (40°F). In addition to visual inspection, concrete specimens were measured at 3-month intervals to determine changes in length, mass and resonant frequency. Some specimens are also being examined using microscopy and XRD. This work is in progress, and is not included here.

For the concretes in field exposure, the solutions were: 15,000 ppm SO<sub>4</sub> (Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>) to represent ACI 318 S3 exposure class for the concretes cast at w/cm = 0.4 and 0.5. For concretes cast at w/cm = 0.7, 1,500 ppm SO<sub>4</sub> (Na<sub>2</sub>SO<sub>4</sub>) solution was used to represent S2 exposure class. The field specimens were buried 2.5 m (8 feet) below ground level in covered, high-density polyethylene containers and the tanks were covered with 1.3 m (4 feet) thick sheets of rigid foam insulation to limit freezing in winter and limit hot temperatures in summer. This resulted in an annual temperature range varying from approximately 3°C to 16°C (38°F to 61°F).

These concrete specimens have been measured annually to determine changes in length, mass and for visual assessment. When removed from the outdoor site, each prism is rinsed in water, and then stored in lime water for 24 to 48 h to condition them to 23° ± 2°C prior to measuring length and mass. Each prism is also photographed.

Visual ratings for the concretes cast at w/cm = 0.40 after 12, 24, 36, and 54 months of exposure are summarized in Table 2.5.

**Table 2.5. Visual Ratings of 0.40 w/cm concretes in outdoor exposure for up to 54 months exposure (updated from Hooton, Ahani, and Fung, 2014)**

Sulfate Type Exposure Period (months)	15,000 mg/L Sodium Sulfate				15,000 mg/L Magnesium Sulfate			
	12	24	36	54	12	24	36	54
<b>GU</b>	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe
<b>GU 40% Slag</b>	Undamaged	Minor	Minor	Minor	Minor	Minor	Minor	Minor
<b>GU 8% Silica Fume</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>GU 6% SF + 25% Slag</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>GU 15%MK</b>	Undamaged	Minor	Minor	Minor	Minor	Minor	Minor	Minor
<b>GU 10% MK+ 25% Slag</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>PLC9</b>	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe
<b>PLC9 40% Slag</b>	Undamaged	Minor	Minor	Minor	Minor	Minor	Minor	Minor
<b>PLC9 50% Slag</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>PLC15</b>	Severe	Severe	Severe	Severe	Severe	Severe	Severe	Severe
<b>PLC15 40% Slag</b>	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor	Minor
<b>PLC15 50% Slag</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>PLC15 8% Silica Fume</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>PLC15 6% SF + 25% Slag</b>	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor	Minor
<b>PLC15 15%MK</b>	Undamaged	Minor	Minor	Minor	Minor	Minor	Minor	Minor
<b>PLC15 10%MK+ 25% Slag</b>	Undamaged	Undamaged	Undamaged	Undamaged	Undamaged	Minor	Minor	Minor
<b>Type II/V</b>	Undamaged	Minor	Moderate	Severe	Undamaged	Minor	Minor	Moderate
<b>Type II/V 5% CaCO<sub>3</sub></b>	Undamaged	Minor	Severe	Severe	Undamaged	Minor	Moderate	Severe
<b>Type II/V 10% CaCO<sub>3</sub></b>	Minor	Moderate	Severe	Severe	Minor	Moderate	Moderate	Severe
<b>MS 30% F-Fly Ash</b>	Undamaged	Minor	Minor	Minor	Minor	Minor	Minor	Minor

**(PC/PLC)-Slag vs Type V/HS/HSb / w/c=0.4 / (54 months) / 15,000 ppm Na<sub>2</sub>SO<sub>4</sub>**

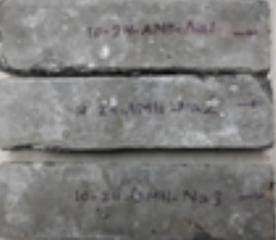
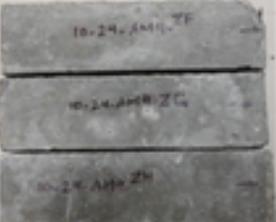
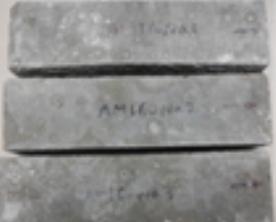
<b>GU-40S</b>	<b>PLC9-40S</b>	<b>PLC15-40S</b>	<b>HS (1)</b>
			
<b>MIN [1]</b>	<b>MIN-MOD [2]</b>	<b>MIN [1]</b>	<b>SEV [5]</b>
	<b>PLC9-50S</b>	<b>PLC15-50S</b>	<b>HSb (30FA)</b>
			
