Investigation of the Long Term Effects of Magnesium Chloride and Other Concentrated Salt Solutions on Pavement and Structural Portland Cement Concrete

Project Number: SD2002-01

Submitted by:

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Quarterly Report

Overview

This Quarterly Report is submitted to outline the work accomplished during the reporting period 10-15-05 to 1-15-07, identify problems (current and anticipated), and to describe any deviations from the agreed Work Plan. This Quarterly Report is arranged by the Tasks described in the project Work Plan. Tasks not listed have been completed and the details of each can be found in previous reports. The following is a summary of results for this reporting period.

- Chloride profiling of samples from Task 6 are proceeding.
- Specimens immersed in calcium chloride solutions exhibit clear distress similar to that seem with mortar specimens during Phase 1 of this study.
- Work at the University of Toronto continues on identifying distress mechanisms and determining scaling potential of various deicers, and measuring diffusivity, sorptivity, and permeability of specimens from Task 6

Task Report

Task 5: Characterization of Field Specimens

Billets used for chloride profiling (reported in the previous quarterly report) have been analyzed. Results are being summarized and will be provided in the next quarterly report.

Task 5 Problems and/or Deviations from Work Plan

There were no problems for Task 5 incurred during the reporting period.

Task 5 Completion -90%

Task 6: Laboratory Experiment

Work Conducted at Michigan Tech

Specimens immersed in $CaCl_2$ brines show a distress similar to that observed in the Phase 1 mortar experiments. As shown in the top portion of Figure 1, a thin layer of $CaCO_3$ precipitate coats the top surface of the specimen immersed in the high concentration $CaCl_2$ brine. $CaCO_3$ precipitate forms in $CaCl_2$ brines within 24 hours, regardless of the presence of concrete. $CaCO_3$ precipitates as the Ca^{2+} ion rich solutions come into equilibrium with atmospheric CO_2. Cracks are readily visible in the specimen shown in Figure 1, which had been immersed for 270 days. Faint cracks were also evident in specimens immersed in high concentration $CaCl_2$ brines when pulled for chloride profiling at 60 days. Additional cracks not immediately evident upon removal from the brine become more visible after drying in the 50 degree C convection oven overnight, as shown on the right hand side of Figure 1.

Figure 1: 0.55 w/c concrete specimen immersed in high concentration $CaCl_2$ brine for 270 days. Left hand side images show specimen immediately after removal from brine, right hand side images show specimen after drying in convection oven overnight at 50 degrees C.

The oven-dried specimen shown in Figure 1 was epoxy impregnated, and then cut into slabs with a kerosene cooled diamond saw. The slabs were immediately cut into billets with a kerosene cooled saw for preparation in thin section. The billets were left in a desiccator cabinet overnight. The next morning, when the billets were removed from the cabinet, droplets of moisture were observed along the edges of billets representing in cross-section the surfaces of the specimen exposed to the brine (see left hand side of Figure 2). Over the period of an hour, these droplets evaporated, leaving behind a salty crust (see right hand side of Figure 2). This same phenomenon was previously observed to spontaneously occur under the optical microscope on thin sections prepared from the mortar cylinders in Phase 1 of this study. At the time it was attributed to humidity present in the air hydrating salts present in the thin sections. Since these droplets appeared overnight in a desiccator cabinet, an alternative explanation is that the droplets represent the instability of calcium oxychloride present in the sample. It is suggested that the droplets may be evidence of calcium oxychloride crystals dissolving in their own waters of hydration. It was a surprise to see indications that some calcium oxychloride may have remained in its original state in the billets, in spite of the fact that the specimen had already been dried in a 50 degree C oven overnight and vacuum impregnated. With this in mind, we have endeavored to preserve any possible remaining calcium oxychloride in the billets by proceeding carefully with the sample preparation. The cut surfaces of the billets, as shown in Figure 2, have since been ground with a mineral oil cooled diamond grinder to expose a fresh surface. The billets were then rinsed with kerosene and dried for 1/2 hour in the 50 degree convection oven prior to another round of vacuum impregnation. No further droplets were observed on the fresh surfaces at any time. The billets have since been in a sealed container under refrigeration. Subsequent cutting, grinding, lapping and polishing will be performed as quickly as possible during evening hours when the lab is not heated. It is hoped to record the phenomenon of the calcium oxychloride dissolving in its own waters of hydration with both the optical microscope and ESEM.

