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The Deleterious Chemical Effects of Concentrated Deicing Solutions on Portland Cement Concrete

Study SD2002-01
Executive Summary

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April 2008

DISCLAIMER

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16. Abstract

This research project investigated the effects of concentrated brines of magnesium chloride, calcium chloride, sodium chloride, and calcium magnesium acetate on portland cement concrete. Although known to be effective at deicing and anti-icing, the deleterious effects these chemicals may have on concrete have not been well documented. As a result of this research, it was determined that there is significant evidence that magnesium chloride and calcium chloride chemically interact with hardened portland cement paste in concrete resulting in expansive cracking, increased permeability, and a significant loss in compressive strength. Although the same effects were not seen with sodium chloride brines, it was shown that sodium chloride brines have the highest rate of ingress into hardened concrete. This latter fact is significant with respect to corrosion of embedded steel. The mechanism for attack of hardened cement paste varies with deicer chemical but in general, a chemical reaction between chlorides and cement hydration products results in the dissolution of the hardened cement paste and formation of oxychloride phases, which are expansive. The chemical attack of the hardened cement paste is significantly reduced if supplementary cementitious materials are included in the concrete mixture. Both coal fly ash and ground granulated blast furnace slag were found to be effective at mitigating the chemical attack caused by the deicers tested. In the tests performed, ground granulated blast furnace slag performed better as a mitigation strategy as compared to coal fly ash. Additionally, siloxane and silane sealants were effective at slowing the ingress of deicing chemicals into the concrete and thereby reducing the observed distress. In general, the siloxane sealant appeared to be more effective than the silane, but both were effective and should be considered as a maintenance strategy.

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Acronym	Definition
ASTM	American Society for Testing and Materials
BSE	Back-Scattered Electron
Ca	Calcium
$Ca(OH)_2$	Calcium Hydroxide
$CaCl_2$	Calcium Chloride
$CaCO_3$	Calcite
Cl	Chlorine
CMA	Calcium Magnesium Acetate
CSH	Calcium Silicate Hydrate
F-T	Freeze-Thaw
GGBFS	Ground Granulated Blast Furnace Slag
MBAP	Magnesium Chloride Based Agricultural Product
Mg	Magnesium
$Mg(OH)_2$	Brucite
$MgCl_2$	Magnesium Chloride
MSH	Magnesium-Silicate-Hydrate
NaCl	Sodium Chloride
Na	Sodium
OH^-	Hydroxide Ion
OPC	Ordinary Portland Cement
psi	Pounds per Square Inch
SCM	Supplementary Cementitious Materials
SDDOT	South Dakota Department of Transportation
SEM	Scanning Electron Microscopy
SHA	State Highway Agency
w/c	Water-to-Cement Ratio
w/cm	Water-to-Cementitious Ratio
XRD	X-ray Diffraction

EXECUTIVE SUMMARY

PROBLEM STATEMENT

Keeping roads safe and passable is a key concern for any State Highway Agency (SHA), especially during the winter season when ice and snow accumulation on roads and bridges can create hazardous driving conditions. To accomplish this, SHAs are constantly seeking out, evaluating, and adapting new winter maintenance strategies that are cost effective and environmentally friendly. One such area where new strategies are being employed is the broad area of deicing and anti-icing. Deicing is defined as any effort to remove ice from road and bridge surfaces after ice deposition has occurred. This is in contrast to anti-icing, which is defined as a surface treatment applied prior to ice formation that eliminates ice accumulation or facilitates ice removal by lessening the bond between the ice and the riding surface. In general, deicing and anti-icing are accomplished through the use of various chemicals including aqueous solutions of chlorides (e.g. magnesium chloride, sodium chloride, and calcium chloride) or other chemicals such as calcium magnesium acetate and urea. Although the efficacy of these chemicals for deicing and anti-icing has been clearly demonstrated, possible detrimental effects to concrete in transportation structures have not been fully examined and documented. In this sense, the true cost effectiveness has not been determined as chemical attack on concrete is a possibility and in turn, the resulting deterioration of the structures from chemical attack may lead to costly rehabilitation or replacement. Based upon published research, the most problematic chemicals appear to be the chlorides of magnesium, calcium, and sodium and other chemicals containing calcium and magnesium (e.g. calcium magnesium acetate). Use of these chemicals has increased given their relatively low cost, ease of use, and effectiveness for deicing and anti-icing, in certain applications. Use of alternative chemicals such as propylene glycol and ethylene glycol have seen limited use given concerns about their environmental impact, whereas potassium acetate, sodium acetate, potassium formate, and sodium formate are used almost exclusively on airports (with some use in automated bridge deicing systems) due to high cost. In the end, chloride-based deicers appear to be the best choice for highway applications if they can be used in such a way as to minimize possible chemical attack to concrete.

The degradation of concrete used in pavements and bridges that may occur as a result of attack by chemical deicers/anti-icers is the result of an increased concentration of dissociated calcium and magnesium ions in the concrete pore water. In theory, these free ions are available to combine with materials in the concrete to form expansive or weak reaction products such as brucite or magnesium silicate hydrates, respectively. Of course, the dissociation of chlorides into ionic species also increases the concentration of chloride in the pore water solution, which has been well documented as a primary cause of scaling and corrosion of reinforcing steel. These possible and known effects must be fully understood if these chemicals are to be used as a mainstay of any deicing or anti-icing strategy. The goal of this research was to examine the effects of deicing and anti-icing chemicals on portland cement concrete and to recommend changes to concrete mixture designs, construction practices, and winter maintenance procedures that will make these solutions non-detrimental to concrete durability.

SUMMARY OF PROJECT TASKS

Task 1: Literature Review
Task 2: Conduct Survey
Task 3: Site Selection
Task 4: Meeting with Technical Panel
Task 5: Characterization of Field Specimens
Task 6: Laboratory Experiment
Task 7: Assessing and Minimizing the Impact of Deicing/Anti-Icing Chemicals
Task 8: Effects of Various Deicing/Anti-Icing Chemicals
Task 9: Life Cycle Cost Analyses
Task 10: Development of Guidelines
Task 11: Submit Interim Report
Task 12: Meeting With Technical Panel at Michigan Tech
Task 13: Prepare and Submit Final Report
Task 14: Executive Presentation to Research Panel
Task 15: Executive Presentation to SDDOT Executive Review Board

REPORT ORGANIZATION AND DISTRIBUTION

The final report for this project is extensive. To facilitate distribution, the report has been broken down into a number of separate volumes and these are listed below.

- **Executive Summary** – Provides a concise overview of the entire project.
- **Final Report** – The final technical report organized into nine sections.

  Section 1: A brief introduction
  Section 2: An abridged background for the project based on the Task 1 literature review
  Section 3: Presents the experimental approach for the entire project
  Section 4: An abridged summary of the Task 5 results
  Section 5: An abridged summary of Task 6 laboratory results for Phase I and Phase II
  Section 6: Presents a discussion of the results of Tasks 5, 6, 7, 8 and 9
  Section *7:* Presents suggested mitigation strategies based upon the results of this study
  Section 8: Conclusions based upon the results of this study
  Section 9: Recommendations based upon the results of this study
  Section 10: Bibliography used as the basis for Section 2
- **Technical Appendices** – The appendices contain details on specific analytical methods used in the study and an unabridged summary of results for the characterization of field specimens and for all laboratory experiments.
- **Full Literature Review** – Provides the unabridged version of the literature review.
- **Implementation Guide** – A practical guideline document to assist DOT personnel in implementing this research.

BACKGROUND

Traditionally, winter maintenance entails plowing snow and applying chemicals and/or abrasives to melt the snow and ice cover. Over the years, traditional snow and ice removal methods have been modified in order to comply with environmental regulations, reduce corrosive damage to vehicles, and provide a more economical method to maintain safe roads. Current methods of snow and ice removal include deicing, pre-wetting salt or abrasive material, and anti-icing.

Concrete consists of coarse aggregate, fine aggregate (i.e. sand), portland cement, water, and typically, entrained air. The water and portland cement react to form hydration products, most notably calcium silicate hydrate (CSH) and calcium hydroxide ($Ca(OH)_2$).

A number of concrete properties affect performance when the concrete is exposed to deicers. The most important characteristics to control are: permeability; air content; cement chemistry; aggregate properties; and cracking.

It is widely understood that the water to cement ratio (*w/c)* has the largest influence on the durability of concrete. By having a relatively low *w/c* ratio, the porosity of the hydration products will decrease and in turn, the concrete will be less permeable.

One important aspect of concrete permeability regarding the application of deicing chemicals is chloride diffusion. The movement of chloride ions in concrete is a function of several variables. These include the concentration of deicer solution at the concrete surface, pore size and spacing, pore volume fraction, changes in pore size with respect to location within the cement paste, and chemical composition of phases present in the hydrated cement paste.

Cracking in concrete significantly increases the permeability and makes the concrete more susceptible to ingress of fluids. Although cracking may not cause immediate structural failure, it may provide for the onset of deterioration that ultimately leads to failure. As cracking spreads, it increases the permeability of concrete, leading to surface scaling and further internal stress-related cracking.

Entrained air has been found to improve the freeze-thaw (F-T) resistance of concrete. It is also known that a disadvantage of increasing the entrained air content is that it lowers the strength and increases the permeability of concrete. However, to have good F-T protection, air entrainment is required.

Both physical and chemical interactions occur within concrete when it is exposed to freeze-thaw conditions and deicing chemicals. Physical interaction is initiated when the saturated concrete freezes, subjecting the concrete to expansion and internal stresses. Additionally, some researchers have reported that the crystallization of salts or other phases within the concrete pore system can also lead to expansive cracking. Chemical interaction results from the interaction of deicing chemicals with the hardened cement paste, leading to possible degradation of the concrete structure. Combined, physical and chemical interactions may lead to distress in concrete pavements.

Deicer scaling/deterioration is typically characterized by scaling or crazing of the slab surface due to the repeated application of deicing chemicals. Although the exact causes of deicer scaling are not known, it is commonly thought to be primarily a form of physical attack, possibly resulting from a combination of factors and the presence of deicing chemicals can magnify or amplify the mechanisms that lead to F-T deterioration of the paste.

Although most research suggests that physical deterioration is the dominant source of distress associated with deicers, some researchers feel strongly that chemical interactions may also be occurring. It is known that the calcium hydroxide dissolution process results in increased porosity at exposed surfaces, increasing the permeability of the concrete, and the dissolved calcium hydroxide reacts with deicers to form deleterious compounds.

Magnesium chloride ($MgCl_2$) effectively reduces the temperature at which water freezes and will have similar physical effects on concrete as sodium chloride (NaCl). However, when the $MgCl_2$ occurs in the melt water on the concrete surface, the subsequent chemical interactions that occur may have a negative impact as the solution ultimately penetrates into the concrete. Some interactions of magnesium and chloride ions with the cement hydration products are known to cause damaging alterations to the cement paste structure, reducing concrete strength while increasing porosity. Magnesium oxychloride compounds can occur as reaction products in concrete samples exposed to concentrated chloride solutions

Magnesium based agricultural product (MBAP) deicers contain agricultural by-products in addition to $MgCl_2$. Some appealing physical properties of MBAP deicers are that they freeze at lower temperatures than most other deicers, they possess a high percentage of deicing solids, and mix readily with liquid chloride brines.

Researchers have concluded that calcium chloride ($CaCl_2$), another common deicer, can be associated with a deleterious chemical reaction with concrete where calcium oxychloride forms, causing cracks as it expands. Other studies have shown that $CaCl_2$ can potentially affect both aggregates and hydrated cement paste within concrete.

Research on calcium magnesium acetate (CMA) has found that it to be not as corrosive as NaCl. However, more recent studies have shown that CMA solutions may be the most deleterious deicing chemicals. It has been reported that concentrated solutions of CMA dissolve hardened cement paste in mortar samples and a reduction in compressive strength is common.

One reported way to mitigate problems with deicing chemicals is the partial replacement of portland cement in the concrete mixture with another cementitious material such as fly ash, silica fume, or ground granulated blast furnace slag (GGBFS). The use of these industrial by-products has many benefits, including their influence on the heat of hydration and strength. More importantly, they aid in the resistance of concrete to chemical attack by improving the chemical nature and microstructure of the hydrated cement paste by decreasing the amount of calcium hydroxide present and decreasing permeability.

In general, physical attack associated with deicing chemicals is not a concern for properly constructed, high quality portland cement concrete. But even if the concrete is properly constructed and cured, deicers may damage concrete with poor mixture characteristics. The two primary mixture design considerations for producing deicer scaling resistant concrete are a relatively low *w/c* ratio (with corresponding high cement content) and air entrainment. State highway agencies standard specifications reflect this, although the specified maximum *w/c* ratio and minimum cement content vary greatly from state to state, indicating that consensus does not exist among the various agencies. It is not clear if chemical attack can be prevented through sound construction practices alone.

EXPERIMENTAL APPROACH

To accomplish the work of this project, a series of field explorations and laboratory experiments were performed, and the results of these form the basis of the conclusions presented.

For samples received from the field sites and samples resulting from the laboratory experiments, a number of analytical methods were used to accomplish a complete microstructural characterization.

Techniques used included visual inspection, stereo optical microscope examination, staining, plus petrographic optical microscope, scanning electron microscope (SEM), and x-ray microscope examination. For the laboratory experiments, mortar and concrete specimens exposed to various deicers were examined by most of these same methods in addition to x-ray diffraction, profile grinding to determine chloride diffusion coefficients, sorptivity testing, and rapid chloride profile testing

STUDY OF FIELD CONCRETE

To accomplish project Task 5, Characterization of Field Specimens, the research team began by meeting with the technical advisory panel and discussing possible sites that 1) represent the range of deicers being currently used and 2) either exhibit some level of distress or represent new pavements that have been exposed only to one specific deicer. The intent of the study was to identify distress mechanisms that are visible in field concrete and study field concrete that has been exposed to a specific deicer, to assess how that one specific deicer is interacting with the concrete. Initially, five sites were identified for coring and analysis by petrographic methods. Later, two additional sites were sampled and core samples from these sites were also examined by petrographic methods.

LABORATORY STUDY

The laboratory study was conducted in two phases. Phase I involved the testing of mortar specimens (i.e. sand, cement, and water only) and Phase II involved performing the same battery of experiments used in Phase I, but with concrete specimens (i.e. sand, cement, aggregate, and water).

Phase I

In Phase I, mortar mixtures were exposed to the deicing chemicals of interest under various temperature regimes to examine how deicing chemicals interact with hardened portland cement paste. Also, the results of these tests were used to help select material parameters for Phase II in which concrete was tested.

The deicer solutions used included aqueous solutions of NaCl, $MgCl_2$, $CaCl_2$, CMA, and MBAP. Solution strengths ranged from 15 – 25% salt by weight. These concentrations represent a 30 – 50% reduction in solution strength as compared to that used in actual anti-icing or deicing of pavements, with the exception of NaCl and CMA that were tested using the same strength used in practice.

Air entrained and non-air entrained mortar mixtures were prepared using 20-30 Ottawa sand (ASTM C778), Type I/II cement, and water with the *w/c* as the independent variable. Three separate groups of tests were performed. In the first group, mortars prepared with *w/c* increments of 0.40, 0.50, and 0.60 were immersed in the various solutions at 40 ºF [4 ºC], 135 ºF [57 ºC], and in a cyclic test that varied from -15 ºF to 135 ºF [-26 to 57 ºC] over a two day cycle. Specimens from each test were examined petrographically for signs of chemical attack. In the second set of tests, mortars prepared with a *w/c* of 0.485 were immersed at a constant 40 ºF [4 ºC] for various times and then physical tests were performed including length change, mass change, change in solution pH, compressive strength, and mercury intrusion porosimetry. In a third group of tests, mortars were exposed to varying concentrations of $MgCl_2$ and $CaCl_2$ to determine the pessimum concentration for these solutions.

The Phase I experiments conducted identified that at least two of the deicing chemicals tested caused damage in portland cement mortar. Also, Phase I identified which testing regimes were ineffective at demonstrating the effects of deicing chemicals on mortar, and by implication, concrete. These ineffective tests were not continued from Phase I to Phase II.

Phase II

Phase II of this research focused on two general areas: chemical attack to concrete and scaling in the presence of deicers. Tests were performed to assess the mechanisms of chemical attack, scaling, and the effects of sealants on preventing distress. Also, fundamental material parameters were determined including the relative diffusivity of the various deicers in concrete and the role of solution strength on concrete degradation.

Various concrete mixtures were used in these experiments. To assess chemical attack, concrete mixtures were made with a *w/c* of 0.45 and 0.55. Additional mixtures were prepared, one with 15 percent replacement of cement with Class F fly ash and another with 35 percent replacement of cement with GGBFS. Specimens cast were standard 4-inch diameter x 8-inch high [100 x 200-mm] cylinders, which in turn were sectioned to produce three 2-in high by 4-in [50 x 100-mm] diameter samples per cylinder. A goal of Phase II was to determine the effect of deicer concentration on observed concrete degradation. To accomplish this, two concentration levels were established for deicer solution exposure. The high concentrations were identical to the concentrations used for each deicer in Phase I with the exception of CMA, which was reduced to 15% for a high concentration. The lower concentration was approximately half of the high concentration, the exact solution concentration being dependent upon the particular deicer. The specimens were submerged in deicer solutions at 40 ºF [4 ºC] and the mass change was monitored. The specimens were analyzed petrographically after 56 and 84 days of submersion.

In other tests, concrete slabs and prisms used for testing were prepared along with 4x8-inch [100 x 200-mm] cylinder specimens cast for compressive strength testing at 28 days of age. The mixtures used were prepared with a *w/c* of 0.45. As a preconditioning period, the concrete slabs were exposed for one year to a solution prepared using the pessimum concentration for $MgCl_2$ and $CaCl_2$ found in the mortar experiments in Phase I. Then the salt scaling resistance was determined following the standard procedure; that is, exposing the concrete surface to either 4% $CaCl_2$ or 4% $MgCl_2$. Reference slabs were exposed to 23% NaCl for a year and then their salt scaling resistance was determined following the standard procedure.

Concrete prisms were subjected to cycles of freezing and thawing using as an exposure solution $CaCl_2$, $MgCl_2$ and NaCl fixed to 3 molar by chloride concentration.

