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 4-15-05 to 7-15-06, 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.

- Thin section specimens from the bridge decks examined in the previous quarterly report have been prepared
- All specimens for Task 6 have been placed in the appropriate solutions.
- Work at the University of Toronto continues on identifying distress mechanisms and determining scaling potential of various deicers.

Task Report

Task 5: Characterization of Field Specimens

Billets used for chloride profiling (reported in the previous quarterly report) have been prepared into thin sections and petrographic examination was begun. No specific details of the petrographic examination are available at this time.

Task 5 Problems and/or Deviations from Work Plan

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

Task 5 Completion -80%

Task 6: Laboratory Experiment

Work Conducted at Michigan Tech

A magnesium-based agricultural product (MBAP) deicer was provided by Syntech Corporation. Samples being tested in those solutions have been started.

The 56-day pulls have occurred for the $MgCl_2$, $CaCl_2$, and NaCl exposed specimens. Fourteen samples from each of the high concentration chloride brines, and four samples from each of the low-concentration brines were obtained for chloride profiling. Visible distress was noted on the $CaCl_2$ specimens.

Work Conducted at the University of Toronto

Salt scaling Resistance

Overview

As stated in the Quarterly Report of the reporting period of July 15, 2005 to October, 15, 2005, the University of Toronto is currently testing laboratory concrete slabs (9 in x 11 in x 3 in) following the ASTM C672 standard and a modified version of C762. Based on preliminary testing done at both the University of Toronto and Michigan Tech, it was clear that the use of $MgCl_2$ deicing salts with concentrations higher than 10% by weight, instead of 3% by weight as recommended in the ASTM C672 standard, prevent them from freezing. Therefore, the nature of any physical attack by ice formation is negligible and also there is no need to follow the recommended freezing temperature range (from -18^{o}C to 23^{o}C) if chemical interaction is expected.

However, the behavior observed on some mortar samples after changing the exposure solution from a diluted concentration of $MgCl_2$ (after a period of chemical interaction between the deicer and the mortar at the surface) to a 30% $MgCl_2$ deicer concentration, gave some insights as to the probable nature of the mechanism of deterioration. That is, it is assumed that there may be two (2) causes of deterioration by $MgCl_2$ deicers.

First, a *chemical-chemical deterioration mechanism* where the deicer interacts first with the surface of the concrete down to approximately 5 mm due to the time dependent diffusion of ions, altering the surface at a higher pace than the core of the concrete (below 5 mm). Any alteration of the surface layer is accompanied by gradual loss of strength and microcracking due to expansion of newly formed products, however, such expansion is not restrained perpendicular to the concrete surface area. In addition, the expansion parallel to the concrete surface area is partially restrained by the surrounding material. Any changes at the concrete matrix surface will be concentration-time dependent. After a period of exposure the concrete matrix will behave as a composite material composed of at least three different matrixes with depth. Later application of salt as anti-icing or deicing will not interact with the surface but will penetrate at a very fast rate into the second layer (below 5 mm) of the concrete due to less binding of the upper layer and higher connectivity (microcracks). Changes in the second layer will happen similar to the first one with the key difference that now the expansion is faster and is mainly restrained in all planes and expansive forces may cause a complete delamination of the first layer.

Second, a *chemical-physical deterioration mechanism* where expansion of new products creates microcracks but instead of restrained expansion being the sole cause of damage, now the ice formation in the microcracks will cause the material to de-bond causing again a dramatic delamination of the surface.

Thus, it was decided to proceed with different experiments where these two mechanisms are simulated separately to confirm whether their occurrence affects the service life of concrete pavements.

In addition, the pessimum concentration of magnesium chloride was determined according to the ASTM C672 standard.

<u>Experimental Procedure</u>

Normal Portland Cement (CSA Type GU, ASTM Type I) was used to prepare a 0.45 water-cement ratio concrete with approximately 5.5 to 8.5% of entrained air. This mix design has been tested previously and proved to comply with the requirements for concrete scaling resistance when exposed to deicing salts. Laboratory concrete slabs (9 in x 11 in x 3 in) were cast and a typical sidewalk broom finish was done on the surface. After de-molding, the slabs were kept in a moist curing room until the age of 28 days. Between the ages of 25 to 28 days, Styrofoam berms were placed along the perimeters of the slab surfaces and sealed with silicone, creating a dyke to retain the salt solution during the test period. At the age of 28 days, the laboratory concrete slabs were placed under different exposure conditions depending on the mechanism of deterioration to be simulated.

Chemical-chemical

For this type of mechanism the concrete slab surfaces were covered with a diluted concentration of magnesium, calcium chloride and sodium chloride deicers (15% $MgCl_2$, 17% $CaCl_2$ and 18% NaCl). The slabs are being kept at an exposure temperature of 5^oC (45^oF) and the solution is changed every three to four weeks to avoid precipitation of carbonated products and degradation of the solution due to possible organics present in the deicer. Visual observation is done at the same time the solution is being replaced.

Chemical-physical

For this type of mechanism the concrete slab surfaces were covered with the same diluted concentration as described above but instead of keeping them at a constant temperature of 5^oC (40^oF), they are cycled every three weeks for 5 days following the ASTM C672 recommended cycle of -18^oC for 16 hours and 23^oC for 8 hours.