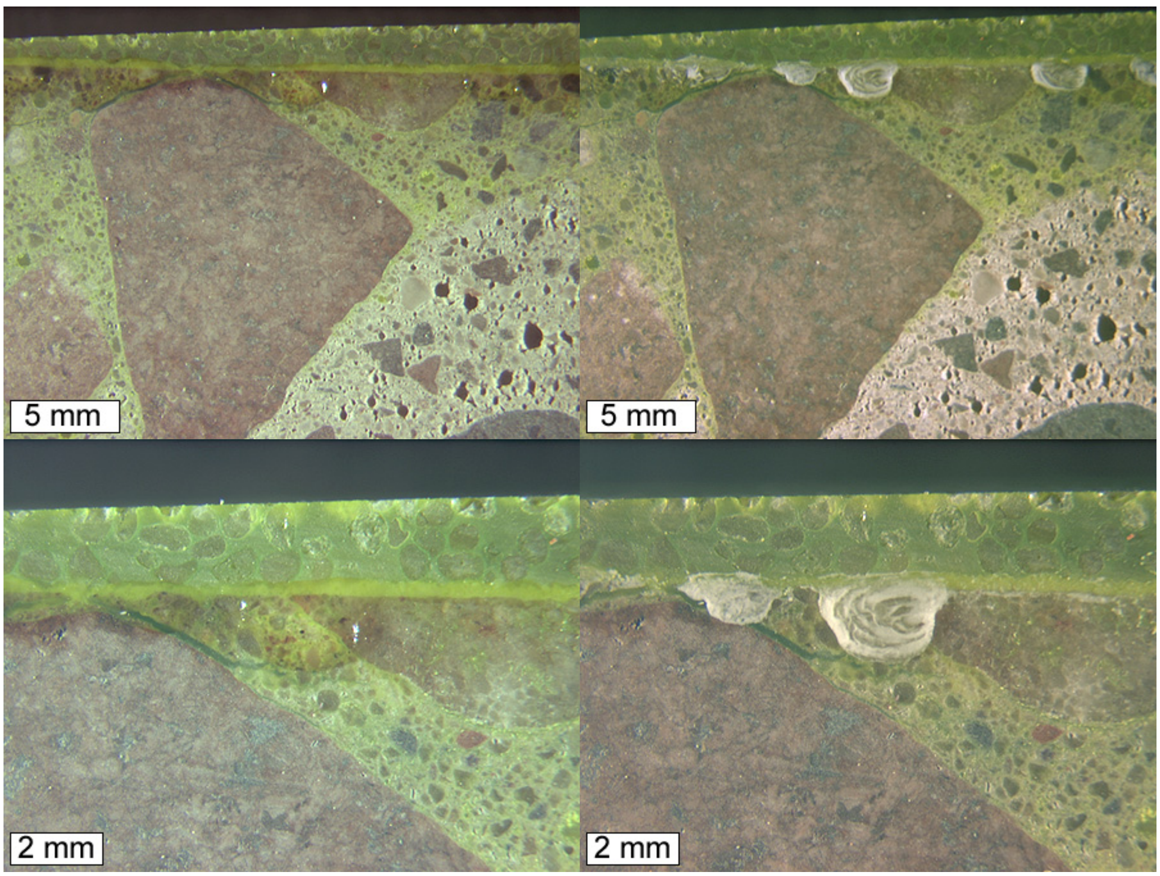

Figure 2: Moisture on billet cut from epoxy impregnated specimen immersed in high concentration $CaCl_2$ solution (left hand side) and salt deposits from evaporated moisture.

Chloride profiling continues on the specimens pulled from brines at 60 days. Table 1 summarizes the progress to date. Two profiles are collected per specimen: one profile from each of two billets prepared from the specimen. To prepare the billets, a slab is cut from the middle of each specimen with a kerosene cooled diamond saw to obtain a rectangular cross-section. The pair of billets is cut from the center portion of each slab, such that the top of each billet represents the top surface of the specimen in cross-section. The billet cross-sectional surfaces are ground flat with a mineral-oil cooled diamond grinder. Each billet is placed in the Oxford/Horiba XGT 2000W x-ray analytical microscope and 54 spectra are collected from points in the cement paste representing 18 depth horizons to a maximum depth of approximately 40 mm. Total x-ray counts in the range of 2.51 to 2.76 KeV (the chlorine K-alpha peak) are recorded at each point. Cement paste wt% chlorine concentrations are determined from a calibration curve, originally derived from spectra collected from 0.50 w/c mortar samples spiked with known concentrations of $CaCl_2$.