CHARACTERIZATION OF FIELD SPECIMENS

In general, the sites initially identified for study lacked unambiguous evidence of distress associated with deicers. To continue the field study, the research team obtained additional cores from a number of bridge decks in Montana that were exhibiting distress. Although these bridge decks are maintained using various non-NaCl deicers, they are all bridge decks that have been in service for numerous years and as a result, have been exposed to NaCl deicers for a significant portion of their service lives. Ultimately, because of this maintenance history, any distress identified would be difficult to associate with a specific deicing chemical. However, the team felt it was important to examine these bridge decks to determine if any visible mechanisms of chemical attack could be identified. Example results from one original field site and one of the additional sites are provided.

SOUTH DAKOTA, SIOUX FALLS, EASTBOUND 26TH STREET LEFT-TURN LANE ONTO NORTHBOUND, INTERSTATE HIGHWAY 29

This pavement was placed on November 1, 1996, and exposed to $MgCl_2$ brine shortly thereafter on November 15, 1996. The coring site is shown in Figure 1. Two of the received cores were cut into slabs and polished: core SD-1 (at a joint), and core SD-4 (mid-panel). Figure 2 shows the slabs as polished, after staining with phenolphthalein (to show areas of carbonation), and after a black and white dye treatment to enhance air voids and cracks. The phenolphthalein stain showed normal carbonation depths. The black and white treatment did not reveal any macro-cracking in either of the cores. Both sets of slabs showed adequate entrained air, with spacing factors of 0.0062 inch [0.158 mm] and 0.0069 inch [0.176 mm] for cores SD-1 and SD-4, respectively. Figure 3 shows an example stereomicroscope image of the air void structure. Water to cement ratio estimations were performed on thin sections prepared from cores taken at the joint and on cores taken at mid-panel. Estimates of the *w/c* value for the concrete were performed using fluorescence microscopy, where thin sections impregnated with fluorescent epoxy are viewed in a microscope with ultra-violet light. The brightness of the fluorescence is proportional to the effective *w/c* value. Figure 4 compares cement paste fluorescence histograms from all cores. The samples prepared from the joint fluoresced consistently brighter than the samples prepared from mid-panel. The effective *w/c* estimates were consistently higher for the cores taken at the joint versus the cores taken at mid-panel. Two companion cores were prepared for chloride profiling: core SD-3 (at a joint), and core SD-7 (mid-panel). Figures 5 and 6 show chloride profiles from cores SD-3 and SD-7.

In general, the cores indicated that the concrete was in satisfactory condition. However, the difference in effective *w/c* between the concrete near the joint and the concrete mid-panel indicates that the concrete near the joint has undergone alteration, most probably dissolution of calcium hydroxide from the hardened cement paste, resulting in a more permeable concrete. There was also significant chloride penetration identified in the chloride profiling that was performed. The depth of chloride penetration is very high for concrete of this age and is most probably due to the concrete being exposed to chlorides only a few weeks after it was placed. Relatively young concrete is more susceptible to chloride ingress because the cement hydration process has not reached completion and the concrete is therefore more permeable.

Figure 1. Photograph of core site.

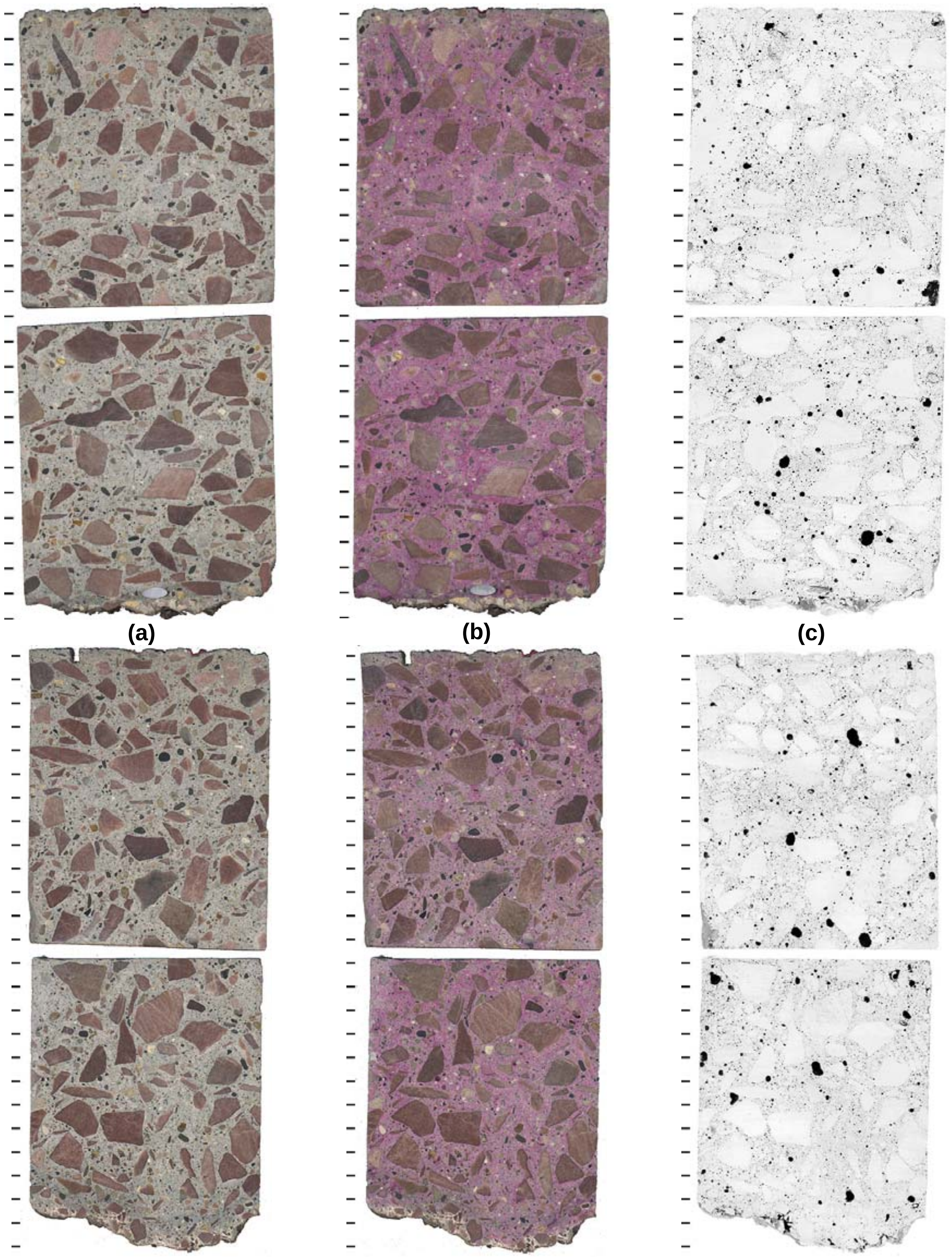


Figure 2. Polished slabs to show complete cross-section through core SD-1 (a-c) and SD-3 (d-e) both before (left) and after application of phenolphthalein stain (center), and after treatment to enhance appearance of air voids and cracks (right) (tic marks every cm).

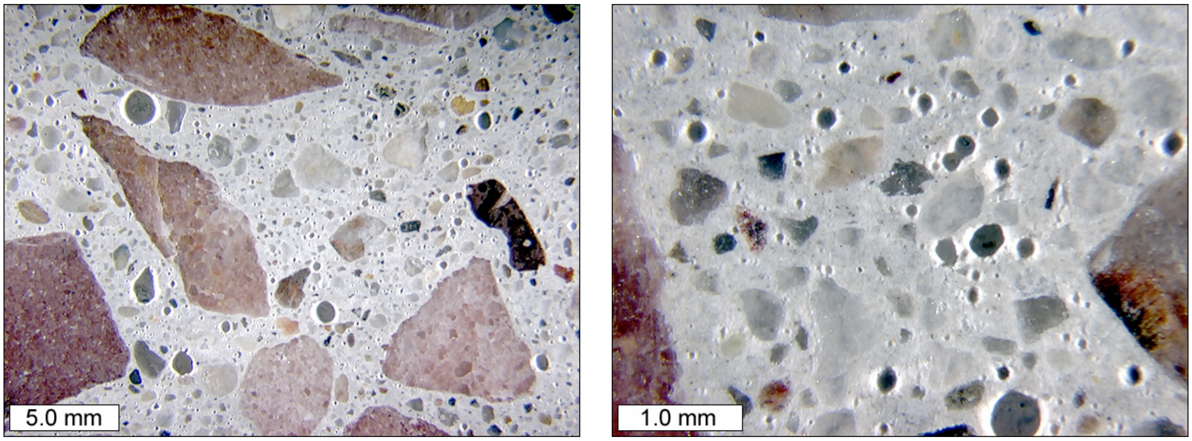


Figure 3. Stereo microscope images to show air-void system from core SD-4.

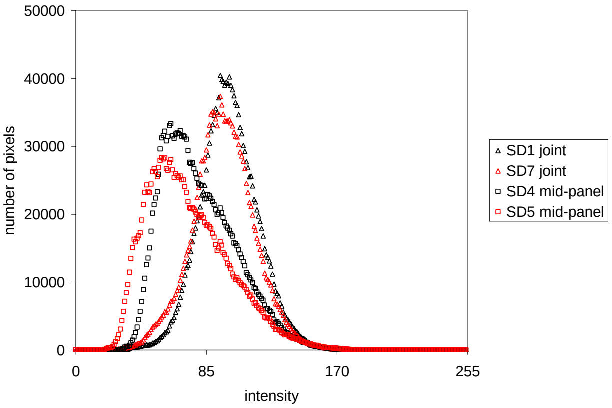


Figure 4. Histogram comparing cement paste pixel intensities using all images collected from thin sections prepared from cores taken at the joint versus cores taken mid-panel.

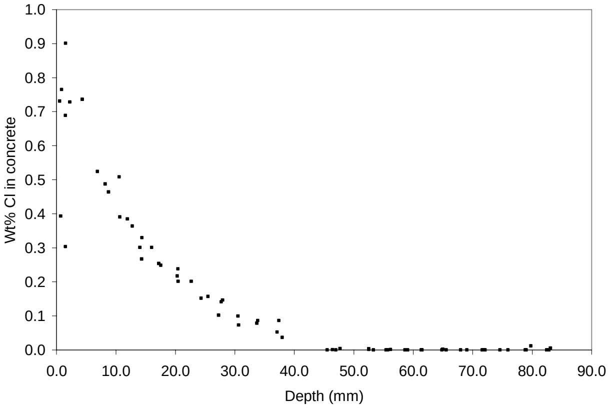


Figure 5. Chloride profile from billet prepared from core SD-3, near joint.

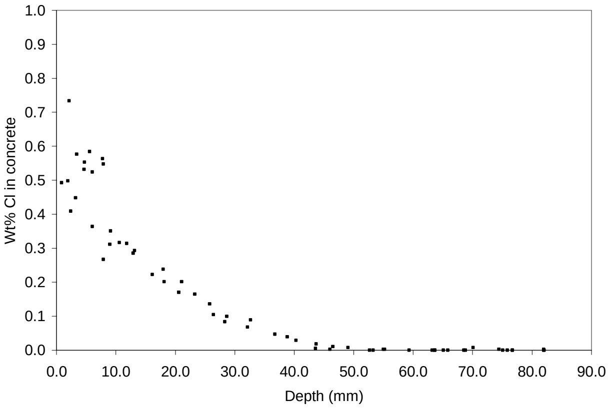


Figure 6. Chloride profile from billet prepared from core SD-7, mid-panel.

MONTANA, EASTBOUND INTERSTATE HIGHWAY 90 BRIDGE DECK, NEAR MILEPOST 61.8, TARKIO INTERCHANGE

The Tarkio interchange was constructed in 1958, and lies at the border of two maintenance areas: 1113, and 1114. Maintenance personnel indicated they used both $MgCl_2$ brine and a combination of NaCl and sand on this bridge deck. Maintenance personnel described spalling at many of the bridge decks in the area that had been coated with a thick (~ ¼ inch [6.4 mm]) layer of epoxy and aggregate. In order to patch the spalls, they had to first scrape away the epoxy layer, which debonded the concrete so it came off in sheets. It was never stated that this was the case at the Tarkio interchange, which appeared to be uncoated. Figure 7 shows the condition of the bridge deck, which is covered with cold patch material, and also the underside of the bridge deck with pronounced efflorescence especially in areas directly below regions covered with cold patch material. Core T-1 exhibited a crack plane at a depth of about 1 ¾ inches [45 mm]. The entire core was vacuum-impregnated with epoxy and used only for thin section preparation. Core T-2 was intact, and cut into slabs and polished. Figure 8 shows the slab as polished, after staining with phenolphthalein, and after treatment to enhance air voids and cracks. The phenolphthalein stain showed normal carbonation at the surface, but pronounced carbonation of over 0.4 inches [1 cm] thick at the base of the deck. The black and white treatment did not reveal significant macro-cracking. The concrete showed inadequate entrained air, with a spacing factor of 0.0116 inch [0.296 mm]. Figure 9 shows an example stereomicroscope image of the air void structure. An effective *w/c* ratio estimation was performed on a thin section prepared from the top of core T-2. The results of the effective *w/c* estimation showed an average value of 0.33. Figure 10 shows a chloride profile from core T-2. Figure 11 shows the location of a thin section prepared from core T-1 that was used for elemental mapping. A region was mapped to represent the pavement surface and the area adjacent. Figure 12 shows the elemental maps from the two regions. The most interesting feature of the elemental maps is the magnesium map in Figure 12 that shows magnesium enrichment at the surface of the bridge deck.

In general, the cores indicated that the concrete was in satisfactory condition for its age. There was strong evidence of brucite formation at the road surface indicating a high exposure to $MgCl_2$. Calcium hydroxide deposits were seen in cracks at depth and calcium hydroxide depletion from within the cement paste near cracks was observed. Although these are all diagnostic features of concrete undergoing chemical attack by deicers, the concrete also had a poor air void system, which contributed to its poor condition. The physical observations regarding the presence of the white efflorescence, is important and will be discussed later.

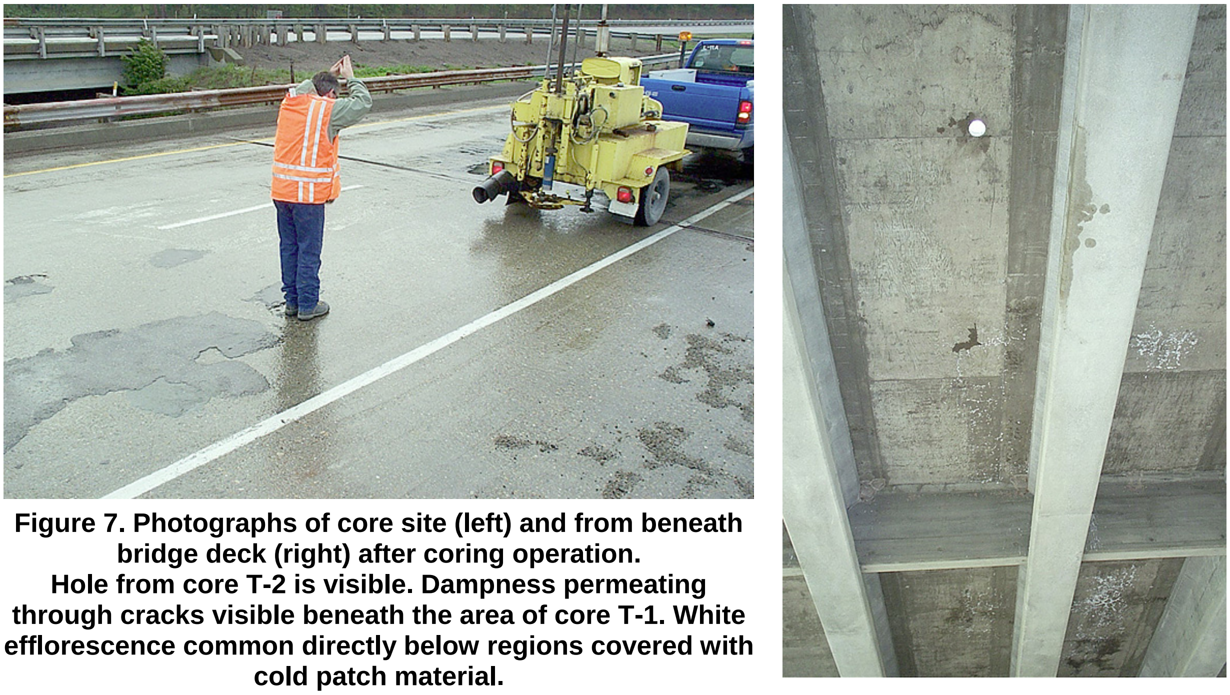


Figure 7. Photographs of core site (left) and from beneath bridge deck (right) after coring operation. Hole from core T-2 is visible. Dampness permeating through cracks visible beneath the area of core T-1. White efflorescence common directly below regions covered with cold patch material.

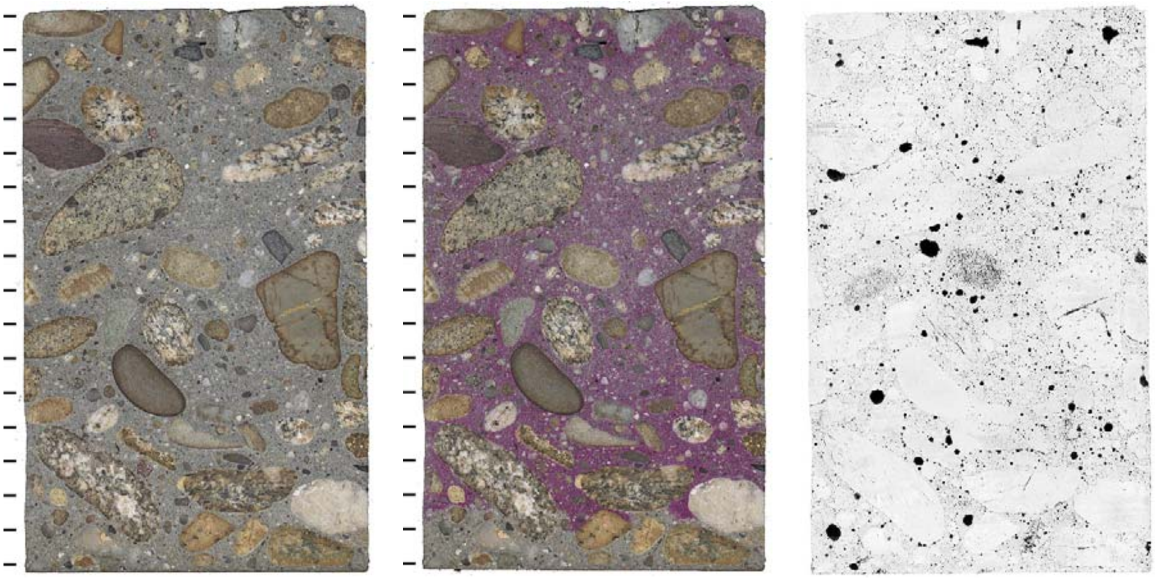


Figure 8. Polished slabs to show complete cross-section through core T-2 before (left), after application of phenolphthalein stain (center), and after treatment to enhance appearance of air voids and cracks (right) (tic marks every cm).