	<b>UND [0]</b>	<b>UND [0]</b>	<b>MIN [1]</b>

Figure 2.1. Visual condition of 0.40 w/cm field exposed concretes in 15,000 ppm sodium sulfate for 54 months

**2.3.1 Visual Condition of 0.40 w/cm concretes exposed to 15,000 ppm Na<sub>2</sub>SO<sub>4</sub> (ACI Exposure S3).** In Figure 2.1, the performance of Type I (GU) cement with 40% slag is similar to those of Type IL PLC-9 and PLC-15 cements with 40% slag. With 50% slag, neither of the PLC-9 or PLC15 cement concretes is showing any damage after 54 months exposure. In comparison all of the mixtures are in far better condition than the Type V (HS) cement concrete. In Figure 2.2, a Type IL cement, PLC-10.5 with 40% slag is performing the same as two Type V (HS) Portland cements, and PLC-10.5 with 50% slag is performing better with no visual damage.

**PLC(10.5)-Slag vs Type V w/c=0.4 / (33 months) 15,000 ppm Na<sub>2</sub>SO<sub>4</sub>**

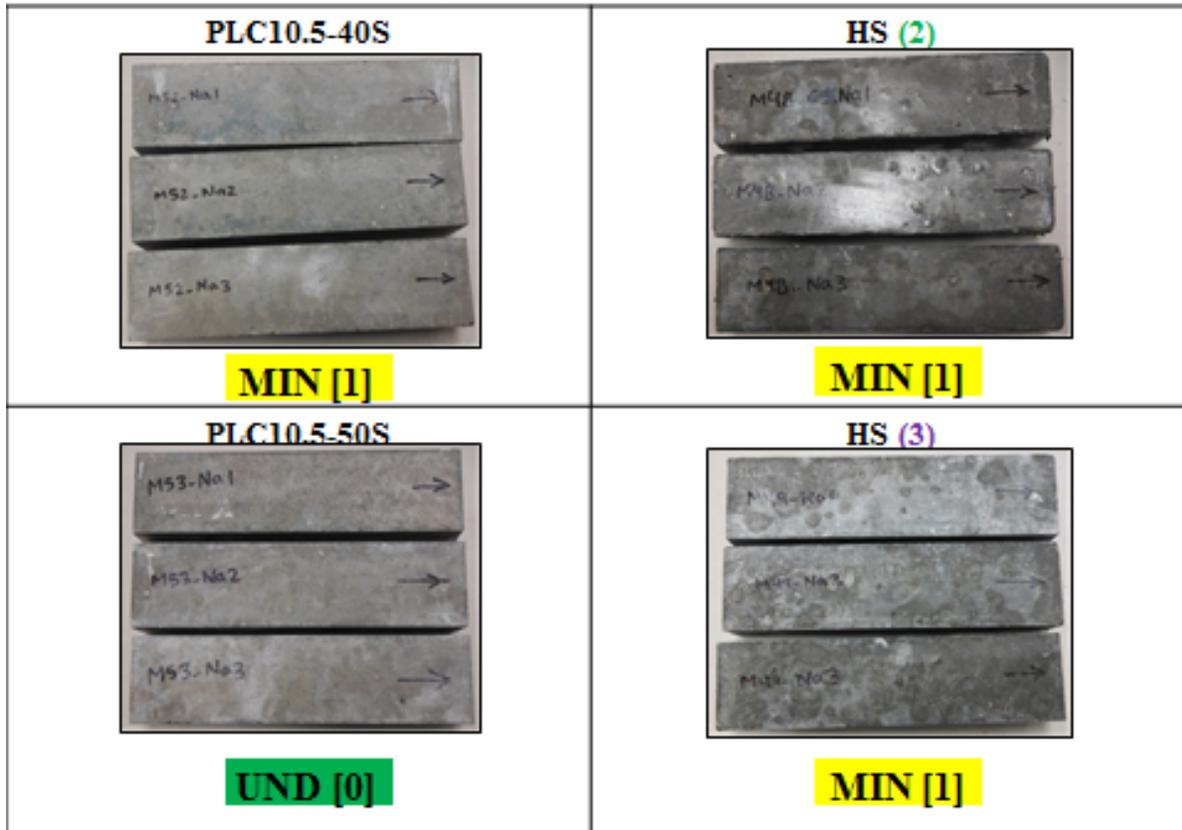


Figure 2.2. Visual condition of 0.40 w/cm field exposed concretes in 15,000 ppm sodium sulfate for 33 months.

In Figure 2.3, photographs of the visual condition of four concretes are shown after periods of sulfate exposure increasing from 12 to 54 months. The only concrete showing progressively increasing damage is the Type V (HS) portland cement.