During a visit this summer from University of Florida staff interested in chloride profiling, we analyzed some 0.35 w/c neat paste samples they had spiked with known amounts of $CaCl_2$. Our procedure over-predicted the chlorine concentrations, since our calibration curve was constructed using standards made from 0.50 w/c mortar. Cement paste density has a profound influence on the magnitude of the measured Cl K-alpha peak. Consider two equal volumes of cement paste, one with a w/c of 0.50, and the other with a w/c of 0.35. The 0.35 w/c volume will have greater mass than the 0.50 w/c volume, since it is denser. Even if both volumes contain the same wt% Cl, the 0.35 w/c volume will contain more Cl than the 0.50 w/c volume. This realization prompted us to prepare $CaCl_2$ spiked mortar standards at 0.45 and 0.55 w/c, and to construct new calibration curves to analyze the data from our 0.45 and 0.55 w/c specimens. The visitors from University of Florida have since sent us a complete set of 0.35 w/c neat paste samples, which will help us to develop appropriate calibration curves over a wider range of w/c values. Thin sections have been prepared from the same billets used in the previous chloride profiling of the field concrete samples. Optical measurements of cement paste fluorescence have been collected from these thin sections to determine which calibration curve to use during the re-calculation of the chloride profiles.

The processing of the collected spectra has been a limiting factor during the chloride profiling procedure. Each individual spectrum had to be opened individually with the OXFORD/HORIBA XGT-2000W software, processed, and the results cut and pasted into a spreadsheet. Faced with the re-analyses of all our spectra collected to date, we recently sought the help of the Computer Science Department to write a program to extract the x-ray count data from the BinHex encoded spectrum files and to report it in a spreadsheet-friendly text format. Now, the process of constructing a chloride profile from 54 spectra has gone from an hour to a few minutes.

Table 1: Progress of chloride profile data collection on billets prepared from specimens pulled from brines at 60 days.

Specimen ID	Profiles collected?	Specimen ID	Profiles collected?
Hi MgCl2 0.45 w/c PC	Y	Hi NaCl 0.45 w/c PC	N
Hi MgCl2 0.55 w/c PC	Y	Hi NaCl 0.55 w/c PC	N
Hi MgCl2 0.55 w/c PC SILANE SEAL	Y	Hi NaCl 0.55 w/c PC SILANE SEAL	N
Hi MgCl2 0.55 w/c PC SILOXANE SEAL	Y	Hi NaCl 0.55 w/c PC SILOXANE SEAL	N
Hi MgCl2 0.45 w/c FLY ASH	Y	Hi NaCl 0.45 w/c FLY ASH	N
Hi MgCl2 0.55 w/c FLY ASH	Y	Hi NaCl 0.55 w/c FLY ASH	N
Hi MgCl2 0.45 w/c SLAG	Y	Hi NaCl 0.45 w/c SLAG	N
Hi MgCl2 0.55 w/c SLAG	Y	Hi NaCl 0.55 w/c SLAG	N
Hi MgCl2 0.45 w/c PC MORTAR	Y	Hi NaCl 0.45 w/c PC MORTAR	N
Hi MgCl2 0.55 w/c PC MORTAR	Y	Hi NaCl 0.55 w/c PC MORTAR	N
Hi MgCl2 0.45 w/c FLY ASH MORTAR	Y	Hi NaCl 0.45 w/c FLY ASH MORTAR	N
Hi MgCl2 0.55 w/c FLY ASH MORTAR	Y	Hi NaCl 0.55 w/c FLY ASH MORTAR	N
Hi MgCl2 0.45 w/c SLAG MORTAR	Y	Hi NaCl 0.45 w/c SLAG MORTAR	N
Hi MgCl2 0.55 w/c SLAG MORTAR	Y	Hi NaCl 0.55 w/c SLAG MORTAR	N
Lo MgCl2 0.45 w/c PC	Y	Lo NaCl 0.45 w/c PC	N
Lo MgCl2 0.55 w/c PC	Y	Lo NaCl 0.55 w/c PC	N
Lo MgCl2 0.45 w/c PC MORTAR	Y	Lo NaCl 0.45 w/c PC MORTAR	N
Lo MgCl2 0.55 w/c PC MORTAR	Y	Lo NaCl 0.55 w/c PC MORTAR	N
Hi CaCl2 0.45 w/c PC	Y	Hi Caliber 0.45 w/c PC	N
Hi CaCl2 0.55 w/c PC	Y	Hi Caliber 0.55 w/c PC	N
Hi CaCl2 0.55 w/c PC SILANE SEAL	Y	Hi Caliber 0.55 w/c PC SILANE SEAL	N
Hi CaCl2 0.55 w/c PC SILOXANE SEAL	Y	Hi Caliber 0.55 w/c PC SILOXANE SEAL	N
Hi CaCl2 0.45 w/c FLY ASH	Y	Hi Caliber 0.45 w/c FLY ASH	N
Hi CaCl2 0.55 w/c FLY ASH	Y	Hi Caliber 0.55 w/c FLY ASH	N
Hi CaCl2 0.45 w/c SLAG	Y	Hi Caliber 0.45 w/c SLAG	N
Hi CaCl2 0.55 w/c SLAG	Y	Hi Caliber 0.55 w/c SLAG	N
Hi CaCl2 0.45 w/c PC MORTAR	Y	Hi Caliber 0.45 w/c PC MORTAR	N
Hi CaCl2 0.55 w/c PC MORTAR	Y	Hi Caliber 0.55 w/c PC MORTAR	N
Hi CaCl2 0.45 w/c FLY ASH MORTAR	Y	Hi Caliber 0.45 w/c FLY ASH MORTAR	N
Hi CaCl2 0.55 w/c FLY ASH MORTAR	Y	Hi Caliber 0.55 w/c FLY ASH MORTAR	N
Hi CaCl2 0.45 w/c SLAG MORTAR	Y	Hi Caliber 0.45 w/c SLAG MORTAR	N
Hi CaCl2 0.55 w/c SLAG MORTAR	Y	Hi Caliber 0.55 w/c SLAG MORTAR	N
Lo CaCl2 0.45 w/c PC	Y	Lo Caliber 0.45 w/c PC	N
Lo CaCl2 0.55 w/c PC	Y	Lo Caliber 0.55 w/c PC	N
Lo CaCl2 0.45 w/c PC MORTAR	Y	Lo Caliber 0.45 w/c PC MORTAR	N
Lo CaCl2 0.55 w/c PC MORTAR	1/2	Lo Caliber 0.55 w/c PC MORTAR	N