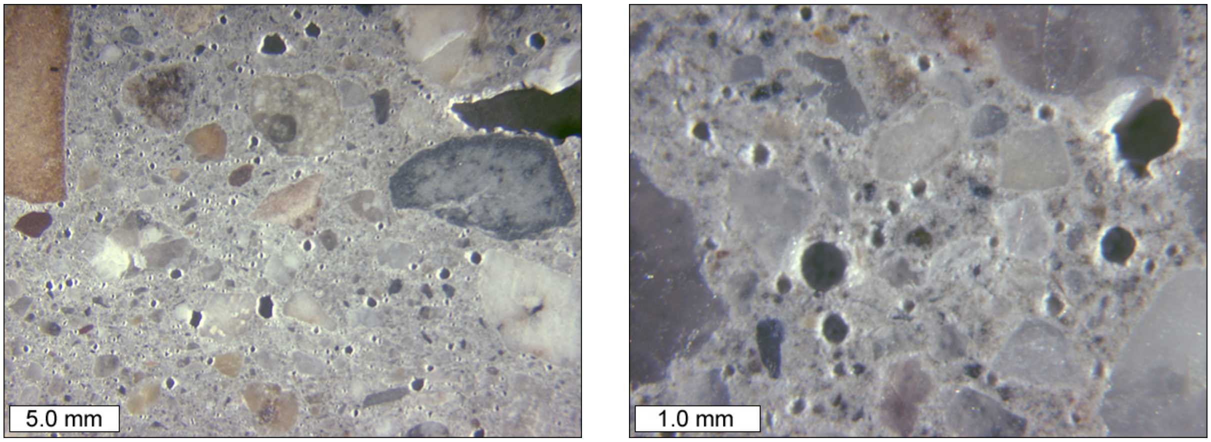


Figure 9. Stereo microscope images to show air void structure on polished slab from core T-2.

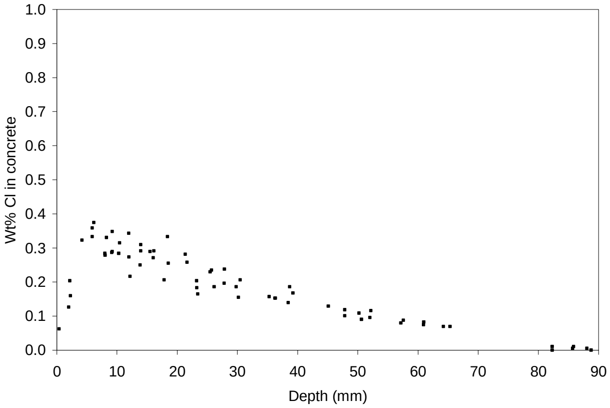


Figure 10. Chloride profile from billet prepared from core T-2.

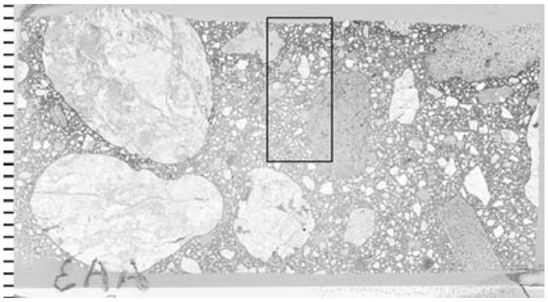


Figure 11. Transmitted light scanned image of thin section to show location of elemental maps shown in Figure 12. The top of the thin section represents the wear surface of the pavement, (tic marks every mm).

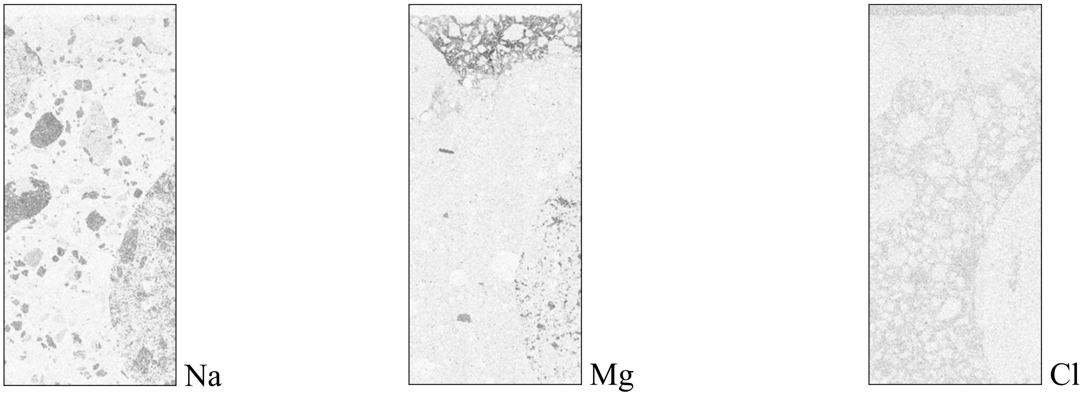


Figure 12. Elemental maps from pavement surface, darker regions indicate higher concentrations.

RESULTS OF THE LABORATORY STUDY

PHASE I LABORATORY EXPERIMENT RESULTS

A constant low temperature experiment was designed to monitor chloride ingress at 28, 56, and 84 days at a temperature of 40°F [4 ºC]. As shown in Figure 13, the cylinders in the NaCl solution showed no deterioration after 84 days. Figures 14 and 15 show cylinders from the $MgCl_2$ and $CaCl_2$ treatments were severely deteriorated by 84 days. The cylinders in the CMA solution showed little to no distress after 84 days as shown in Figure 16, although there was some staining evident in the 0.60 *w/c* cylinders. The control cylinders in the lime water solution, as shown in Figure 17, showed no signs of distress after 84 days.

**Figure 13. Cylinders exposed to NaCl solution after 84 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 *w/c* mortar cylinders.**

**Figure 14. Cylinders exposed to MgCl2 solution after 84 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.**

**Figure 15. Cylinders exposed to CaCl2 solution after 84 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.**

**Figure 16. Cylinders exposed to CMA solution after 84 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.**

Figure 17. Control cylinders exposed to lime water solution after 84 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders.

Petrographic Analysis

Thin sections were prepared from the 0.50 *w/c* mortar cylinders subjected to 56 days of immersion in the five solutions. One cylinder was selected from each of the five solutions: $MgCl_2$, $CaCl_2$, NaCl, CMA, and lime water. The thin sections represent a cross-sectional plane oriented parallel to the finished surface to a depth of about 3/4 inch, [19 mm] from the finished surface. Figure 18 consists of SEM back-scattered electron images of representative areas from all five exposures to illustrate the extensive crack networks of the $MgCl_2$ and $CaCl_2$ immersed cylinders, as compared to the cylinders immersed in the other three solutions. Near the exteriors of the $MgCl_2$ and $CaCl_2$ exposed cylinders, the cracks are empty. However, cracks further towards the interior of the cylinders are filled with calcium oxychloride or the altered remnants of calcium oxychloride. Figures 19 and 20 show close-up views of regions of the cement paste disrupted by cracks filled with calcium oxychloride for both the $MgCl_2$ and $CaCl_2$ immersed samples. The deterioration of these samples appears very similar. Both samples exhibit a region of calcium oxychloride filled cracks and voids associated with calcium hydroxide depleted cement paste. Figure 21 shows elemental maps for magnesium for all of the thin sections. These maps show that a magnesium crust is present at the exterior of the $MgCl_2$ immersed sample as well as the CMA immersed sample. Magnesium is sequestered at the exterior of the $MgCl_2$ immersed cylinders, likely resulting in a $CaCl_2$ solution in the interior that is similar to the solution in the interior of the $CaCl_2$ immersed cylinders. Finally, Figures 22 and 23 correspond to the cylinder immersed in lime water showing no sign of cracking or any other deterioration.

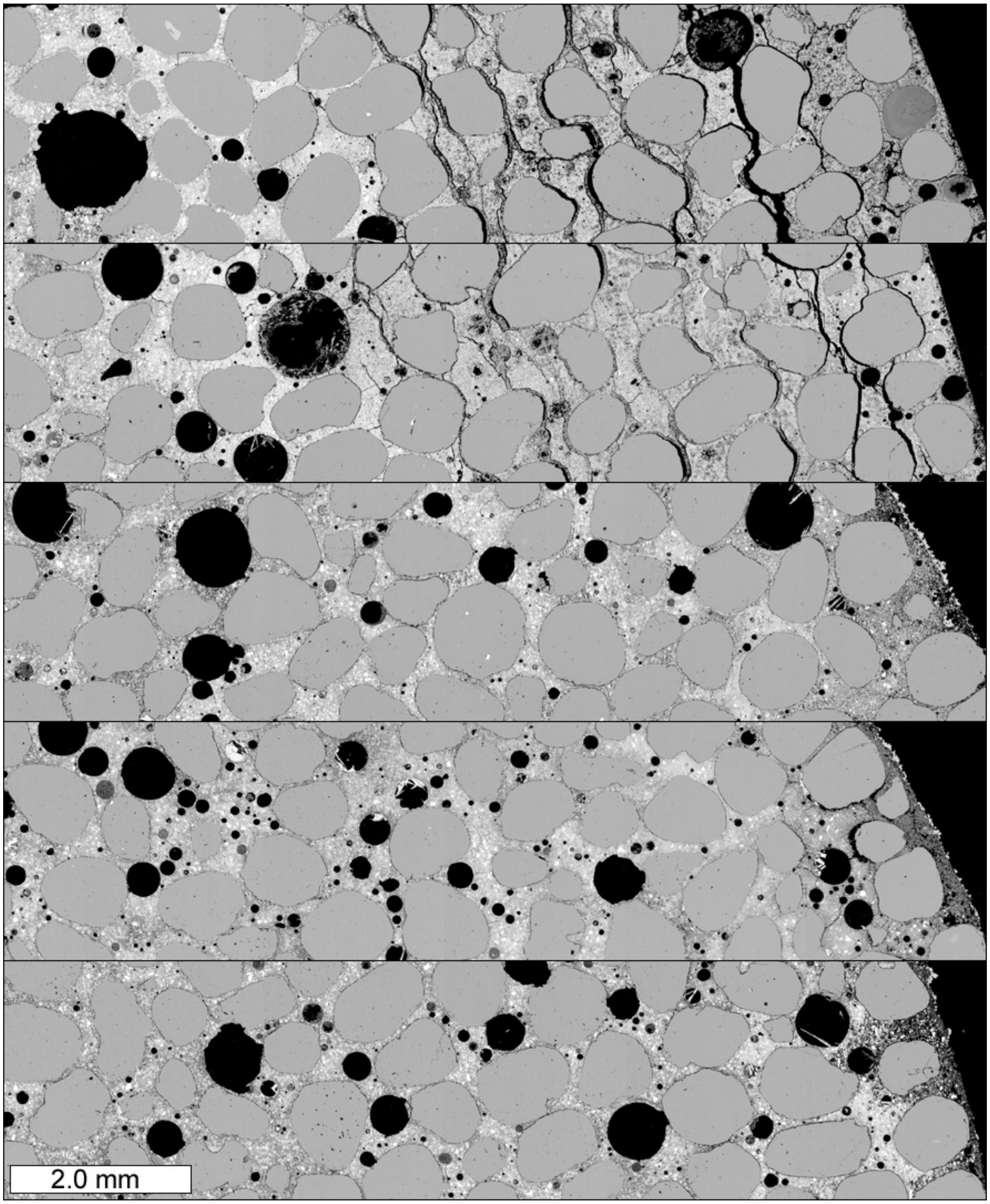


Figure 18. SEM back-scattered electron images of thin sections prepared from mortar cylinders immersed in chemical solutions showing the sub-parallel cracking that results from exposure to $MgCl_2$ and $CaCl_2$.
From top to bottom: magnesium chloride, calcium chloride, sodium chloride, calcium magnesium acetate, and lime water.

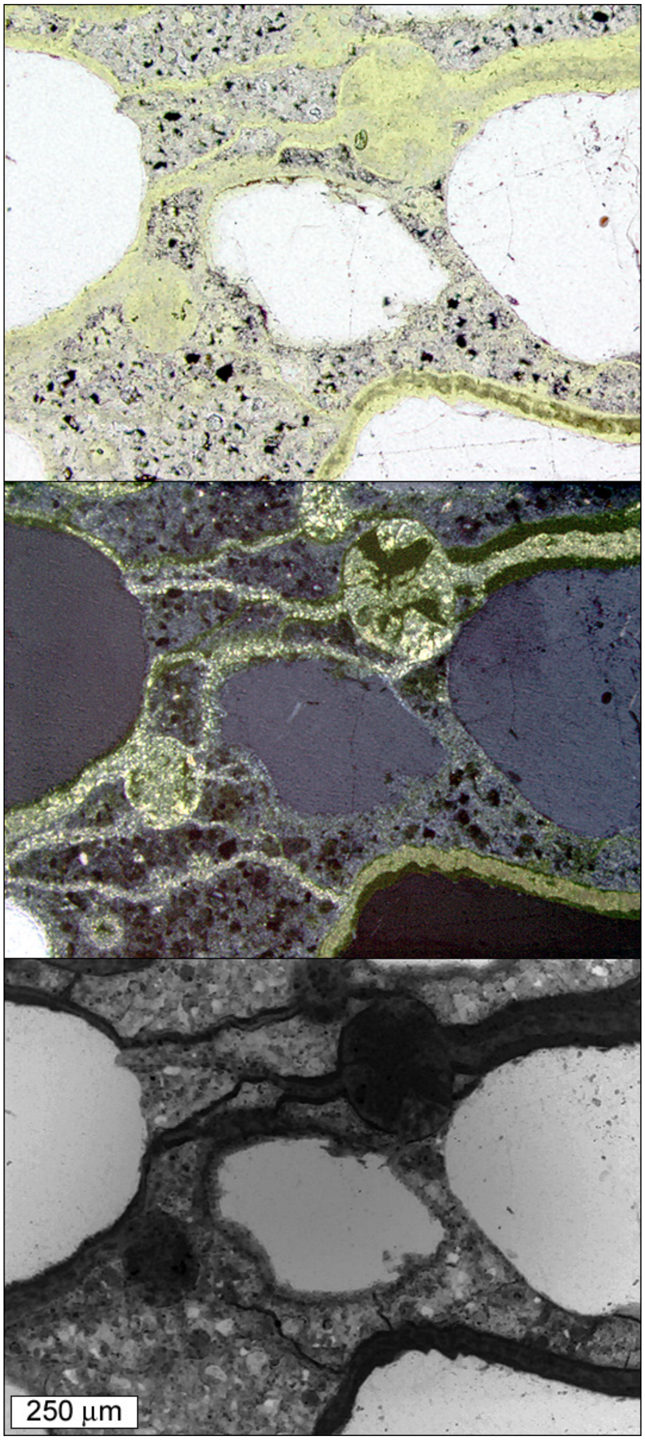


Figure 19. Cracks and air voids filled with remnant calcium oxychloride crystals in thin section prepared from magnesium chloride solution immersed sample.
From top to bottom: plane polarized light, cross polarized light, and epifluorescent mode.

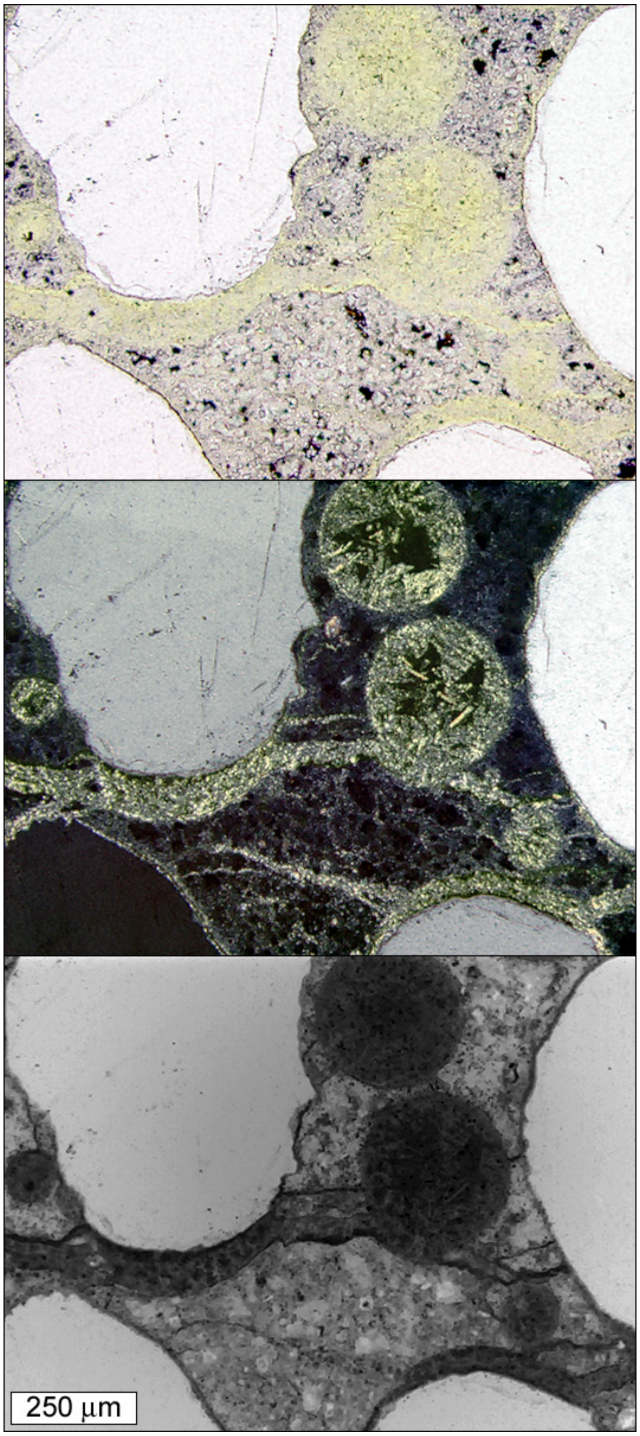


Figure 20. Cracks and air voids filled with remnant calcium oxychloride crystals in thin section prepared from calcium chloride solution immersed sample.
From top to bottom: plane polarized light, cross polarized light, and epifluorescent mode.