**Progress of Deterioration / w/c=0.4 / 15,000 ppm Na<sub>2</sub>SO<sub>4</sub>**

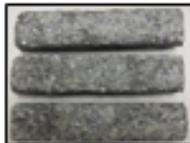
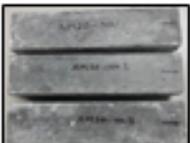
	(12 months)	(22 months)	(30 months)	(43 months)	(54 months)
<b>GU-40S</b>	 UND [0]	 MIN [1]	 MIN [1]	 MIN [1]	 MIN [1]
<b>PLC15-50S</b>	 UND [0]	 UND [0]	 UND [0]	 UND [0]	 UND [0]
<b>HS (I)</b>	 UND [0]	 MIN-MOD [2]	 MOD-SEV [4]	 SEV [5]	 SEV [5]
<b>HSb (30EA)</b>	 UND [0]	 MIN [1]	 MIN [1]	 MIN [1]	 MIN [1]

Figure 2.3. Visual condition of 0.40 w/cm field exposed concretes in 15,000 ppm sodium sulfate increasing from 12 to 54 months.

**2.3.2 Visual Condition of 0.50 w/cm concretes exposed to 1,500 ppm Na<sub>2</sub>SO<sub>4</sub> (ACI Exposure S3).** Figure 2.4 shows the excellent condition at 54 months of 30% slag blended with high-C<sub>3</sub>A clinker Type I (GU) cement and Type IL cements made from the same clinker, PLC-9 and PLC-15. The Type II (MS) portland cement is showing moderate damage with or without 12% interground limestone.