Work Conducted at University of Toronto

Diffusion and Permeability assessment

Concrete and mortar specimens cast at Michigan Tech and sent to the University of Toronto for an assessment of their penetrability are being tested. Below are the preliminary results.

<u>Bulk diffusion test</u> **<u>(ASTM C 1556-03)</u>**

In previous quarterly reports, a summary of results for mortar samples exposed to calcium chloride and magnesium chloride at approximately 5^{o}C were presented. At this time the results for the concrete samples are shown in Table 2 and 3.

This task is still in progress with samples exposed to sodium chloride and those with sealed surfaces remaining for chloride profiling.

<u>Exposure Conditions</u>: 17% Calcium Chloride at 5^{o}C for 35 days (Table 2)
15 % Magnesium Chloride at 5^{o}C for 35 days (Table 3)

Table 2. Summary of Results - Concrete samples – 17% $CaCl_2$

	w/cm=0.45			w/cm=0.55		
Code	PCC	FCC	SGC	PCC	FCC	SGC
Concrete Samples						
Da (m^2/s)	4.28e-12	6.00e-12	3.60e-12	2.38e-11	1.27e-11	7.65e-12
Cs (%)	0.97	1.12	1.11	0.66	1.55	1.24
P [0.1%] (mm)	8.53	10.51	8.09	17.75	16.60	12.19
r^2	0.9803	0.9848	0.9987	0.9752	0.9875	0.9911

Table 3. Summary of Results - Concrete samples – 15% $MgCl_2$

	w/cm=0.45			w/cm=0.55		
Code	PCC	FCC	SGC	PCC	FCC	SGC
Concrete Samples						
Da (m^2/s)	4.04e-12	6.73e-12	3.21e-12	2.35e-11	1.39e-11	7.89e-12
Cs (%)	1.12	0.85	1.45	0.59	0.82	0.84
P [0.1%] (mm)	8.62	10.29	8.20	16.97	14.60	11.08
r^2	0.9952	0.9839	0.9996	0.9944	0.9828	0.9961

Da: Apparent Diffusion Coefficient
Cs: Surface Concentration
P (0.1%): Penetration depth for 0.1% chloride concentration
r^2: r-squared from fitting Fick's 2nd law equation to experimental data
PCC: Portland cement concrete
FCC: Portland cement + 15% fly ash concrete
SGC: GGBFS blended cement concrete

Sorptivity test **(ASTM C 1585-04)**

In previous quarterly reports, summary of results for concrete samples exposed to tap water, sodium chloride, calcium chloride and magnesium chloride were presented. At this time a summary of the results for mortar samples are shown in Table 4. Thus, this task is now complete.