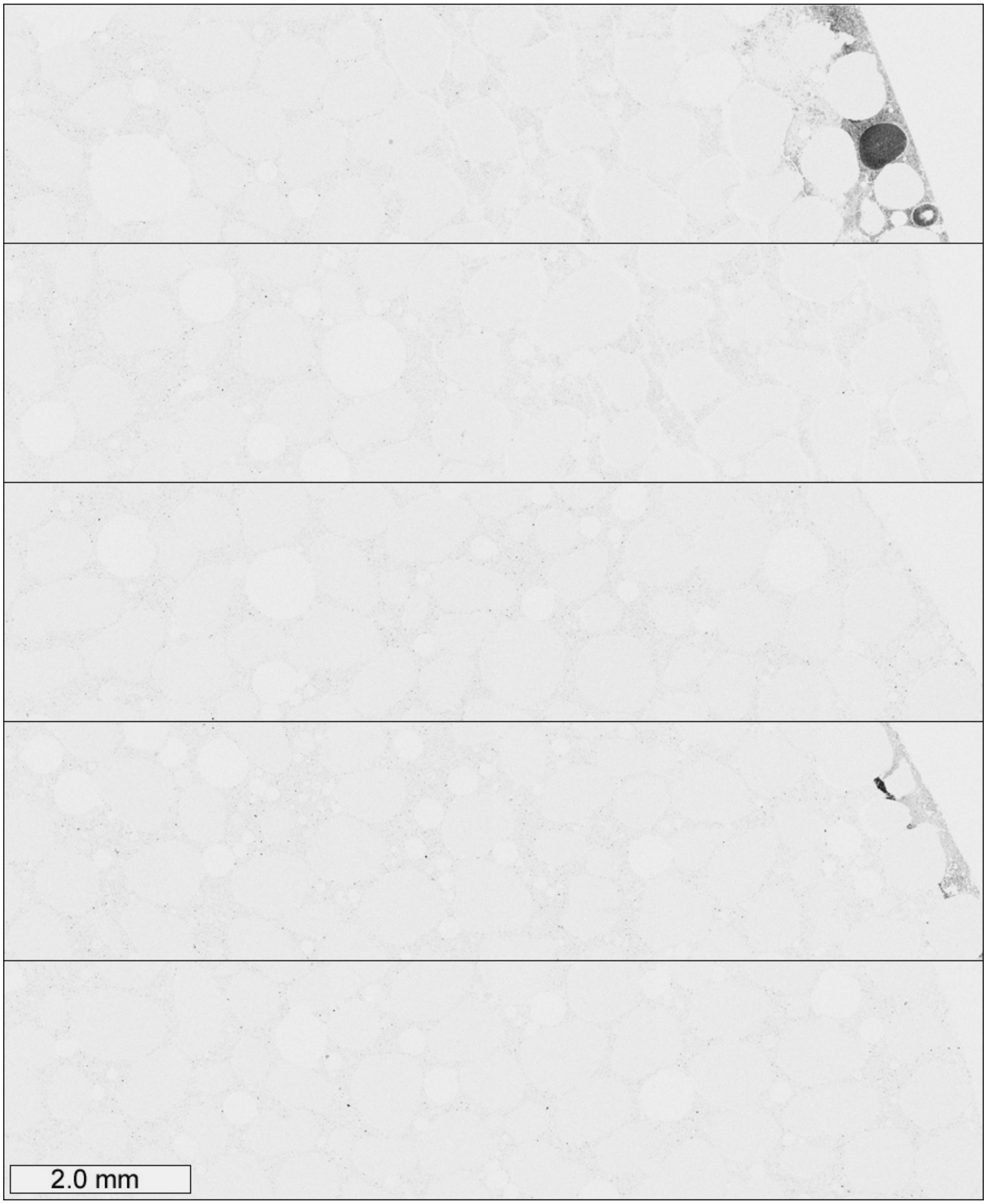


Figure 21. Elemental map for magnesium collected from thin sections prepared from mortar cylinders immersed in chemical solutions.
From top to bottom: magnesium chloride, calcium chloride, sodium chloride, calcium magnesium acetate, and lime water. Dark areas indicate higher concentrations.

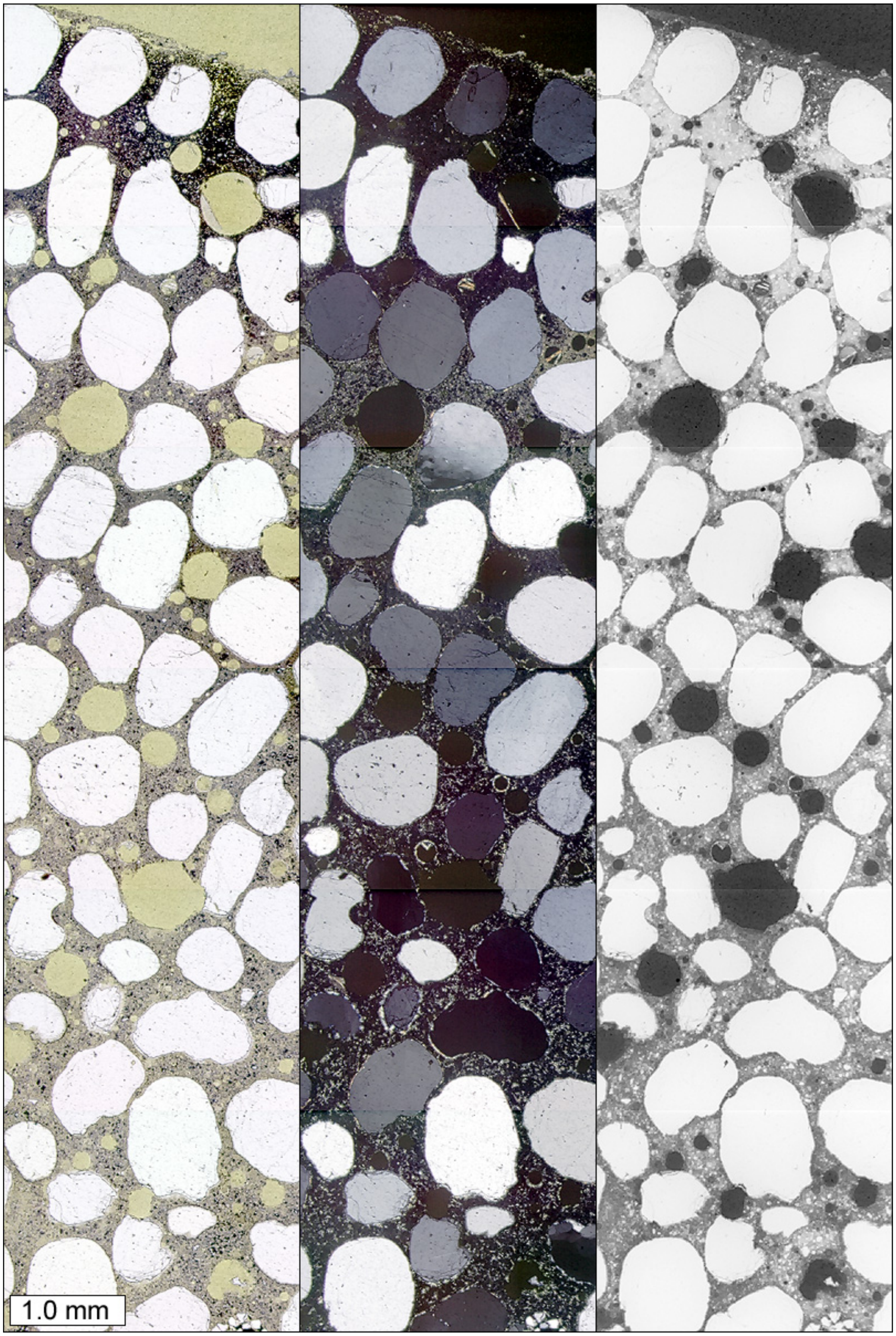


Figure 22. From left to right: plane polarized light, cross polarized light, and epifluorescent mode images of a thin section prepared from a cylinder immersed in lime water.

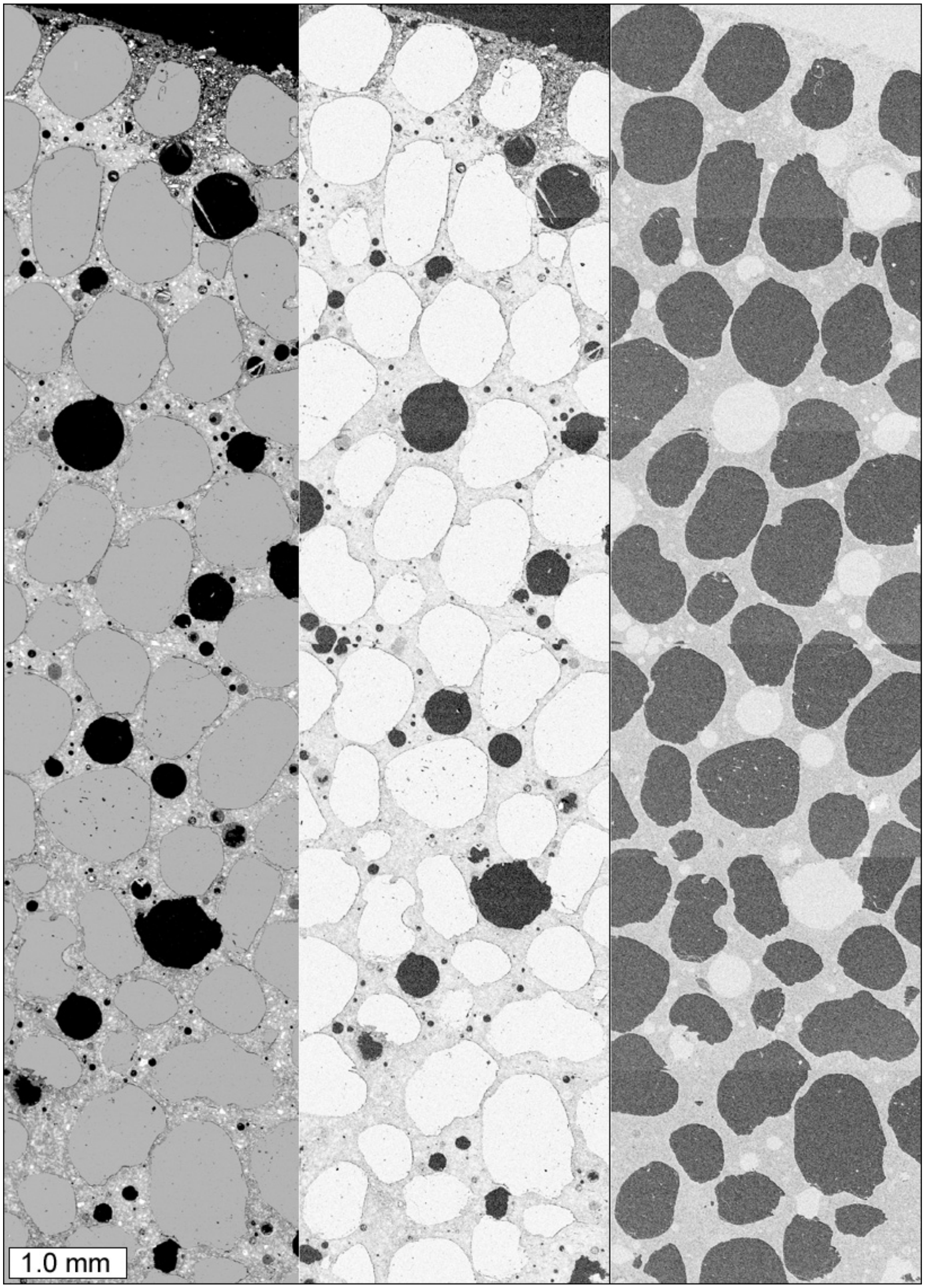


Figure 23. From left to right: back scattered electron image, elemental map for carbon, and elemental map for oxygen all intended to highlight any cracks.
Images were collected from a thin section prepared from a cylinder immersed in lime water.

Additional tests were performed to determine the effect of solution concentration on the observed distress. New constant low temperature $CaCl_2$ samples were exposed to the solutions at varying concentrations. For this experiment, solution concentrations were chosen at 3, 7, 10, and 14 weight percent salt for each solution. The specimens were left in solution for 54 days with random samples being pulled every 7 days for inspection and analysis. As can be seen clearly in Figures 24 through 28, concentration clearly has an effect on the observed damage at a given time for mortars exposed to the low temperature test.

**Figure 24. Cylinders exposed to CaCl2 solution after 56 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders. Solution strength was 3% CaCl2.**

**Figure 25. Cylinders exposed to CaCl2 solution after 56 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders. Solution strength was 7% CaCl2.**

**Figure 26. Cylinders exposed to CaCl2 solution after 56 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders. Solution strength was 10% CaCl2.**

**Figure 27. Cylinders exposed to CaCl2 solution after 56 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 w/c mortar cylinders. Solution strength was 14% CaCl2.**

Figure 28. Cylinders exposed to $CaCl_2$ solution after 56 days of constant low temperature test.
From left to right: 0.40, 0.50, and 0.60 *w/c* mortar cylinders.
Solution strength was 17% $CaCl_2$.

Compressive Strength

Mortar cubes with a constant *w/c* were prepared for these tests and were tested at 28 days of age to determine the baseline average compressive strength of the mortar cubes. After exposure to the different deicers, the compressive strength decreased for those samples exposed to MBAP, $MgCl_2$ and $CaCl_2$. The mortar cubes exposed to NaCl did not show a decrease in compressive strength and to the contrary, their behavior was similar to those samples exposed to calcium hydroxide. The samples exposed to MBAP and $MgCl_2$ showed similar trends in their compressive strength evolution with time. The results of this test are shown in Figure 29.

Expansion

Exposure of mortar bars to MBAP, $MgCl_2$ and $CaCl_2$ resulted in considerable expansion while those subjected to NaCl showed negligible expansion even after 500 days of exposure, as illustrated in Figure 30. Although MBAP and $MgCl_2$ caused the compressive strength to decrease to a similar degree, a similar correlation was not observed with the rate of expansion. The MBAP samples expanded almost twice as much as samples exposed to $MgCl_2$, with the same exposure period.

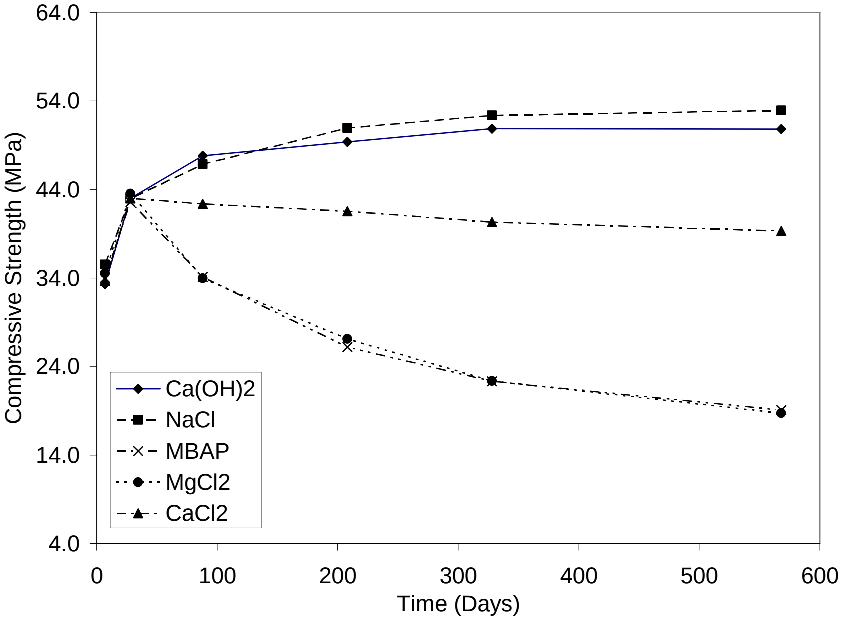


Figure 29. Compressive strength evolution with time of mortar cubes exposed to different deicers.

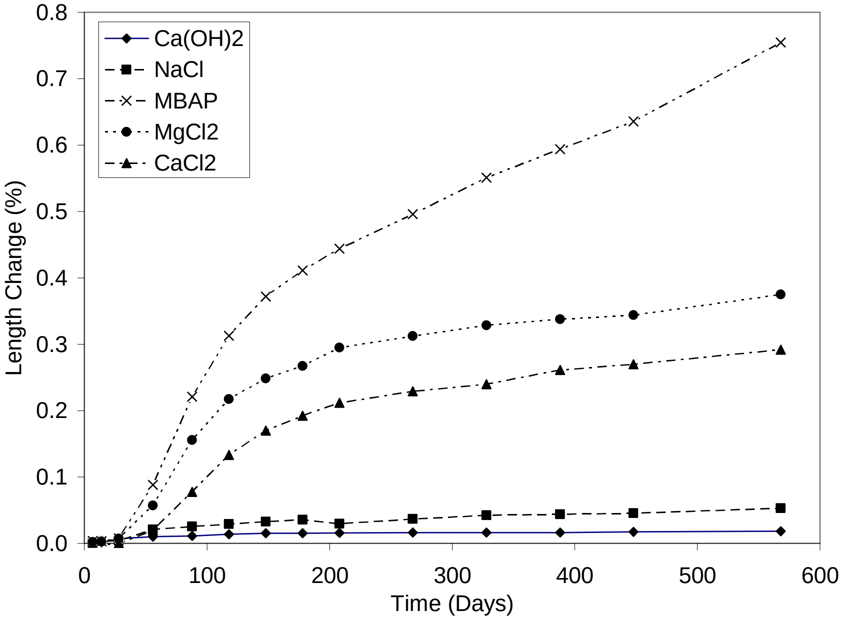


Figure 30. Length change of mortar bars with time exposed to different deicers.

Mass Change

For those specimens exposed to MBAP, $MgCl_2$ and $CaCl_2$, expansion of mortar bars was accompanied by considerable mass gain as shown in Figure 32. The greatest mass gain was 5.9% observed for those samples exposed to MBAP, followed by $MgCl_2$ with 3.6% and $CaCl_2$ with 2.4% mass gain. The specimens exposed to NaCl and calcium hydroxide did not show considerable mass gain.