**(PC/PLC)-Slag vs Type II/MS w/c=0.5 / 4.5 years (54 months) /1,500 ppm Na<sub>2</sub>SO<sub>4</sub>**

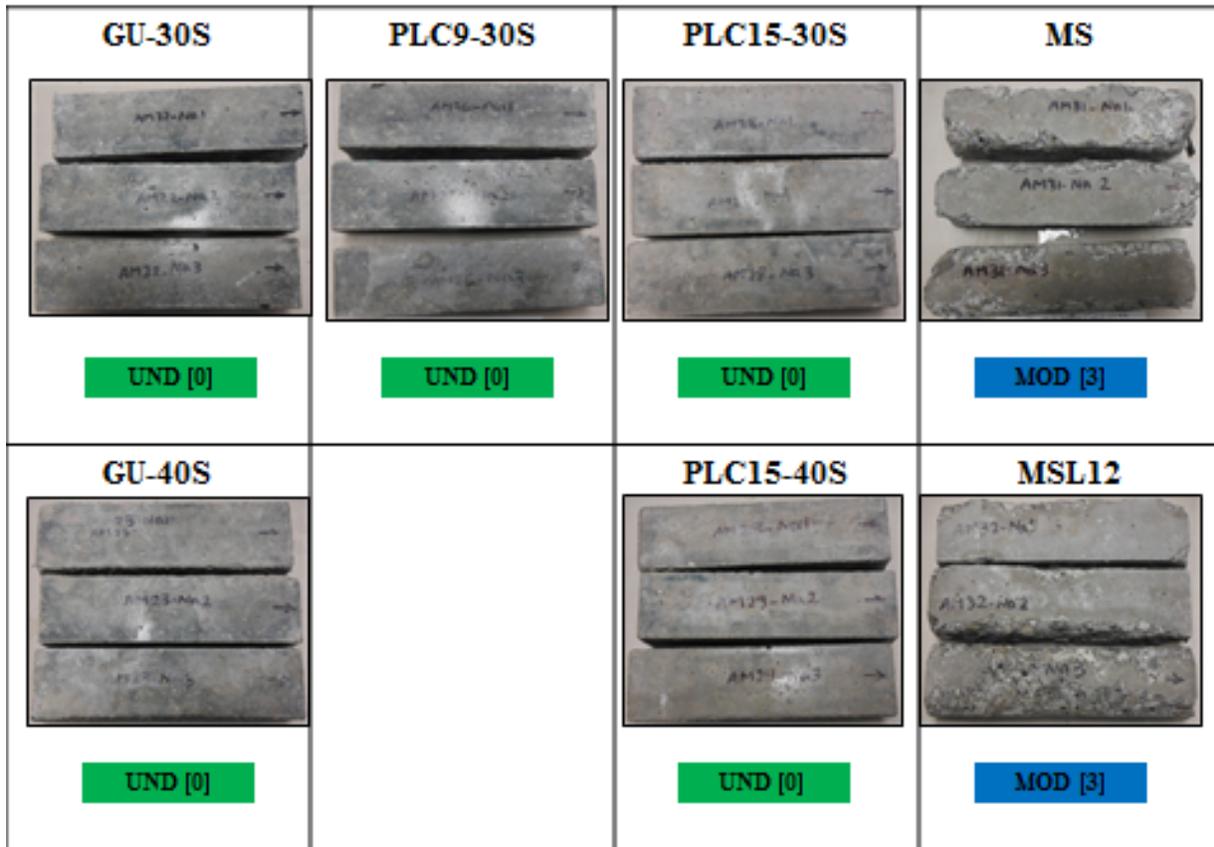


Figure 2.4. Visual condition of 0.50 w/cm field exposed concretes in 1,500 ppm sodium sulfate for 54 months.

## 2.4 Discussion of Concrete Performance

Concrete testing in the laboratory at 5°C and in field exposure indicates that in most cases concrete with blends of PC-SCM and PLC-SCM perform at least as well, if not better, than concrete with Type II (MS) or Type V (HS) cement at the same w/cm and in the same exposure condition. Similar to the findings in the UNB study, in its current form, the cold-temperature version of the ASTM C1012 test currently adopted in the Canadian CSA standard does not appear to predict the good performance of these blended cements when tested in concrete. As stated earlier, it is thought that this is due to the relatively low level of maturity when the bars are first placed in in cold-temperature sulfate solution. Mortars with slowly-reacting SCMs are unlikely to gain maturity rapidly in such low temperatures.

## 2.5 Conclusions from the University of Toronto Concrete Studies

1. 100% Type I, II, and V portland cement and Type IL blended cement concretes cannot resist low temperature sulfate attack without SCMs.
2. Regardless of limestone content, SCMs greatly improve the resistance of concrete to low temperature sulfate attack, as with normal sulfate attack.

3. Concretes made with Type IL+SCM binders are performing as well or better than Type V (HS) and HSb blended cements.
4.  $\text{MgSO}_4$  attack is more aggressive than  $\text{Na}_2\text{SO}_4$ , but Western soils are thought to be mainly  $\text{Na}_2\text{SO}_4$ .

### **3. UNIVERSITY OF NEW BRUNSWICK STUDIES**

#### **3.1 Introduction**

Studies at the University of New Brunswick (UNB) have included testing of mortars and concrete with a range of materials at various temperatures. The results of the mortar studies have been published in a series of journal articles (Hossack and Thomas, 2015a; 2015b; 2015c) and are only discussed briefly here. The concrete studies have included exposure of concrete samples in the laboratory and buried outdoors in simulated field conditions. These data have not been published with the exception of some preliminary data in a PhD thesis (Hossack, 2015). This report will focus on the concrete data.

#### **3.2 Mortar Studies at University of New Brunswick**

Two series of mortar bar tests were conducted: Series 1 used a moderate- $\text{C}_3\text{A}$  cement (8% to 9%  $\text{C}_3\text{A}$ ) and Series 2 used a high- $\text{C}_3\text{A}$  cement (11% to 12%  $\text{C}_3\text{A}$ ). Mortars were produced with portland-limestone cements (PLC) with a range of limestone contents in combination with a range of supplementary cementing materials (SCM). The testing followed ASTM C1012 except that mortars were exposed to 5% sulfate solution at a temperature of  $5^\circ\text{C}$  ( $40^\circ\text{F}$ ) in addition to the standard  $23^\circ\text{C}$  ( $73.5^\circ\text{F}$ ).

Mortar bars produced with PC or PLC without SCM failed the tests (defined as more than 0.10% expansion at 12 months) at all test temperatures. In general the time to failure decreased with increasing limestone content, but this did not affect the outcome of the test. Combinations of PC or PLC combined with SCM performed well in sulfate solution at  $23^\circ\text{C}$  ( $73.5^\circ\text{F}$ ) provided sufficient SCM was present. However, the performance at  $5^\circ\text{C}$  ( $40^\circ\text{F}$ ) was very different as shown in Figure 3.1. The data show that the rate of deterioration is strongly influenced by the SCM type and content, the  $\text{C}_3\text{A}$  content of the cement and the temperature, with the amount of limestone having little consistent impact.

Some of the test results at  $5^\circ\text{C}$  ( $40^\circ\text{F}$ ) are surprising, as mixtures that have shown excellent long-term performance in published studies on mortars and concrete, for example blends with 25% Class F fly ash or 8% silica fume, expand to more than 0.10% rapidly when tested at  $5^\circ\text{C}$  ( $40^\circ\text{F}$ ).