Table 4. Summary of Preliminary Results – Mortar samples

Exposure solution / Code	w/cm=0.45		w/cm=0.55	
	Initial Absorption Si (mm/s^{½}) / [r^2]	Secondary Absorption S_s (mm/s^{½}) / [r^2]	Initial Absorption Si (mm/s^{½}) / [r^2]	Secondary Absorption S_s (mm/s^{½}) / [r^2]
Water				
PCMW	4.3 x 10^{-3} [0.99]	2.5 x 10^{-3} [0.99]	5.9 x 10^{-3} [0.99]	3.4 x 10^{-3} [0.98]
FCMW	3.3 x 10^{-3} [0.99]	1.9 x 10^{-3} [0.99]	4.0 x 10^{-3} [0.99]	2.5 x 10^{-3} [0.99]
SGMW	2.4 x 10^{-3} [0.97]	0.9 x 10^{-3} [0.99]	3.4 x 10^{-3} [0.98]	1.7 x 10^{-3} [0.99]
NaCl				
PCMN	4.6 x 10^{-3} [0.99]	2.5 x 10^{-3} [0.98]	7.1 x 10^{-3} [0.99]	3.0 x 10^{-3} [0.94]
FCMN	3.7 x 10^{-3} [0.99]	1.9 x 10^{-3} [0.99]	4.4 x 10^{-3} [0.99]	2.5 x 10^{-3} [0.98]
SGMN	2.4 x 10^{-3} [0.99]	0.8 x 10^{-3} [0.98]	4.3 x 10^{-3} [0.99]	1.2 x 10^{-3} [0.96]
$CaCl_2$				
PCMC	3.5 x 10^{-3} [0.99]	1.0 x 10^{-3} [0.98]	4.4 x 10^{-3} [0.99]	1.7 x 10^{-3} [0.99]
FCMC	1.7 x 10^{-3} [0.98]	0.5 x 10^{-3} [0.99]	2.0 x 10^{-3} [0.99]	0.6 x 10^{-3} [0.98]
SGMC	1.0 x 10^{-3} [0.95]	0.2 x 10^{-3} [0.99]	1.4 x 10^{-3} [0.96]	0.2 x 10^{-3} [0.98]
$MgCl_2$				
PCMM	0.4 x 10^{-3} [0.75]	0.5 x 10^{-3} [0.99]	1.0 x 10^{-3} [0.98]	1.1 x 10^{-3} [0.99]
FCMM	0.3 x 10^{-3} [0.64]	0.4 x 10^{-3} [0.99]	0.8 x 10^{-3} [0.99]	0.7 x 10^{-3} [0.99]
SGMM	0.3 x 10^{-3} [0.96]	0.3 x 10^{-3} [0.99]	0.7 x 10^{-3} [0.88]	0.3 x 10^{-3} [0.99]

PCMW: Portland cement mortar - tap water
PCMM: Portland cement mortar - magnesium chloride
FCMW: Portland cement + 15% fly ash mortar - tap water
FCMM: Portland cement + 15% fly ash mortar - magnesium chloride
SGMW: GGBFS blended cement mortar - tap water
SGMM: GGBFS blended cement mortar - magnesium chloride
PCMC: Portland cement mortar – calcium chloride
PCMN: Portland cement mortar - sodium chloride
FCMC: Portland cement + 15% fly ash mortar - calcium chloride
FCMN: Portland cement + 15% fly ash mortar - sodium chloride
SGMC: GGBFS blended cement mortar - calcium chloride
SGMN: GGBFS blended cement mortar - sodium chloride