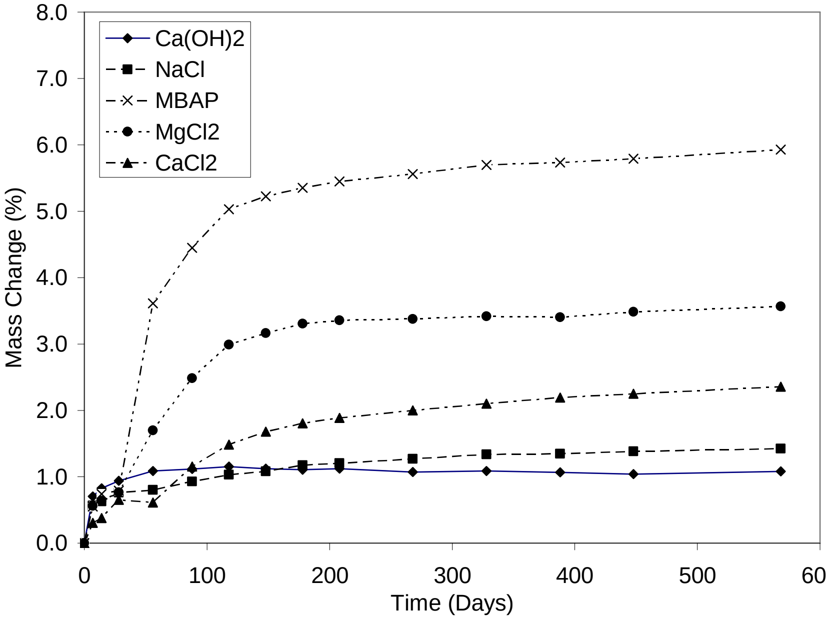


Figure 31. Mass change of mortar bars with time exposed to different deicers.

Visual Observations

Visual observations of the specimens exposed to MBAP and $MgCl_2$ that experienced loss of strength, expansion and mass gain revealed a clear feature. Defined zones of chemical interaction of 0 to 0.2 inches [0 to 5 mm] through the cross sectional area of the mortar bar were visible. These zones are easily identified by the changes in color from a light gray in the core of the specimen to a yellowish color at the surface. The presence of microcracks was confirmed using the stereo optical microscope.

At early ages (less than 118 days) a white layer developed on the surface of specimens exposed to $MgCl_2$ and MBAP and it was subsequently identified by x-ray diffraction as brucite. The deterioration front seemed to move deeper into the specimen with exposure time. Softening of the surface and debonding of sand grains were identified. None of these features were identified in samples exposed to either $CaCl_2$ or NaCl.

X-ray Diffraction

For mortar bars exposed to $MgCl_2$ and $CaCl_2$, X-ray diffraction analysis of powder samples taken from the surface up to a depth of 0.2 inches [5 mm] showed the formation of new phases and the depletion of others. In the case of the samples exposed to calcium hydroxide, no sign of chemical attack was found with the main calcium hydroxide peaks clearly defined in the diffractogram.

Those samples exposed to NaCl solutions had phases similar to those exposed to calcium hydroxide solutions, the only difference being the presence of Friedel's salt. In the case of MBAP, besides Friedel's salt, some peaks of magnesium oxychloride were identified. This phase was not detected in the samples exposed to $MgCl_2$ but instead defined peaks of brucite were found. For both MBAP and $MgCl_2$ the intensity of the main peaks of calcium hydroxide diminished suggesting depletion of this phase due to chemical attack, leaching or both.

Determination of Pessimum Concentration for MgCl2 and CaCl2

Mortar cubes were exposed to different concentrations of $MgCl_2$ and $CaCl_2$ to determine the effect of exposure solution concentration on the 30 day compressive strength of the mortar. The effect of concentration on compressive strength is shown in Figure 32. A minimum in compressive strength was seen at solution concentrations of 20% $MgCl_2$ and 22% $CaCl_2$. Examples of the distress observed are shown in Figures 33 and 34.

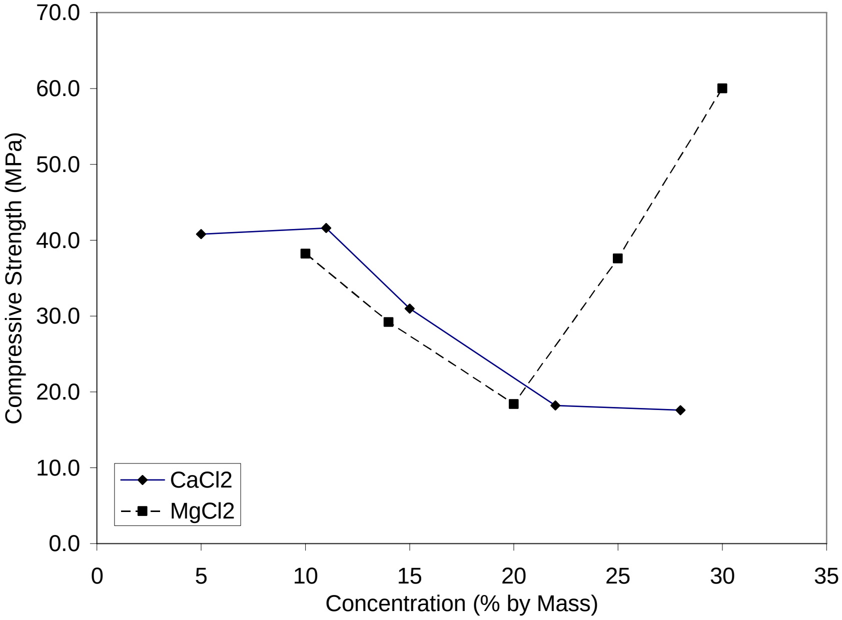


Figure 32. Effect of $MgCl_2$ and $CaCl_2$ on compressive strength after 30 days of exposure.

X-ray diffraction analysis of samples exposed to the pessimum concentration of $MgCl_2$ (i.e. 20%) and $CaCl_2$ (i.e. 22%) showed that the phase formed during the deterioration process of the mortar was magnesium oxychloride for $MgCl_2$ exposure and calcium oxychloride for $CaCl_2$ exposure.

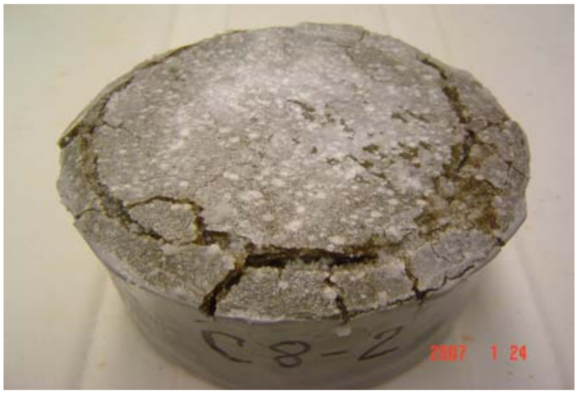


Figure 33. Deteriorated disc sample exposed to 20% MgCl2 after 150d of exposure.

Figure 34. Deteriorated disc sample exposed to 28% CaCl2 after 150d of exposure.

PHASE II LABORATORY EXPERIMENT RESULTS

Physical Characterization of Mortar and Concrete Mixtures

Concrete mixtures prepared for use in Phase II were analyzed to determine their sorptivity and bulk diffusion properties. These properties were compared to specimens coated with siloxane and silane sealants to determine the effectiveness of these sealants at preventing chloride ingress. Bulk diffusion is a measure of the overall rate of transport of an ionic species into concrete. Sorptivity is a measure of the permeability of the concrete and is a function of the concrete but also the solution being absorbed.

Bulk Diffusion

Concrete samples coated with siloxane did not allow the penetration of chloride ions. Therefore, the experimental data could not be fitted to determine a diffusion coefficient. Concrete samples coated with silane exhibited minor penetration of chloride ions. Both sealants were very effective at reducing chloride ion ingress into the concrete specimens.

Sorptivity

The sorptivity of mixtures prepared with GGBFS were less than that measured for mixtures prepared with Class F fly ash, which in turn were less than that measured for plain portland cement mixtures. Water and NaCl brine showed the highest sorptivity rate while MgCl2 showed the lowest sorptivity rate.

Macroscopic Observations

Concrete and mortar specimens were removed from the brine solutions at 60 and 500 days. None of the specimens showed any obvious external signs of deterioration at 60 days. At 500 days, many of the specimens from the high-concentration $CaCl_2$, $MgCl_2$, and MBAP brines exhibited external cracking, examples of which are shown in Figure 35.

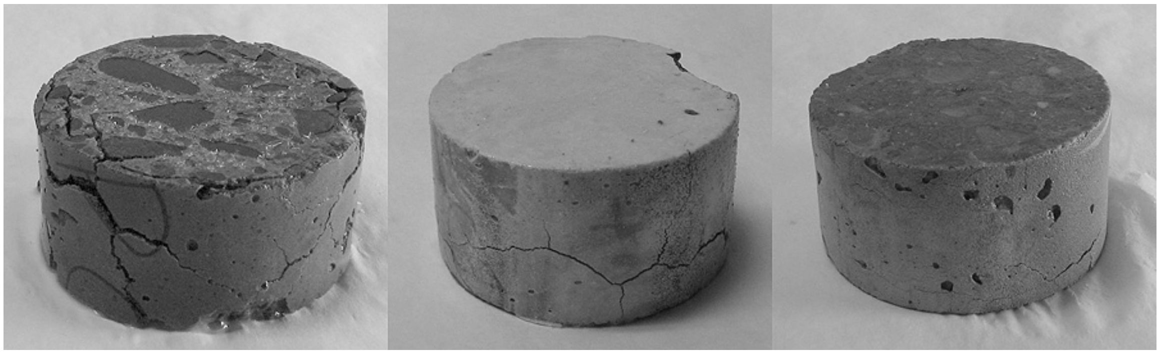


Figure 35. Photographs of 4 inch (100 mm) diameter 0.45 w/c OPC concrete specimens after 500 days in high concentration brines.
From left to right: CaCl2, MgCl2, and MBAP brines.

Coatings of oxychloride crystals were typically observed on specimens from the $CaCl_2$, $MgCl_2$, and MBAP brines. External precipitates were not observed on specimens from the other brines, with the exception of specimens immersed in the low-concentration CMA brine. Figures 36 and 37 illustrate the precipitates present on the surface of a specimen from the high-concentration $CaCl_2$ solution and the low-concentration CMA brine, respectively.

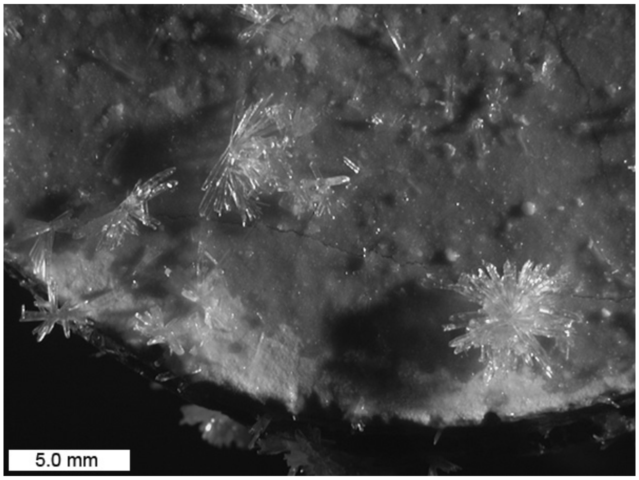


Figure 36. Crystals on exterior of concrete specimen after 500 days immersion in high-concentration CaCl2 solution.

Figure 37. White precipitate on exterior of 4 inch (100 mm) diameter concrete specimen after 500 days immersion in low-concentration CMA solution.

Digital images were used to make visual estimates of the degree of alteration of saw-cut cross-sections of the specimens. The perimeters of each specimen cross-section were outlined and any zones of visible alteration were outlined. Figure 38 shows example images from the 0.45 *w/c* mortar specimens from the five high-concentration brine solutions showing visible alteration. The high-concentration $CaCl_2$, $MgCl_2$, and MBAP solutions were more aggressive than the NaCl and CMA solutions in terms of the visual alteration.

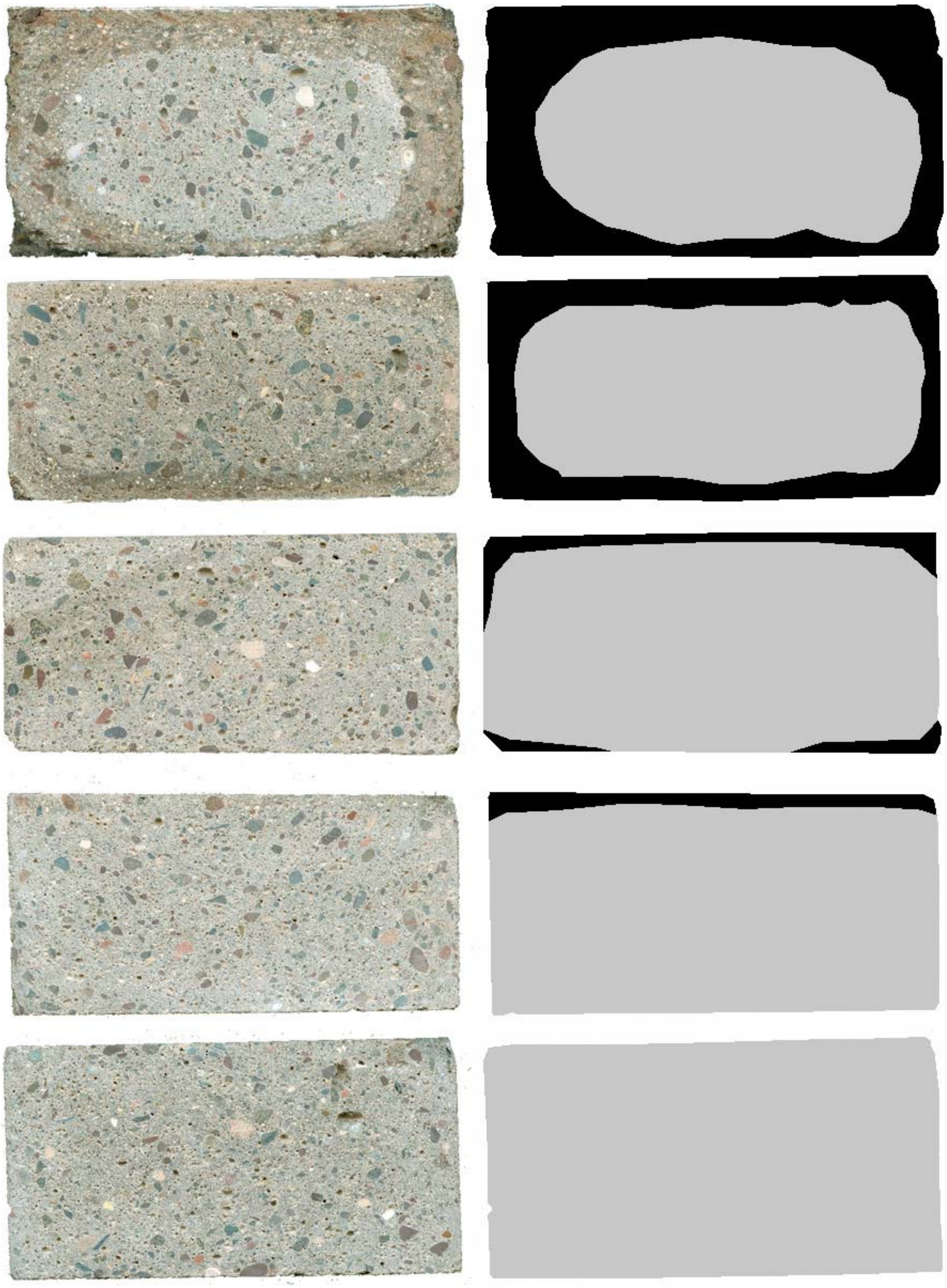


Figure 38. Visible alteration on saw-cut plane through 0.45 *w/c* mortar specimens, from top to bottom: $CaCl_2$, $MgCl_2$, MBAP, NaCl & CMA high-concentration brines at 500 days.

X-ray Diffraction

Cement paste was extracted from the deteriorated concrete samples exposed for 500 days to the high concentration $MgCl_2$ and $CaCl_2$ brines. XRD patterns were collected from the samples in both the wet and dry condition. An XRD pattern from the wet paste extracted from the concrete exposed to the $CaCl_2$ brine showed that the primary phase is calcium oxychloride.

Experiments were performed to determine how the oxychloride phase changed when exposed to different environmental conditions. At high temperature, the calcium oxychloride reverted to low water (i.e. 2 waters of hydration) calcium oxychloride phase. This altered material was then immersed overnight in distilled water at room temperature, in equilibrium with atmospheric carbon dioxide. The XRD pattern of the resultant material from this experiment showed that the low water calcium oxychloride phase was converted to calcite ($CaCO_3$). A second sample of calcium oxychloride was subjected to a brine cure treatment where it was heated to 122°F [50°C] overnight in a sealed container filled with $CaCl_2$ brine. After treatment, the XRD pattern showed that some calcium oxychloride remained, but there were also new peaks present for calcium hydroxide. In another experiment, the extracted cement paste sample was allowed to air dry for one week and re-analyzed. Peaks for calcite were observed in the dried paste, and no peaks were observed for calcium oxychloride or the low water calcium oxychloride.

Optical Microscopy

Thin sections were prepared from 0.45 *w/c* portland cement concrete specimens to represent all of the high-concentration brines and the limewater control after 500 days of immersion. Thin sections were also prepared from 0.45 *w/c* concrete specimens with supplementary fly ash and slag, but only those exposed to the $CaCl_2$, $MgCl_2$, and MBAP brine solutions for 500 days. An additional thin section was also prepared from a 0.55 *w/c* concrete specimen that had been sealed with silane and immersed in high-concentration $MgCl_2$ brine for 500 days.

Comparison of the 0.45 w/c Portland Cement Concrete Specimens from the Six Solutions

Figure 39 shows epifluorescent mode images from all of the 0.45 *w/c* plain portland cement concrete specimens. The images depict the specimens in cross-section, with the top surfaces of each specimen facing towards the right hand-side. Cracking planes sub-parallel to the surface are evident in the specimens exposed to the $CaCl_2$, $MgCl_2$, and MBAP brines, while the specimens exposed to the CMA and NaCl brines, and the specimen exposed to the lime water, do not show any cracking. Figure 40 shows further close-up epifluorescent mode images from the same areas outlined in pink from Figure 39. Figures 41 through 43 show close-up images of the cracks in the specimens exposed to $CaCl_2$, $MgCl_2$, and MBAP brines. In all of these specimens, a similar pattern of blocky birefringent crystals is observed in the cracks and air voids in the deteriorated regions. The crystals have the same birefringence colors as calcium hydroxide, but their blocky appearance departs from the usual calcium hydroxide morphology, which generally occurs as stacks of thin hexagonal plates, or as isolated thin hexagonal plates. The cement paste in the deteriorated portions is generally devoid of calcium hydroxide. Figures 44 through 46 show images of cement paste with abundant calcium hydroxide. These images were taken from areas just below the surfaces of the 0.45 *w/c* plain portland concrete specimens exposed to the NaCl, CMA, and lime water solutions. Secondary calcium hydroxide deposits are present in the air voids of the specimen immersed in lime water, as shown in Figure 46. The shape of these calcium hydroxide crystals, long and thin in cross-section, is a typical morphology for secondary calcium hydroxide, and in contrast to the blocky morphology demonstrated in the air voids and cracks of the deteriorated specimens (Figures 41 through 43).