#### **3.3 Concrete Studies at University of New Brunswick**

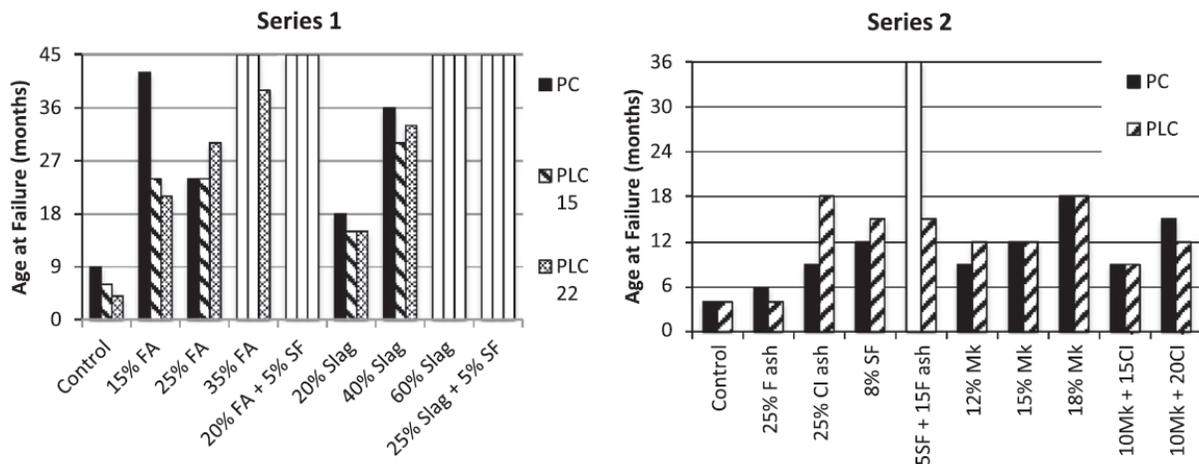
For the concrete studies, mixtures were produced with a water-to-cementing-materials ratio (w/cm) of 0.40 or 0.50 and concrete prisms cast with either a 50 mm  $\times$  50-mm (2 in.  $\times$  2-in.) or 75 mm  $\times$  75-mm (3 in.  $\times$  3-in.) cross-section for laboratory or field exposure, respectively. The mixture proportions used are shown in Table 3.1. Cements designated as PC-4, PLC-9 and PLC-

15 were produced from a high-C<sub>3</sub>A (12%) clinker with, respectively, 4%, 9% and 15% by mass interground limestone. Cements designated as GU, GUb and GULb were produced with a high-C<sub>3</sub>A clinker (11%). Cements GU and GUb contained 4% limestone and GULb contained 12% limestone. Cements GUb and GULb also contained 15% slag. In all cases the clinker, gypsum, limestone and slag were interground. In each case the fineness of the finished cements was targeted such that the cements produced from each of the two clinkers achieved equivalent 28-day mortar strengths.

**Table 3.1 Proportions used for control mixtures\***

W/CM	0.40	0.50
Cementing materials (kg/m <sup>3</sup> )	400	360
Water (kg/m <sup>3</sup> )	160	180
Coarse aggregate (kg/m <sup>3</sup> )	980	970
Fine aggregate (kg/m <sup>3</sup> )	750	741
Target air (%)	6	6

\*For SCM mixtures adjustments were made to the sand content to compensate for differences in the specific gravity of the SCMs).



**Figure 3.1 Time to 0.10% expansion or fracture for mortar bars produced with PLC and SCM – white bars indicate mortars that did not exceed 0.10% expansion during the test period of 45 months and 36 months for Series 1 and 2, respectively. (Note: Series 1 produced with moderate-C<sub>3</sub>A cement with 4% (PC), 15% (PLC 15) and 22% interground limestone; Series 2 produced with high-C<sub>3</sub>A cement with 4% (PC) and 10% (PLC) limestone).**

Concrete prisms were exposed to sulfate solutions after moist curing at 23°C (73°F) for 28 days. The following sulfate concentrations were used for laboratory exposure: 5% Na<sub>2</sub>SO<sub>4</sub> (33,800 ppm SO<sub>4</sub>), 1.8% MgSO<sub>4</sub> (14,400 ppm SO<sub>4</sub>), and 0.21% CaSO<sub>4</sub> (1,500 ppm SO<sub>4</sub>). All solutions were maintained at 5°C (40°F). For the field exposure the solutions were: 15,000 ppm SO<sub>4</sub> (Na<sub>2</sub>SO<sub>4</sub> and MgSO<sub>4</sub>) to represent S3 exposure class and 1,500 ppm SO<sub>4</sub> (CaSO<sub>4</sub>) to represent S2 exposure class. The field specimens were buried 2.1 m (7 ft) below ground level and this resulted in a temperature range varying from approximately 2° to 12°C (36° to 54°F).