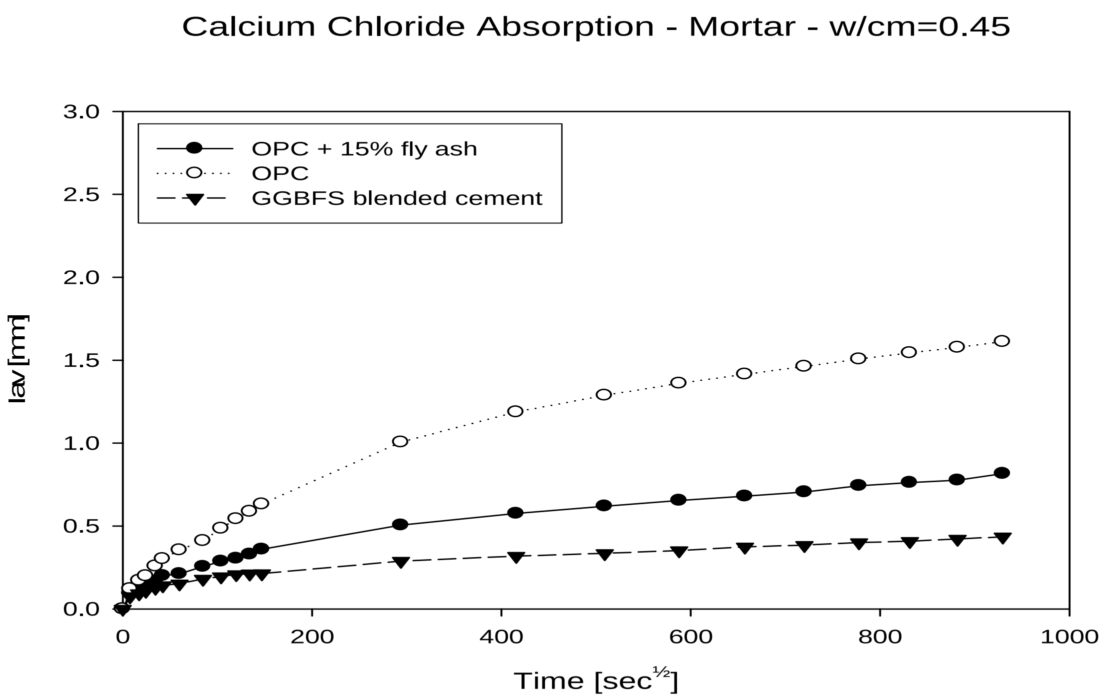

Figure 3. Absorption rate change with time for different mortars (w/cm=0.45) exposed to $CaCl_2$.

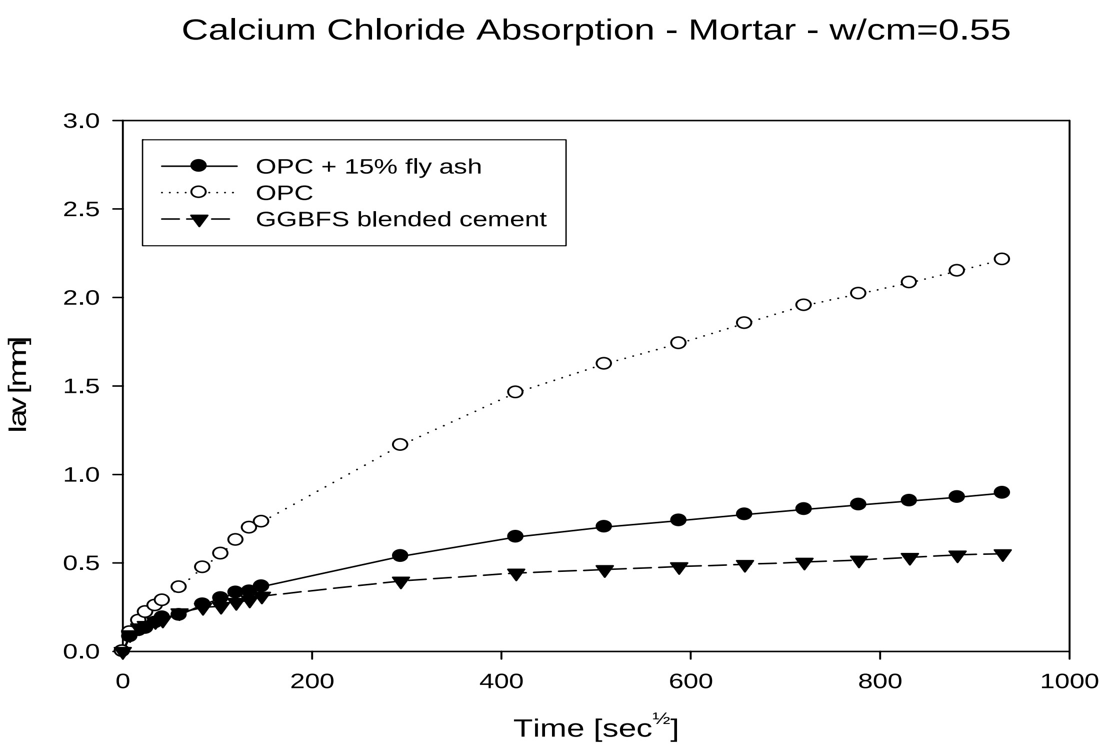

Figure 4. Absorption rate change with time for different mortars (w/cm=0.55) exposed to $CaCl_2$.