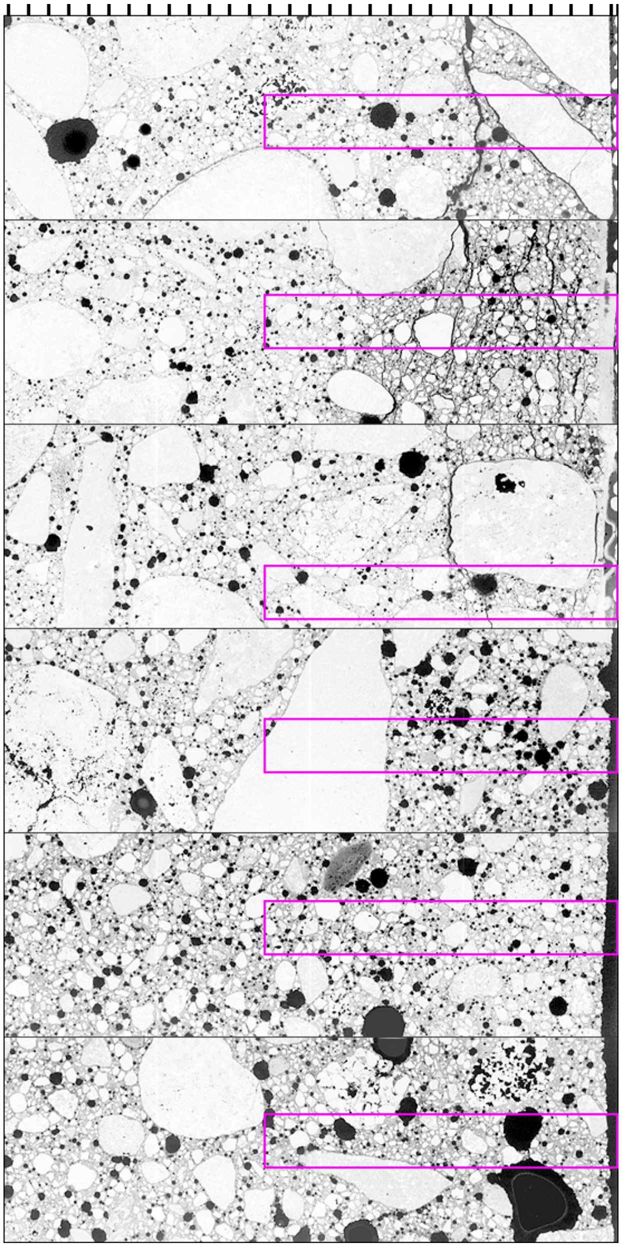


Figure 39. Epifluorescent thin section views of the 0.45 *w/c* concrete specimens immersed in solution for 500 days, exterior surfaces to the right. From top to bottom: $CaCl_2$, $MgCl_2$, MBAP, NaCl, CMA, and lime water. Pink boxes highlight close-up regions shown in Figure 40. (tic marks every mm)

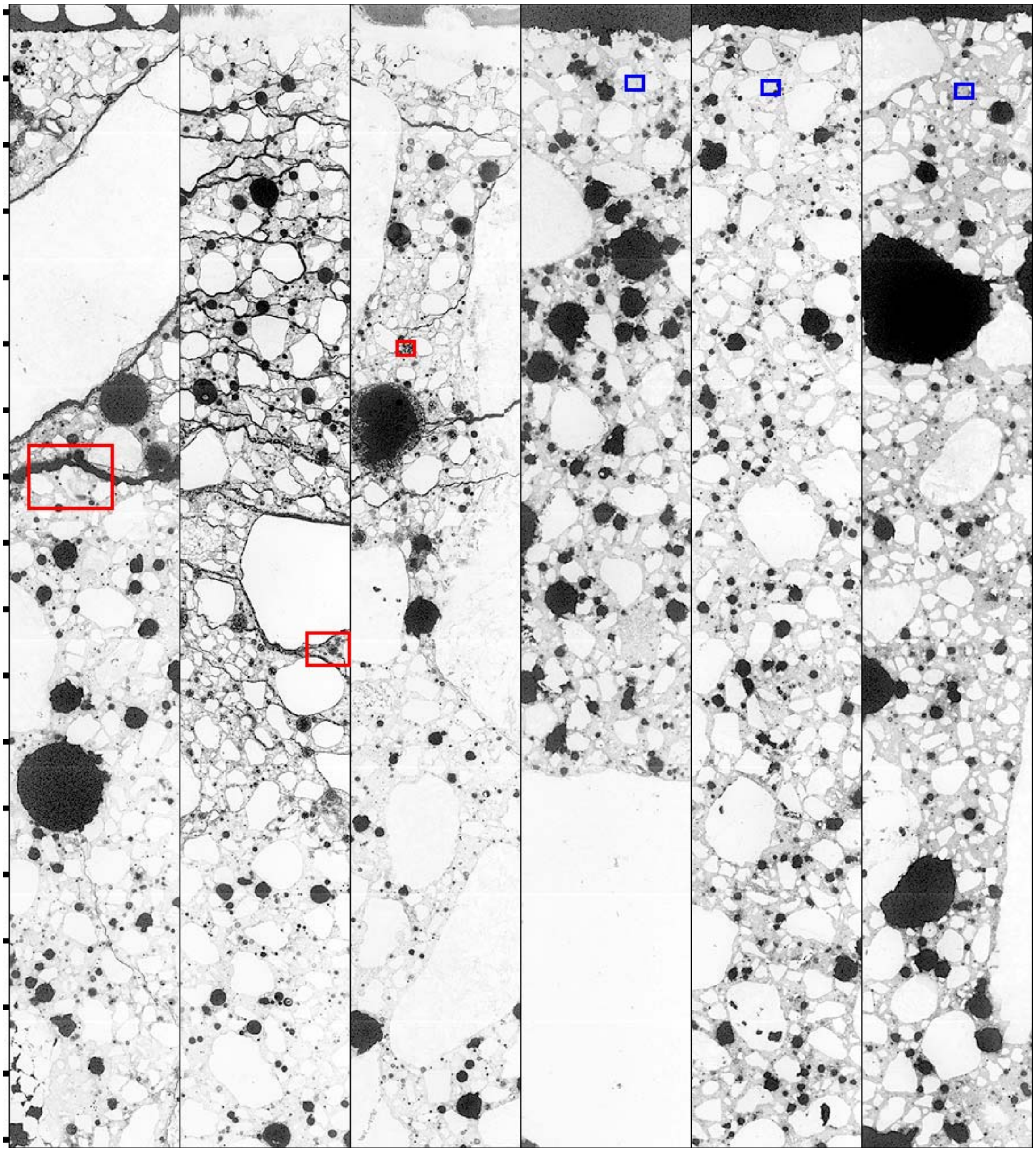


Figure 40. Close-up views of regions outlined in pink in Figure 39, but with exterior surfaces oriented towards the top. Cross-sectional epifluorescent mode images of the 0.45 *w/c* concrete specimens after 500 days of immersion in solution.
From left to right: CaCl2, MgCl2, MBAP, NaCl, CMA, and lime water, tic marks every mm. Red boxes highlight locations of close-up images of deterioration in Figures 41 through 43. Blue boxes show locations of close-up images of calcium hydroxide in the cement paste in Figures 44 through 46.

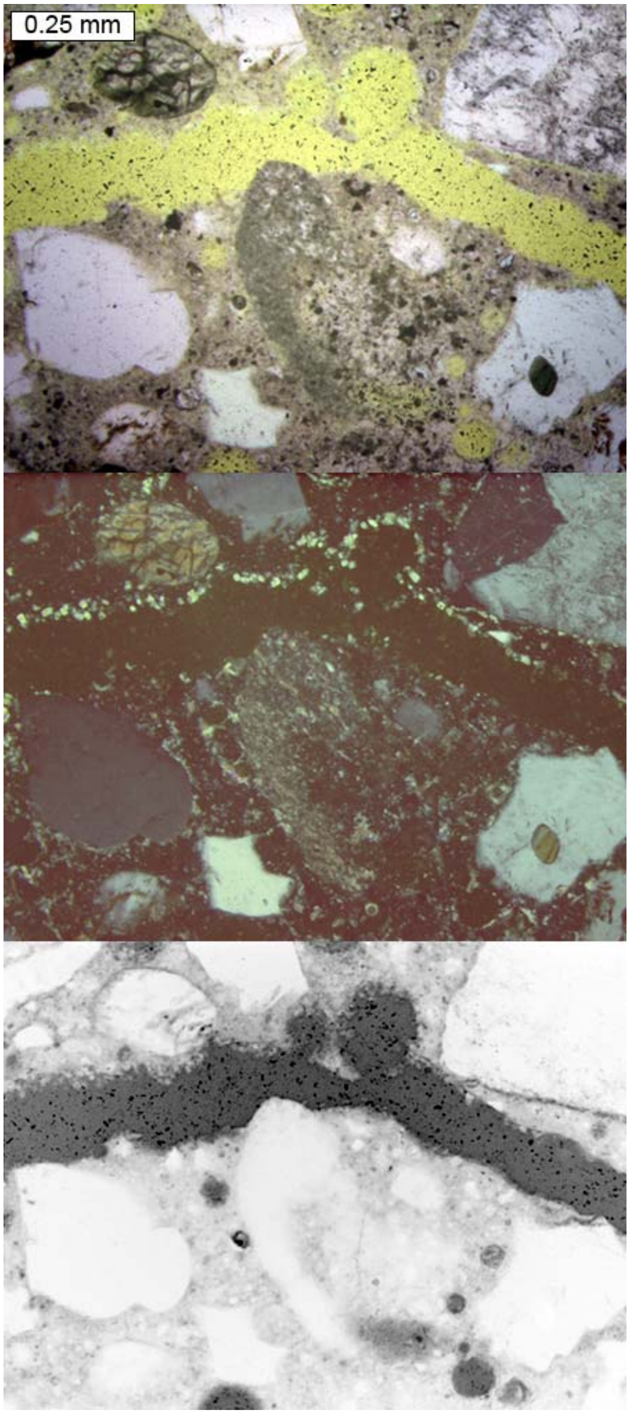


**Figure 41. Close-up view of deteriorated portion from 0.45 w/c plain portland concrete specimen exposed to CaCl2 brine.
From top to bottom: transmitted light, crossed-polars, and epifluorescent mode images.**

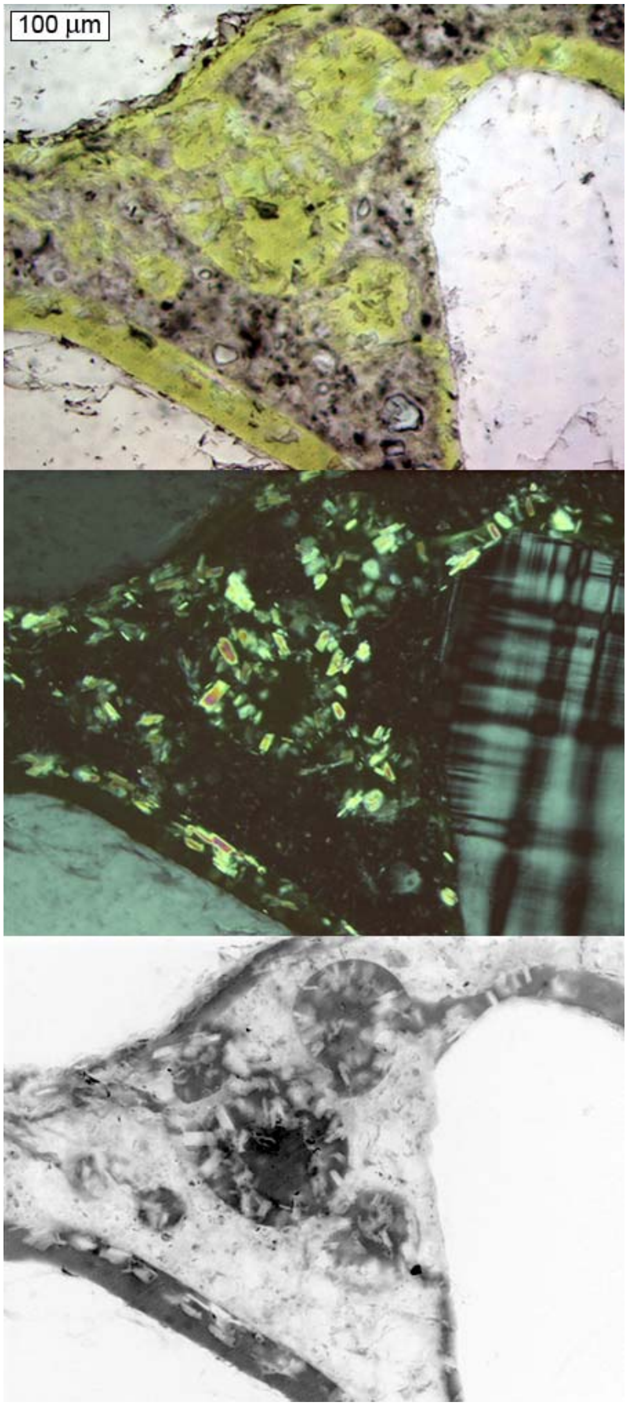


**Figure 42. Close-up view of deteriorated portion from 0.45 w/c plain portland concrete specimen exposed to MgCl2 brine.
From top to bottom: transmitted light, crossed-polars, and epifluorescent mode images.**

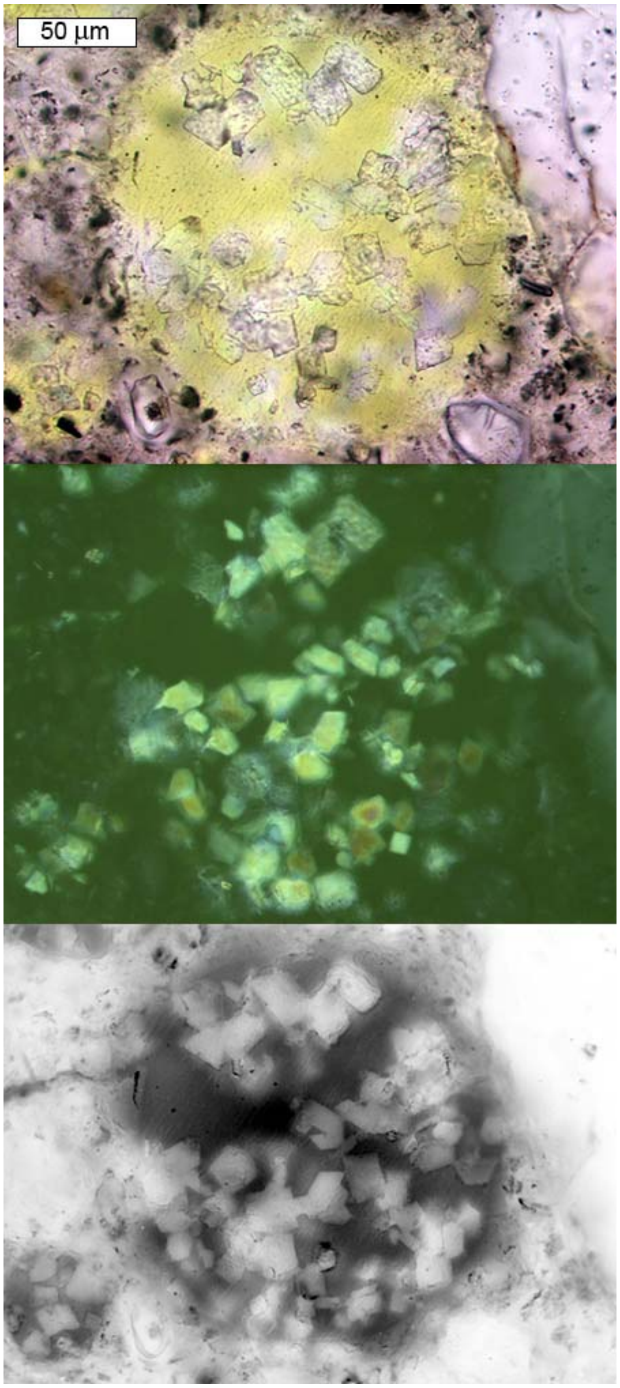


Figure 43. Close-up view of deteriorated portion from 0.45 w/c plain portland concrete specimen exposed to MBAP brine.
From top to bottom: transmitted light, crossed-polars, and epifluorescent mode images.