Although concrete specimens were periodically measured to determine changes in length, mass and resonant frequency these data are not presented here as, for most mixes, the duration of exposure has not yet been sufficiently long for significant changes in the bulk properties to have occurred. What is most evident after 4 to 5 years is surface damage which ranges from no visible damage to a loss of corners, edges, complete loss of the surface concrete and finally to complete deterioration. Consequently, a visual rating was developed and this will be used to present the findings of the study. The visual rating is shown in Figure 3.2 and may be summarized as follows: 1 – no damage; 2 – loss of one or two corners; 3 – loss of all corners and “rounding” of ends; 4 – loss of edges and moderate scaling of surfaces; 5 – complete loss of surface ranging to complete disintegration of sample. Note that these numeric visual ratings differ slightly from the ones adopted in the University of Toronto studies.

Tables 3.2 and 3.3 show the visual ratings for, respectively, laboratory-exposed concretes in 2015 and field-exposed concretes in 2014. The results show that concrete with blends of PC or PLC with SCM generally perform as well, if not better, than concrete with Type MS or Type HS cement with the same w/cm in the same exposure. An example of this is shown in Figure 3.3 where it can be seen that the concrete produced with PLC-SCM blends are generally in better condition than the concrete produced with a Type HS cement. The exception to this is the occasional poor performance of concrete with blends of PLC-9 cement and SCM. Control concretes produced with PLC-9 had lower 28-day strengths (by approximately 1500 psi) than control concretes produced with PC-4 and PLC-15 and it is suspected that this cement was not optimized to achieve equivalent 28-day strength.

### **3.4 Discussion of University of New Brunswick Results**

The performance of blends of PC-SCM and PLC-SCM when tested in mortar in sodium sulfate solution at 5°C (40°F) is poor with mortar bars often exceeding the 0.10% expansion limit in relatively short periods of time. The same blends show a high level of sulfate resistance when tested at the standard testing temperature of 23°C (73.5°F). Concrete testing in laboratory and field exposure indicates that in most cases concrete with blends of PC-SCM and PLC-SCM perform at least as well, if not better, than concrete with Type MS or Type HS cement at the same w/cm and in the same exposure condition. The cold-temperature test currently used in Canada does not appear to properly predict the performance of blended cements when tested in concrete. It is suspected that this is due, at least in part, to the relatively low level of maturity when the bars are first placed in cold sulfate solution. Mortars with slowly-reacting SCMs are unlikely to gain maturity rapidly at low temperature.

**Table 3.2 Visual Ratings for Laboratory Exposure (2015)**

SCM Type and Amount	W/CM = 0.40							
	Lab Exposure: 5% Na <sub>2</sub> SO <sub>4</sub>							
	PC-4	PLC-9	PLC-15	GU	GUb-15S	GULb-15S	Type HS	Type MS
Control	5	5	4	5	5	5	4	
25% CI ash	2.5	5	2					
15% F ash				5	3.5	4		
8% SF	1	3	1					
5% SF + 15% CI ash	1	1	1					
	Lab Exposure: 1.8% MgSO <sub>4</sub>							
Control	5	5	3	5	2	5	2	
25% CI ash	2	2	2					
15% F ash				2	3	3		
8% SF	1	2	2					
5% SF + 15% CI ash	2	2	2					
	W/CM = 0.50							
	Lab Exposure: 5% Na <sub>2</sub> SO <sub>4</sub>							
Control	5	5	5					5
25% CI ash	2	2	2					
15% F ash								
8% SF	2	3	2					
5% SF + 15% CI ash								
	Lab Exposure: 1.8% MgSO <sub>4</sub>							
Control	5	5	5					5
25% CI ash	3	1	1					
15% F ash								
8% SF	1	5	5					
5% SF + 15% CI ash								

**Table 3.3 Visual Ratings for Field Exposure (2014)**

SCM Type and Amount	W/CM = 0.40							
	Field Exposure: 2.22% Na <sub>2</sub> SO <sub>4</sub>							
	PC-4	PLC-9	PLC-15	GU	GUb-15S	GULb-15S	Type HS	Type MS
Control	5	5	3	5	2	5	2	
25% CI ash	2	2	1					
15% F ash				3	2	2		
8% SF	1	1	1					
5% SF + 15% CI ash	1	1	1					
	Lab Exposure: 1.8% MgSO <sub>4</sub>							
Control	5	5	3	5	3	5	2	
25% CI ash	2	3	2					
15% F ash				3	1	2		
8% SF	3	2	2					
5% SF + 15% CI ash	2	3	1					
	W/CM = 0.50							
	Field Exposure: 0.21% CaSO <sub>4</sub>							
Control	5	5	3					4
25% CI ash	1	1	1					
15% F ash								
8% SF	1	1	1					
5% SF + 15% CI ash								
	Lab Exposure: 1.8% MgSO <sub>4</sub>							
Control	5	5	5					5
25% CI ash	2	2	2					
15% F ash								
8% SF	2	5	3					
5% SF + 15% CI ash								