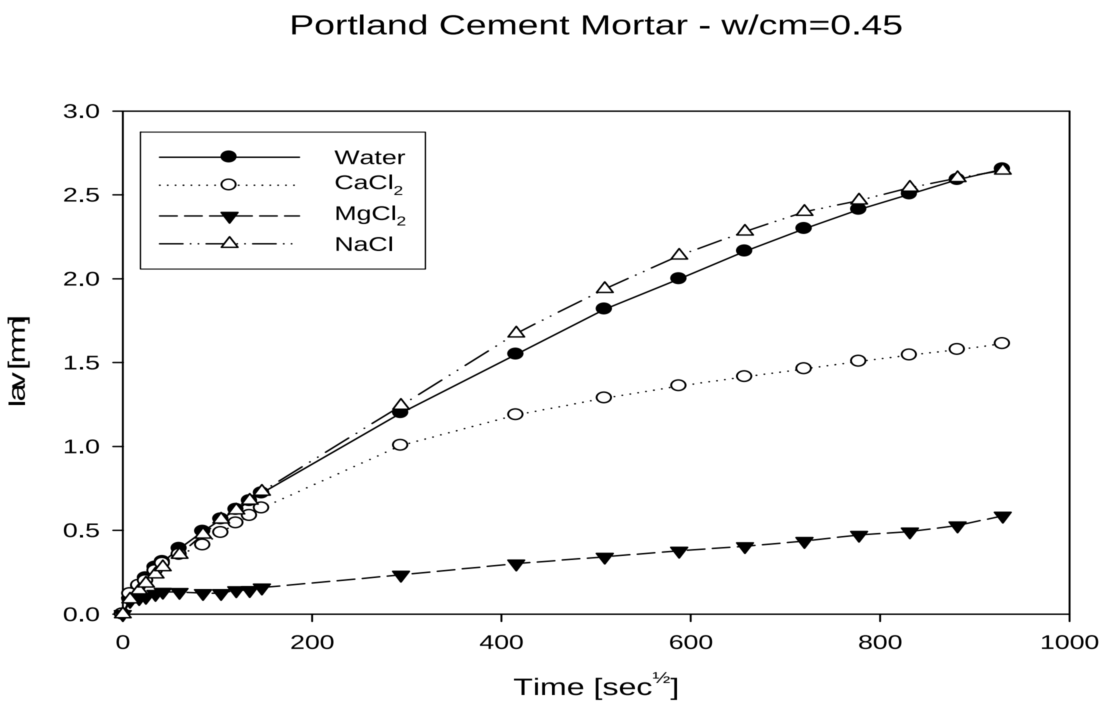

Figure 5. Absorption rate change with time for different exposure solutions-mortar (OPC w/cm=0.45).

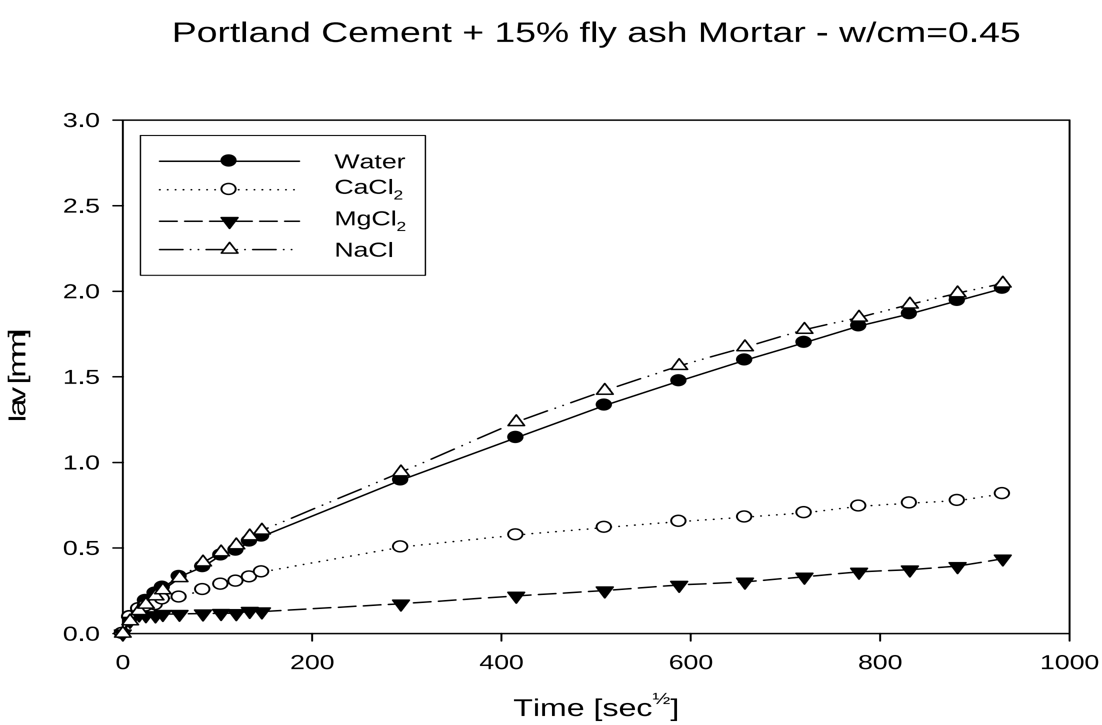

Figure 6. Absorption rate change with time for different exposure solutions-mortar (OPC + 15% fly ash w/cm=0.45).