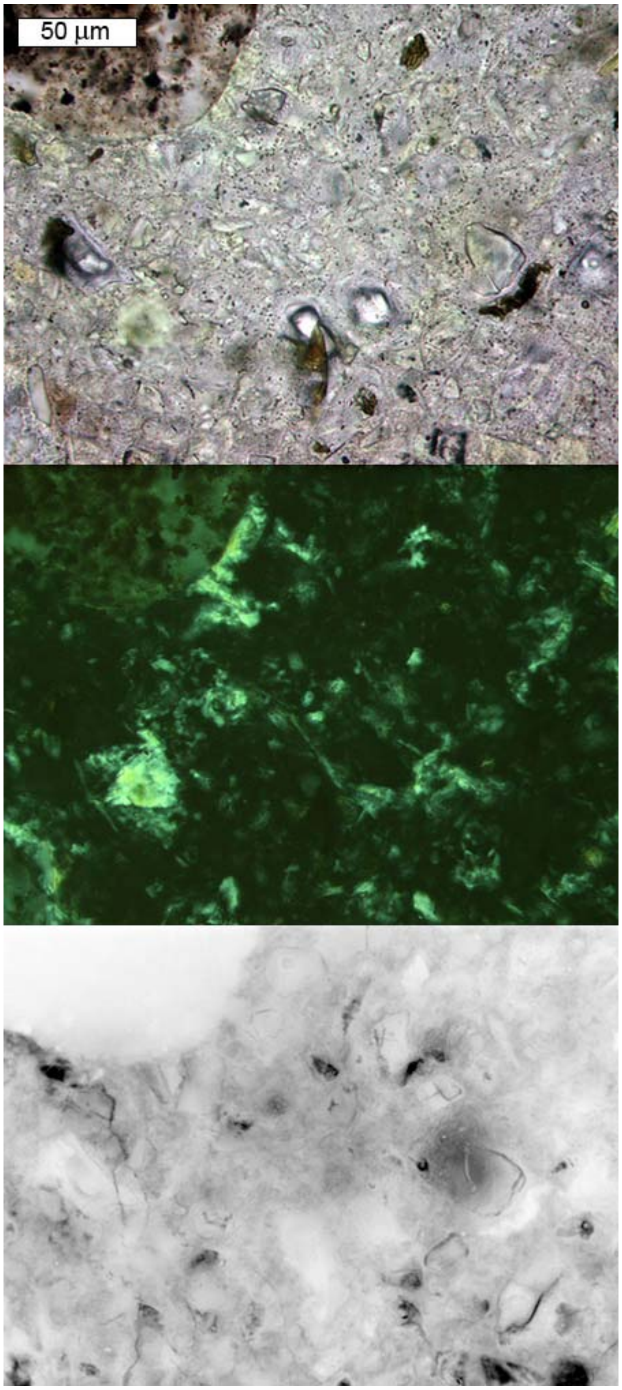


Figure 44. Cement paste just below the surface from 0.45 w/c plain portland cement concrete specimen exposed to NaCl brine.
From top to bottom: transmitted light, crossed-polars, and epifluorescent mode images.

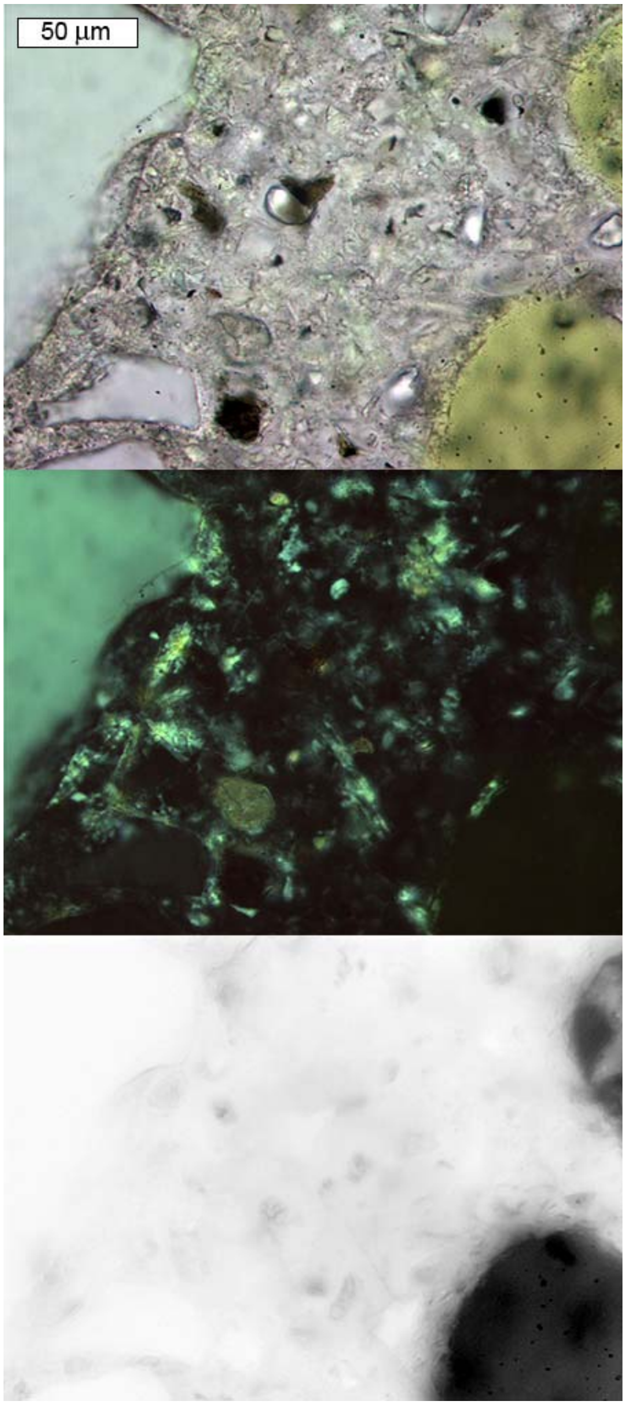


Figure 45. Cement paste just below the surface from 0.45 w/c plain portland cement concrete specimen exposed to CMA brine.
From top to bottom: transmitted light, crossed-polars, and epifluorescent mode images.

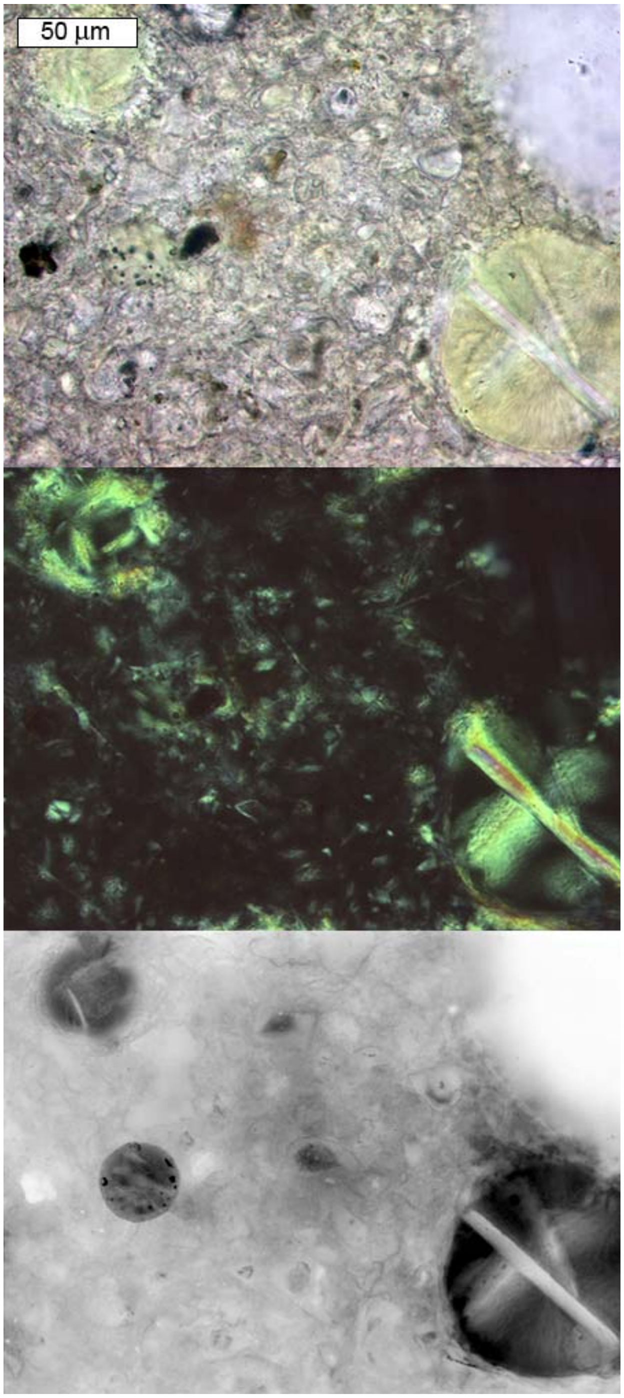


Figure 46. Cement paste just below the surface from 0.45 w/c plain portland cement concrete specimen exposed to lime water.Secondary calcium hydroxide deposits also present in air voids.
From top to bottom: transmitted light, crossed-polars, and epifluorescent mode images.

Comparison of the 0.45 w/c Concrete Specimens Immersed in $CaCl_2$ Brine

The plain portland cement concrete specimen showed the most severe cracking. Cracks were also present in the fly ash concrete specimen, but to a lesser degree. Cracks were not observed in the slag concrete specimen. Calcium hydroxide was depleted from the cement paste near the specimen surface. In the non-depleted regions of cement paste, calcium hydroxide appears most abundant and well-distributed in the plain portland cement concrete. Calcium hydroxide in the cement paste of the fly ash concrete appeared slightly less abundant overall than in the plain portland cement concrete, but tended to be more dispersed and occurred in larger patches. Calcium hydroxide was least abundant in the cement paste of the slag concrete. All of the specimens exhibited blocky secondary calcium hydroxide crystals in air voids within the zone of calcium hydroxide-depleted cement. Blocky calcium hydroxide crystals were present in the large cracks of the plain portland cement concrete specimen but were not present in the tighter cracks of the fly ash and slag concrete specimens.

Comparison of the 0.45 w/c Concrete Specimens Immersed in $MgCl_2$ Brine

As with the plain portland cement specimens exposed to $CaCl_2$ brine, the plain portland cement concrete specimens exposed to $MgCl_2$ brine showed the most severe cracking. Cracks were also visible in the slag concrete specimen, but to a lesser degree. Cracks were not observed in the fly ash concrete specimen. The silane-sealed specimen appeared to be in good condition. The same trend noted from the $CaCl_2$ brine, of calcium hydroxide depletion coupled with blocky secondary deposits of calcium hydroxide in air voids and large cracks in the depleted zone, was observed in the plain portland cement, fly ash, and slag specimens exposed to $MgCl_2$ brine. However, in contrast to the specimens exposed to the $CaCl_2$, the specimens exposed to the $MgCl_2$ brine all exhibited fibrous mineral precipitates on the surface and in the air voids and cracks near the surface. Calcium hydroxide was observed in the cement paste just below the surface of the concrete specimen treated with silane indicating little penetration has occurred (i.e. no dissolution has occurred). Neither calcium hydroxide depleted paste nor blocky secondary calcium hydroxide crystals were observed in the silane-sealed specimen.

Comparison of the 0.45 w/c Concrete Specimens Immersed in MBAP Brine

The only specimen to show signs of severe cracking was the plain portland cement concrete specimen. The same trend noted from the $CaCl_2$ and $MgCl_2$ brines of calcium hydroxide depletion, coupled with blocky secondary deposits of calcium hydroxide in air voids and large cracks in the depleted zone, was observed in the plain portland cement, fly ash, and slag specimens exposed to MBAP brine. As with the specimens exposed to the $MgCl_2$ brine, all of the specimens from the MBAP brine exhibited fibrous mineral precipitates on the surface and in the air voids and cracks near the surface.

ASTM C666 Freeze Thaw Testing

Concrete prisms subjected to freeze-thaw testing showed behavior similar to the mortar samples tested in Phase I. That is, concrete prisms exposed to $MgCl_2$ and $CaCl_2$ expanded above 0.1%, which is considered by ASTM C666 to represent failure. Figure 47 shows the length change of the specimens. While prisms exposed to NaCl did not expand more than 0.04% for 300 cycles, prisms exposed to $MgCl_2$ and $CaCl_2$ expanded considerably. Note that the concentration of the exposure solution did not allow freezing during the test, eliminating physical attack as the sole mechanism of deterioration. The specimens exposed to NaCl showed negligible expansion even after 300 cycles.

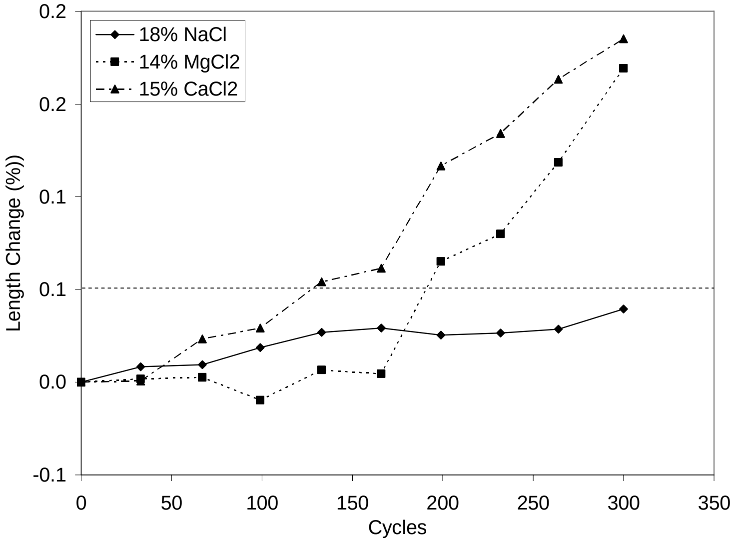


Figure 47. Length change of concrete prisms exposed to deicers under freezing and thawing cycles.

After determining the durability factor in accordance with ASTM C666, it is clear that $MgCl_2$ and $CaCl_2$ solutions reduce the concrete's resistance to freezing and thawing when compared with NaCl as shown in Figure 48. The durability factors of 60 for $CaCl_2$ and 51 for $MgCl_2$ show the negative impact of these deicers on the resistance of concrete to freezing and thawing. Note that although there is no universally accepted limit for the durability factor, 80 is typically accepted as the threshold between durable and non-durable concrete.

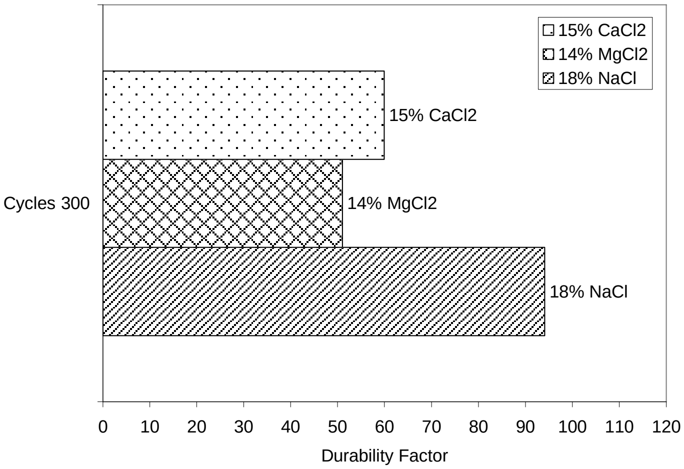


Figure 48. Durability factor of concrete prisms exposed to deicers under freezing and thawing cycles.

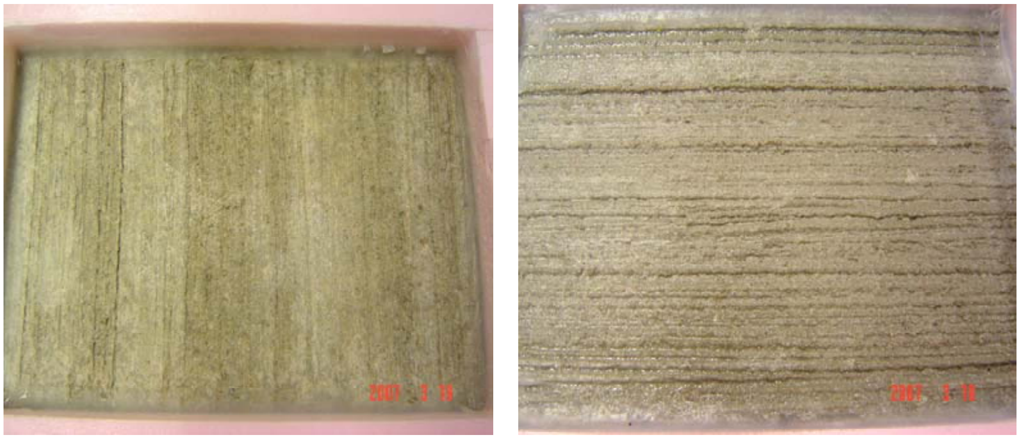
Figures 49 and 50 show photographs of the concrete prism specimens exposed to $CaCl_2$ and $MgCl_2$ and used for determining the resistance to freeze-thaw action. Both deicers caused the prisms to expand and crack along the edges but it was observed that in addition to this, the prisms exposed to $MgCl_2$ precipitated a white gel compound that started to fill the cracks.

Figure 49. Photographs of concrete prisms subjected to 133 freezing and thawing cycles in 15% $CaCl_2$ solution.

Figure 50. Photographs of concrete prisms subjected to 133 freezing and thawing cycles in 14% $MgCl_2$ solution.

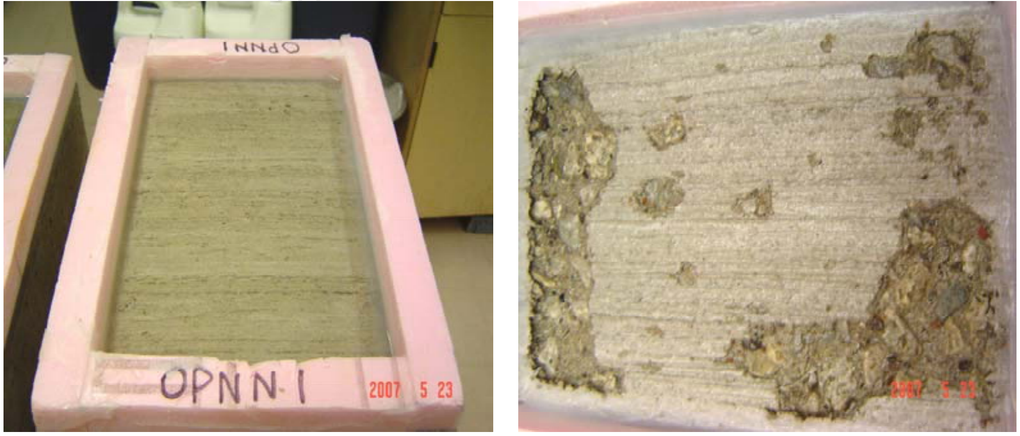
Scaling Resistance

It was observed that after exposing concrete slabs to $CaCl_2$ solutions, the chemical interaction of this deicer with the concrete surface diminished the concrete's ability to properly withstand environmental conditions involving application of deicers during winter.



(a) **(b)**

Figure 51. Photographs of concrete surfaces at cycle 0 (a) pretreated with 23% NaCl and tested with 3% NaCl and (b) pretreated with 22% $CaCl_2$ and tested with 4% $CaCl_2$.



(a) **(b)**

Figure 52. Photographs of concrete surfaces at cycle 50 (a) pretreated with 23% NaCl and tested with 3% NaCl and (b) pretreated with 22% $CaCl_2$ and tested with 4% $CaCl_2$.

(a) **(b)**

Figure 53. Photographs of concrete surfaces at cycle 100 (a) pretreated with 23% NaCl and tested with 3% NaCl and (b) pretreated with 22% $CaCl_2$ and tested with 4% $CaCl_2$.