Physical

In addition to the mechanism mentioned above, some slabs are being tested following the ASTM C672 and they will be used as control ones so a pure physical mechanism of deterioration is compared with the other two mechanisms.

Lower range pessimum concentration (1 to 10% by weight) – Physical attack

Some slabs are being exposed to magnesium chloride at different concentrations in the range between 1 to 10% by weight and cycled until the first visual rating of 5 is reached in one of the concentrations. At that time the test will be discontinued and the pessimum concentration will de determined.

Higher range pessimum concentration (10 to 30% by weight) – Chemical attack

Some slabs are being exposed to magnesium chloride at different concentrations in the range between 10 to 30% by weight and cycled until the first visual rating of 5 is reached in one of the concentrations. At that time the test will be discontinued and the pessimum concentration will de determined.

Diffusion and Permeability Assessment

Overview

Concrete and mortar specimens cast at Michigan Tech were sent to the University of Toronto for an assessment of their penetrability, which in turn helps defines their performance when exposed to aggressive environments. The specimens are discs saw cut from cylinders (100 by 200 mm) without the finished surface. A total of 162 samples were provided to be used on three (3) different tests: sorptivity as per ASTM C 1585-04, *"Measurement of rate of absorption of water by hydraulic cement concretes"*, bulk diffusion tests as per ASTM C 1556-03, *"Determining the apparent chloride coefficient of cementitious mixtures by bulk diffusion"*, and the rapid chloride permeability test as per ASTM C1202-97, *"Electrical indication of concrete's ability to resist chloride ion penetration"*. The following are the type of mixes to be tested.

Concrete samples: 90 discs
18 discs - slag + OPC - w/c=0.55
12 discs - slag + OPC - w/c=0.45
18 discs - OPC - w/cm=0.55
12 discs - OPC - w/cm=0.45
18 discs - 15% fly ash + OPC - w/cm=0.55
12 discs -15 % fly ash + OPC - w/cm=0.45

Mortar samples: 72
12 discs - slag + OPC - w/c=0.55
12 discs - slag + OPC - w/c=0.45
12 discs - OPC - w/cm=0.55
12 discs - OPC - w/cm=0.45
12 discs – 15% fly ash + OPC - w/cm=0.55
12 discs – 15% fly ash + OPC - w/cm=0.45

Sorptivity test

For this test, five (5) specimens will be tested per mix for a total of 60 specimens. Besides the rate of absorption of water, three deicing salts were included: magnesium chloride, calcium chloride and sodium chloride for analysis. The testing will be carried out in three phases due to the high number of samples. At this time all samples for the first run of sorptivity are being conditioned and tested according to the ASTM C1585-04 standard (as defined in 8.0 and 9.0).

Bulk diffusion test

This test has two components; first, the determination of the apparent chloride diffusion coefficient on exposed sawn surfaces, and second, the determination of the apparent chloride diffusion coefficient on sealed, sawn surfaces. The types of salt exposure, solution concentration and exposure temperature have been modified to replicate the conditions used under Phase I of the same project. That is, 15% magnesium chloride, 17% calcium chloride and 18% NaCl will be the exposure solutions to be used at a constant 5^{o}C (45^{o}F) exposure temperature. For the first part five (5) specimens will be tested per mix for a total of 60 specimens.

For the second component only concrete mixtures with w/cm=0.55 will be tested. The same exposure conditions as mentioned above will be used. Two type of sealers will be evaluated, Tri-siloxane 12% (aliphatic hydrocarbon) and Tri-silane 40% (2-propanol). Both products are manufactured in the states by TK products. For this part six (6) specimens will be tested for a total of 18 specimens. At this time all specimens for part one are being exposed to the salt solution and will remain there for 35 days.

Rapid chloride permeability test

This test will give a relative indication of the chloride penetrability and conductivity of the sample so all the mortar and concrete mixture can be ranked relative to each other based on the charge passed during the test. To avoid misleading results due to heating of the specimen during the test, the total charge reported will be based on the 30 minutes charge (the 30minute coulomb value was multiplied by 12 to obtain an equivalent 6 h value). Two specimens per mixture were tested for a total of 24 specimens. Table 1 summarizes the results showing the charged passed and the chloride ion penetrability.

Table 1. Chloride ion penetrability results

Code	w/cm=0.45		w/cm=0.55	
	Charge (coulombs)	Chloride ion penetrability	Charge (coulombs)	Chloride ion penetrability
Concrete Samples				
PCC	4413	High	5236	High
FCC	3397	Moderate	4446	High
SGC	2787	Moderate	3103	Moderate
Mortar Samples				
PCM	5380	High	6151	High
FCM	5219	High	5871	High
SGM	3309	Moderate	4208	High

PCC: Portland cement concrete
FCC: Portland cement + 15% fly ash concrete
SGC: GGBFS blended cement concrete
PCM: Portland cement mortar
FCM: Portland cement + 15% fly ash mortar
SGM: GGBFS blended cement mortar

Task 6 Problems and/or Deviations from Work Plan

There were no problems for Task 6 incurred during the reporting period with the exception of obtaining the MBAP deicer.

Task 6 Completion -70%

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%