Figure 3.2 Visual Ratings used in UNB Study



Type HS



40 PLC-9



40 PLC-9 + 25% fly ash



40 PLC-15 + 8% SF



40 PC-4 ternary

Figure 3.3 Visual condition of selected concrete specimens (w/cm = 0.40) after 3 years of simulated field exposure in 15,000 ppm Na<sub>2</sub>SO<sub>4</sub> solution (S3 Exposure).

## 4. DISCUSSION OF ALL DATA

Testing mortars for sulfate resistance at 5°C was adopted in Canadian CSA standards to address concerns related to the perceived increased risk of the thaumasite form of sulfate attack (TSA) in concrete containing portland-limestone cement (PLC). Since 2014, when CSA A23.1 was revised, PLC-SCM blends are now permitted for use in concrete in sulfate exposure classes, but only if: (i) the blend passes an 18-month expansion criteria in the cold-temperature (5°C) mortar test, (ii) a minimum level of specific SCMs is used, and (iii) the w/cm of the concrete is reduced compared to the requirements for PC and PC-SCM blends. Thus the requirements for PLC-SCM blends are considerably more onerous than those for PC or PC-SCM blends. Recent research does not support the more conservative CSA approach for PLC-SCM blends, as the presence of up to 15% limestone appears to have little impact on the performance of mortars or concretes in sulfate solutions at cold temperature (5°C) in the laboratory or concrete buried in tanks of sulfate solutions in simulated field-exposure conditions.

Many cementitious systems with excellent sulfate resistance when tested in mortars at normal laboratory temperature show extremely variable and poor performance when tested at 5°C. The reasons for this are not completely understood. Mortar mixtures produced with sulfate-resistant (Type V) portland cement or mixtures produced with either PC or PLC blended with Class F fly ash or slag cement failed to pass the 18-month expansion limit at 5°C and often deteriorated with 6 to 12 months; this behaviour was observed regardless of the quantity of limestone in the cement. Unpublished data collected by UNB and U of T from some of the cement companies (not presented here) showed failure of systems at 5°C with slag levels as high as 50% or, in one case, 65%.

The ongoing concrete testing in laboratory and field conditions at the University of Toronto and the University of New Brunswick may not be sufficiently advanced to draw firm conclusions at this time, but certain observations can be made. Firstly, the concrete data support findings from mortar testing: PC-SCM and PLC-SCM blends generally perform in a similar manner and the quantity of limestone does not appear to have consistent impact on performance, at least not up to the 15% addition used in these tests. Secondly, concrete containing PC-SCM or PLC-SCM blends generally perform at least as well, if not better, than concrete containing Type II or Type V cement at the same w/cm and in the same sulfate-exposure condition. This is significant as there is a long history of satisfactory field performance of Type V cement in concrete exposed to sulfates in the field and, in the absence of any established performance criteria for concrete in sulfate exposure, it seems rational at this time to use concrete with Type V cement as the benchmark for evaluating PC-SCM and PLC-SCM blends. Thirdly, the 5°C mortar test, as adopted in the CSA standards, does not seem to provide a reliable indication of how blends of cementing materials are going to perform in concrete exposed to sulfate at cold temperature in the laboratory or in field exposure.

Overall, the existing data do not support a wider adoption of the 5°C mortar test and suggest that the use of the Canadian test in its current form needs to be re-evaluated to improve the correlation with concrete testing. Furthermore, the more restrictive testing and concrete mix proportioning required for PLC-SCM blends when used in sulfate-exposure classes in Canada appears to be overly conservative.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The following conclusions can be drawn from the sulfate-resistance testing at the Universities of Toronto and New Brunswick:

1. Many blends of cementitious materials that are sulfate resistant when tested in mortars at 23°C show poor performance in sulfate solution at 5°C; this includes sulfate-resistant (Type V) portland cements and blends of PC and SCM or PLC and SCM.
2. PC-SCM and PLC-SCM blends generally show similar performance in mortars and there appears to be little consistent impact of the limestone content (up to 15%) on the outcome of tests where sufficient levels of SCMs were used at 5°C or 23°C.
3. For concretes exposed to sulfate solutions at low temperature either in the laboratory or in “field conditions,” PC-SCM and PLC-SCM blends show similar behavior and the performance is generally equivalent or superior to Type V or Type II portland cements with the same w/cm and exposure conditions.
4. The low temperature mortar bar test does not reliably predict the performance of concrete produced with PC-SCM or PLC-SCM blends.
5. By mitigating classic sulfate attack using materials meeting traditional expansion limits based on ASTM C1012 or CSA A3004-C8, Procedure A, thaumasite sulfate attack is also mitigated.