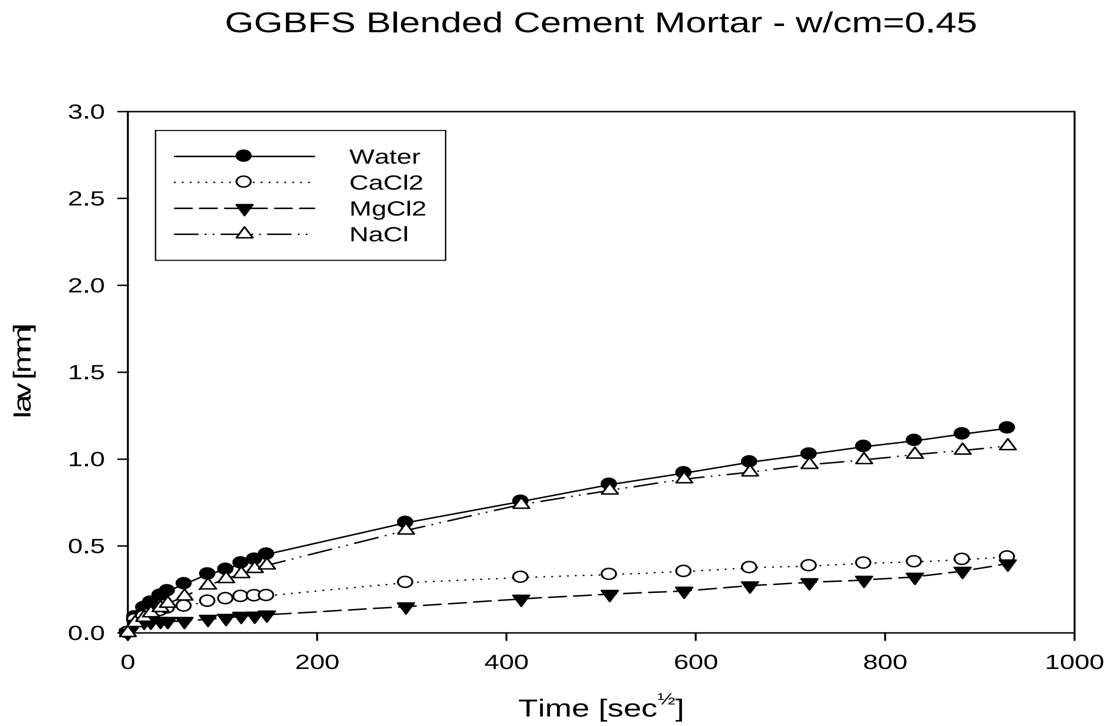

Figure 7. Absorption rate change with time for different exposure solutions-mortar (GGBFS blended cement w/cm=0.45).

Task 6 Problems and/or Deviations from Work Plan

There were no problems for Task 6 incurred during the reporting period.

Task 6 Completion -80%

Task 7: Assessing and Minimizing the Impact of Deicing/Anti-Icing Chemicals

Task 7 Problems and/or Deviations from Work Plan

None

Task 7 Completion -0%

Task 8: Effects of Various Deicing/Anti-Icing Chemicals

No additional work has been conducted on Task 8. Further work will continue once specimens from the Phase II experiments are ready for analysis.

Task 8 Completion -25%

Task 9: Life Cycle Cost Analysis

Task 9 Problems and/or Deviations from Work Plan

None

Task 9 Completion -0%

Task 10: Development of Guidelines

Task 10 Problems and/or Deviations from Work Plan

None

Task 10 Completion -0%

Task 13: Final report

Task 13 Problems and/or Deviations from Work Plan

None

Task 13 Completion -0%

Task 14: Present to Panel

Task 14 Problems and/or Deviations from Work Plan

None

Task 14 Completion -0%

Task 15: Present to Review Board

Task 15 Problems and/or Deviations from Work Plan

None

Task 15 Completion -0%