The following recommendation is made on the basis of these ongoing studies:

It is recommended that the standard ASTM C1012 test method, *not* modified to be conducted at 5°C, be used for determining the sulfate resistance of ASTM C595 Type IL and IT cements. That method should also be used to evaluate sulfate resistance of cementitious mixtures with supplementary cementing materials.

## 6. ACKNOWLEDGEMENTS

The research reported in this paper (PCA R&D SN3285a) was conducted by the University of New Brunswick and the University of Toronto. The contents of this report reflect the views of the authors, who are responsible for the facts and accuracy of the data presented. The contents do not necessarily reflect the views of the Portland Cement Association.

## 7. REFERENCES

Barcelo, L.; Gartner, E.; Barbarulo, R.; Hossack, A.; Ahani, R.; Thomas, M.; Hooton, R. D.; Brouard, E.; Delagrave, A.; and Blair, B., "A Modified ASTM C1012 Procedure for Qualifying Blended Cements containing Limestone and SCMs for use in Sulfate-Rich Environments," *Cement and Concrete Research*, Vol. 63, 2014, pages 75 to 88.

Hooton, R. D.; Ahani, R. M.; and Fung, R., "Durable & Sustainable Concretes with Portland-limestone Cements and Supplementary Cementing Materials," *2014 International Concrete Sustainability Conference*, National Ready Mixed Concrete Association, Boston, May 12-15, 2014, 15 pages.

Hooton, R. D.; Ahani, R. M.; and Ramezaniapour, A. M., "Prevention of Thaumasite Sulfate Attack in Binders Containing Interground Limestone," DVD-Proceedings, *The 8th International Symposium on Cement & Concrete (ISCC2013)*, Nanjing, China, September 20-23, 2013, 7 pages.

Hooton, R. D., Nokken, M. R., and Thomas, M. D. A., 2007. *Portland-Limestone Cement: State-of-the-Art Report and Gap Analysis for CSA A3000*, Portland Cement Association, Skokie, Illinois, USA, SN3053, 2007, 59 pages. Available at: [http://www2.cement.org/pdf\\_files/sn3053.pdf](http://www2.cement.org/pdf_files/sn3053.pdf).

Hossack, A. M., *Producing Sulfate-Resistant Concrete and Achieving Equal Performance with low-CO<sub>2</sub> Portland Limestone Cement*. Ph.D. Thesis, University of New Brunswick, 2015.

Hossack, A. M. and Thomas, M. D. A., "The Effect of Temperature on the Rate of Sulfate Attack of Portland Cement Blended Mortars in Na<sub>2</sub>SO<sub>4</sub> Solution," *Cement and Concrete Research*, Vol. 76, 2015a, pages 136 to 142.

Hossack, A. M. and Thomas, M. D. A., "Varying Fly Ash and Slag Contents in Portland Limestone Cement Mortars Exposed to External Sulfates," *Construction and Building Materials*, Vol. 78, 2015b, pages 333 to 341.

Hossack, A. M. and Thomas, M. D. A., "Evaluation of the Effect of Tricalcium Aluminate Content on the Severity of Sulfate Attack in Portland Cement and Portland Limestone Cement Mortars," *Cement and Concrete Composites*, Vol. 56, 2015c, pages 115 to 120.

Ramezaniapour, A. M. and Hooton, R. D., "Sulfate Resistance of Portland-Limestone Cements in Combination with Supplementary Cementitious Materials," *Materials and Structures*, Vol. 46, No. 7, 2013a, pages 1061 to 1073.

Ramezaniapour, A. M. and Hooton, R. D., "Thaumasite Sulfate Attack in Portland and Portland-Limestone Cement Mortars Exposed to Sulfate Solution," *Construction and Building Materials*, Vol. 40, 2013b, pages 162 to 173.

Thomas, M. D. A. and Hooton, R. D., *The Durability of Concrete made with Portland-Limestone Cement: Canadian Studies*, Portland Cement Association, SN3142, Skokie, Illinois, USA, 2010, 26 pages. Available at: [http://www2.cement.org/pdf\\_files/sn3142.pdf](http://www2.cement.org/pdf_files/sn3142.pdf).

Thomas, M. D. A., *Supplementary Cementitious Materials in Concrete*, CRC Press, 2013, 190 pages.