Figures 51, 52 and 53 show photographs of the concrete surface of slabs tested at different cycles, illustrating the unusual scaling of those preconditioned with 22% $CaCl_2$ and the excellent state of the slabs that were pretreated with 23% NaCl before starting the salt scaling test.

DISCUSSION

EFFECTS OF SODIUM CHLORIDE (NACL) ON CONCRETE PAVEMENTS AND BRIDGE DECKS

A variety of tests were performed where distress would be visible, if it were occurring. In all of these tests, no visible distress was detected when specimens were exposed to concentrated NaCl solutions. For the laboratory specimens exposed to NaCl, and examined by petrographic methods, no evidence of chemical interaction was observed except for the formation of Friedel's salt in voids. Calcium hydroxide depletion was seen near the surface of some mortar specimens, but not at depth in the sample as seen in the case of exposure to other deicers. No evidence of oxychloride formation was observed. From a practical perspective, the chemical interaction between NaCl and hardened cement paste was minimal to none existent. In the mortar tests conducted in Phase 1, expansion as a result of exposure to NaCl was negligible, there was no loss in strength, and there appeared to be no demonstrable freeze-thaw durability problem with concrete exposed to NaCl as a result of this testing. Regarding scaling performance, there were no significant scaling problems associated with NaCl exposure.

In general, NaCl was the most chemically benign of the three principal deicers (i.e. NaCl, $MgCl_2$, and $CaCl_2$) in terms of attacking the concrete. There were minimal negative effects identified with exposure of mortar and concrete to concentrated solutions of NaCl. It should be noted however that there is ample evidence in the literature regarding the detrimental effects of NaCl deicers with respect to corrosion of embedded steel in concrete and corrosion of vehicles. Work performed in this study showed that NaCl had the highest sorptivity rate of all the deicers and this is a major concern regarding corrosion in concrete. Therefore, NaCl should not be viewed as a completely benign alternative and mitigation strategies should be employed when using this chemical including a reduction in chemical use and achieving decreased concrete permeability through the use of SCMs in the concrete mixture and sealants on in-place concrete.

EFFECTS OF MAGNESIUM CHLORIDE ($MGCL_2$) ON CONCRETE PAVEMENTS AND BRIDGE DECKS

For all tests conducted, visible distress was commonly associated with exposure of mortar and concrete to concentrated solutions of $MgCl_2$. In Phase I laboratory experiments, mortar cylinders significantly expanded and cracked. In Phase II laboratory experiments similar behavior was observed. One area where only negligible physical damage was observed was in the scaling tests. Those slabs pretreated with $MgCl_2$ and tested for salt scaling resistance did not scale and their visual rating and behavior was similar to those exposed to NaCl.

There was strong petrographic evidence of detrimental chemical interactions between $MgCl_2$ and hardened cement paste. At depth in mortar specimens, calcium hydroxide depletion was common as were deposits of calcium and magnesium oxychloride. X-ray diffraction confirmed the presence of oxychloride phases as did petrographic microscopy and scanning electron microscopy. Strong evidence was found linking the dissolution of calcium hydroxide and re-deposition of calcium and magnesium oxychloride. The proposed reaction path is shown below in equation 1.

$$3Ca(OH)_2 + CaCl_2 + 12H_2O \rightarrow 3CaO{\cdot}CaCl_2{\bullet}15H_2O \qquad (1)$$

The $CaCl_2$ can come directly from the deicer or, in the case of $MgCl_2$ deicers, through a two step process where the $MgCl_2$ first reacts to form brucite producing CaCl2 as a reaction product as shown in equation 2 or with calcium silicate hydrate (CSH) (i.e. hardened cement paste) as shown in equation 3 where magnesium silicate hydrate (MSH) is a reaction product.

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 + CaCl_2 \tag{2}$$

$$C\text{–}S\text{–}H + MgCl_2 \rightarrow M\text{–}S\text{–}H + CaCl_2 \tag{3}$$

Magnesium oxychloride forms in a reaction similar to equation 1. Many researchers have reported the presence of brucite ($Mg(OH)_2$) and also MSH in concrete or mortar exposed to $MgCl_2$. The oxychloride phases are easily overlooked as they are not stable in laboratory conditions. Special care must be exercised and special sample preparation techniques must be utilized to identify these phases by petrography or x-ray diffraction.

Further evidence was presented in this research that the transition from calcium oxychloride to calcium carbonate occurs and therefore calcium carbonate deposits seen in field concrete are possibly oxychloride phases that have been converted to calcium carbonate.

In the mortar tests conducted in Phase 1, expansion as a result of exposure to $MgCl_2$ was significant. The samples exposed to $MgCl_2$ expanded the most of the three principal deicers. Only samples exposed to the MBAP deicer expanded more but that deicer is also $MgCl_2$ based. Also, for samples exposed to $MgCl_2$ solutions, there was a very significant strength loss and poor performance in freeze-thaw testing.

It is clear from the results of these laboratory experiments that $MgCl_2$ based deicers chemically attack mortar and concrete causing expansion, volume change, loss of compressive strength, and microcracks. The chemical attack appears to be temperature and concentration dependent with 20% $MgCl_2$ being the pessimum concentration at temperatures below 72^{o}F [22^{o}C]. The lower the temperature, the greater is the deterioration process.

The phases associated with the damage of mortar and concrete samples observed are the highly hydrated basic salts calcium oxychloride and magnesium oxychloride. These phases are formed by the chemical reaction of the deicer with calcium hydroxide in the hardened cement paste. The formation of brucite at the surface of a specimen may slow down the ingress of deicing chemicals. However, it is expected that this layer will not indefinitely protect the mortar and concrete against chemical attack.

EFFECTS OF CALCIUM CHLORIDE ($CACL_2$) ON CONCRETE PAVEMENTS AND BRIDGE DECKS

As was the case with $MgCl_2$, visible distress was commonly associated with exposure of mortar and concrete to concentrated solutions of $CaCl_2$. In all cases, the visible distress was more pronounced and occurred more quickly with exposure of mortar and concrete to concentrated solutions of $CaCl_2$ then was seen with any other deicer. For example, in the Phase 1 tests, visible distress was apparent at 56 days with $CaCl_2$ exposure where it was only beginning to manifest in specimens exposed to $MgCl_2$ at the same point in time. In Phase II experiments similar behavior was observed. Based upon visual assessment alone, $CaCl_2$ exposure created the most distress.

Specimens exposed to $CaCl_2$ also exhibited conclusive evidence of calcium oxychloride formation in all occurrences of distress. These observations were confirmed by multiple techniques including petrography, x-ray diffraction, and scanning electron microscopy. Calcium hydroxide dissolution was identified and the effects of this could be seen not only through petrography, but also by monitoring the pH of the exposure solutions during Phase I testing.

In the mortar tests conducted in Phase 1, expansion as a result of exposure to CaCl2 was significant but not as severe as was seen with the MgCl2 exposed samples. Likewise, for samples exposed to CaCl2 solutions, there was strength loss but not as severe as was seen with MgCl2. The concrete specimens exposed to CaCl2 also performed poorly in freeze-thaw testing. With respect to scaling, the CaCl2 specimens scaled severely.

Results of the laboratory experiments indicate that $CaCl_2$ based deicers chemically attack mortar and concrete causing expansion, volume change, loss of compressive strength, and cracking. The phase associated with the damage of mortar and concrete samples observed was calcium oxychloride. This phase is formed by the chemical reaction of the deicer with phases in the hardened cement paste, certainly calcium hydroxide and possibly CSH.

The formation of calcium oxychloride in the concrete matrix decreases dramatically the salt scaling and freeze-thaw resistance of concrete mixtures that are otherwise immune to the effect of freezing and thawing cycles in the presence of low concentration $CaCl_2$ solutions. Calcium chloride is not exacerbating a physical attack; it is creating a chemical attack that slowly weakens the hardened cement paste by attacking the CSH in addition to the calcium hydroxide.

EFFECTS OF CALCIUM MAGNESIUM ACETATE (CMA) ON CONCRETE PAVEMENTS AND BRIDGE DECKS

Samples exposed to CMA showed mixed results, but did show some visible signs of deterioration. In Phase I experiments, cylinders in the CMA solution at 40 ºF [4 ºC] showed little to no distress after 84 days, although there was some staining evident in the 0.60 *w/c* cylinders. However, in other experiments, samples exposed to CMA at room temperature disintegrated approximately 30 days after immersion. There is no explanation available for why the two tests had such different results. The only petrographic evidence of chemical interaction was the formation of calcium acetate hydrate phases in the separate Phase I experiments.

Evidence of detrimental effects of CMA is mixed. Based upon this work it is not possible to draw hard conclusions regarding how this deicer affects concrete. There is evidence to indicate that there may be a concern but additional testing would be required to establish any conclusive relationship between CMA and chemical attack to hardened concrete.

EFFECTS OF MAGNESIUM CHLORIDE BASED AGRICULTURAL PRODUCT (MBAP) ON CONCRETE PAVEMENTS AND BRIDGE DECKS

As part of the Phase I laboratory experiments, observations were made that specimens exposed to MBAP experienced loss of strength, expansion and mass gain. Defined zones of chemical interaction of 0 to 0.2 inches [0 to 5 mm] through the cross sectional area of the mortar bar were visible. The presence of microcracks was confirmed using the stereo optical microscope. Softening of the surface and debonding of sand grains were identified.

In the mortar tests conducted in Phase 1, expansion as a result of exposure to MBAP was extensive. Samples exposed to MBAP expanded more than specimens in any other exposure condition. For samples exposed to MBAP solutions, there was also a strength loss almost identical to specimens exposed to $MgCl_2$.

In general, MBAP performed in a manner very similar to $MgCl_2$. Although it was not taken through every test performed using $MgCl_2$, enough testing was performed including, volume change, loss of compressive strength, and petrography, to establish that MBAP will most likely cause distress in a manner similar to concentrated $MgCl_2$.

ASSESSING AND MINIMIZING THE IMPACT OF DEICING/ANTI-ICING CHEMICALS

A clear mechanism for chemical attack by at least two deicers – $CaCl_2$ and $MgCl_2$ - seems clear. Therefore, it is necessary that SHAs examine mitigation strategies. One simple strategy is to use less of these chemicals for anti-icing and deicing. The other strategy is to construct concrete pavements and bridge decks that are less susceptible to attack. This research examined different approaches to modifying the concrete itself, in particular decreasing the permeability of the concrete.

In general, a reduction in concrete or mortar permeability resulted in less damage in the same amount of exposure time for similar mixtures and exposure solutions. The only inconsistency, which cannot be fully explained at this time, is that for Phase II testing on concrete, and to some extent for Phase I on mortars, a reduction in *w/c* did not improve performance. It is not clear why the lower *w/c* mixtures did not perform better but it is clear that lowering *w/c* by itself is not a reasonable strategy for mitigating deicer attack.

However, the use of supplementary cementitious materials (SCMs) did significantly improve the concrete performance. It is thought that this is the result of SCMs consuming calcium hydroxide in the pozzolanic reaction thereby providing less calcium hydroxide in the cement paste to chemically react. The mitigation effects associated with the use of SCMs also results from a decrease in concrete permeability for these mixtures.

Petrographic evidence also supports the fact that the use of SCMs greatly improved performance. Evidence is presented that reduced cracking was seen for mixtures containing, in order of effectiveness, ground slag and fly ash.

Likewise, sealants proved to be effective at reducing the impact of deicing chemicals. Concrete samples coated with the siloxane sealer did not allow the penetration of chloride ions. Silane sealants allowed a small amount of ingress but it was still very significantly lower than the chloride penetration for plain portland cement concrete.

Clearly, as a mitigation strategy, SHAs that use these deicing chemicals should begin developing concrete mixtures that utilize ground slag and fly ash. As a maintenance strategy, sealants should be employed to help slow the ingress of the deicing chemicals, thereby minimizing the impact these chemicals will have on concrete pavement and structures.

LIFE CYCLE COST ANALYSIS

As part of the original proposal, it was stated that a life cycle cost analysis would be performed to describe the potential impacts of the various deicers relative to the service life of the pavement. This proposal was predicated on having the necessary data to accomplish the analysis, which includes in general two types of information. The first is laboratory data describing the behavior of the laboratory prepared mixtures when exposed to the various deicers. This would include information such as the rate of ingress and the rate at which observed distresses progressed. To a large extent, the research was successful in obtaining this information.

The second type of information required is field examples of distressed pavements, coupled with adequate maintenance records to establish the amount and type of deicer used, and preferably examples of distressed pavements that had been exposed to one type of deicer exclusively. This research was unable to identify pavements that provided this second type of information. None of the pavements examined as part of the field examination could be absolutely identified as ones exhibiting distress solely as a result of deicer application. In addition, most of the pavements sampled and examined have been exposed to different deicers over their service life making the association of distress with any one deicer impossible.

As a result, the research team is only left with laboratory results on which to base a life cycle model. In the opinion of the research team, any predictions made solely on the basis of laboratory tests would be flawed and it would be counter-productive to present an analysis that was based on inadequate data.

It can be said that clearly, chemical attack of concrete from the use of $CaCl_2$ and $MgCl_2$ based deicers occurs. Conversely, NaCl appears to have little to no potential for chemical interaction with the cement but its corrosive nature is well documented. The results for CMA were inconclusive.

The distress mechanisms identified in the laboratory are real, they have been confirmed through multiple experiments at different institutions, and are most certainly active in field concrete.

What is also clear from review of the literature and from the survey performed early in this project, $CaCl_2$ and $MgCl_2$ are effective deicers and are a tool any maintenance engineer wants to have available to keep roads safe and passable. Therefore, it is recommended that SHAs adopt mitigation strategies to minimize the impacts of these chemicals and maximize the service life of pavements and bridge decks. Even with these strategies, a reduction in service life should be expected when $CaCl_2$ and $MgCl_2$ based chemicals are used for deicing and anti-icing.

MITIGATION STRATEGIES

Mitigation strategies that can be implemented from a maintenance perspective are three-fold. They are 1) use less deicing chemicals, 2) use NaCl brines whenever possible, and 3) use concrete sealants and concrete mixture designs incorporating SCMs to slow deicer ingress.

1) *Use Less Chemicals* – The research conducted here shows that regardless of the distress mechanism, reducing deicer solution concentrations reduces the distress and distress rate. Therefore, any effort to reduce deicer application concentrations or rates will result in less damage to concrete structures.

2) *Use NaCl Brines* – All evidence from this study indicates that NaCl brines have a minimal impact on concrete from a chemical attack perspective. However, they are known to be highly corrosive to steel. Maintenance strategies should consider using NaCl brines as much as possible, and investigating methods of depressing the freezing point of these brines to extend their useful temperature range. However, mitigation strategies such as sealants and the inclusion of SCMs in the concrete mixture still need to be adopted when using NaCl brines to prevent corrosion.

3) *Use Sealants and SCMs* – The siloxane sealant studied in this research was very effective at significantly slowing the ingress of deicing chemicals into concrete or mortar. To a lesser extent the silane sealant was also effective. The effectiveness of either sealant is lost after some time (e.g. 3-5 years) and as result, maintenance strategies should include periodic reapplication of sealants to pavements and bridge decks.

The only certain engineering solution is to utilize SCMs in pavement concrete. For this study, 30% ground slag substitution for portland cement greatly improved the durability of the mixtures tested. Fly ash as a concrete admixture also improved durability. State Highway Agencies need to develop concrete mixture designs with a higher percentage substitution of SCMs for portland cement.

Reducing the *w/c* should provide increased durability but it could not be proven conclusively with this study.

CONCLUSIONS

Based on the review of the the literature, the following conclusions are presented:

- Both physical and chemical interactions occur within concrete when it is exposed to freeze-thaw conditions and deicing chemicals.
- Damage from physical mechanisms of attack are most commonly scaling, map cracking, or paste disintegration.
- Chemical interaction results from the application of deicing chemicals, leading to possible degradation of the concrete structure.
- One interaction resulting from the long-term application of chloride deicers is the dissolution of calcium hydroxide ($Ca(OH)_2$).
- A number of studies have concluded that calcium chloride ($CaCl_2$), another common deicer and a product of the reaction between magnesium chloride ($MgCl_2$) and $Ca(OH)_2$, is associated with a deleterious chemical reaction with concrete. The chemical attack is accompanied by the formation of a hydrated calcium oxychloride.

Based on the characterization of field specimens, the following conclusions are presented:

- No definitive correlation could be made between observed distress in field concrete and the use of deicers.
- The petrographic analysis of these cores did not reveal any specific degradation related to chemical attack from deicers. The only significant observations included the common occurrence of calcium hydroxide dissolution and in some cases a marginal air-void system, which may have contributed to the observed distress.
- Magnesium enrichment at the surface of some concrete field specimens was observed, similar to that seen on laboratory specimens exposed to MgCl2 brine.
- Calcium carbonate deposits in field concrete and on concrete structures were observed and these may be the result of calcium oxychloride converting to calcium carbonate.

Based on the overall project results, the following conclusions are presented:

- Exposure of concrete and mortar to NaCl results in little to no chemical interaction or related distress. NaCl is known to cause severe corrosion problems that can affect the durability of concrete structures.
- Exposure of concrete and mortar to $MgCl_2$ and $MgCl_2$ based deicing chemicals results in significant chemical interaction and related distress. $MgCl_2$ appears not to be safe for use as a deicing and anti-icing chemical with respect to possible damage to concrete structures.

- Exposure of concrete and mortar to $CaCl_2$ and $CaCl_2$ based deicing chemicals results in significant chemical interaction and related distress. $CaCl_2$ appears not to be safe for use as a deicing and anti-icing chemical with respect to possible damage to concrete structures.
- In all cases, the observed distress decreases as the concentration of deicer is reduced. Therefore, if $MgCl_2$ and $CaCl_2$ based deicing chemicals are to be used, they should be used at the lowest possible concentration.
- The pessimum concentration determined for $MgCl_2$ and $CaCl_2$ based deicing chemicals are 20% and 22% by weight $MgCl_2$ and $CaCl_2$, respectively.
- It is not conclusive if CMA is detrimental to concrete or mortar.
- Results were mixed regarding the effect of w/c on performance of concrete and mortars exposed to deicing chemicals. Although the general parameters (i.e. sorptivity, bulk diffusion, rapid chloride permeability) improved with decreasing w/c as expected, the performance in low temperature immersion was the opposite as expected. That is, the low w/c mixtures often performed worse.
- In general, concrete mixtures containing ground granulated blast furnace slag showed the lowest susceptibility to deicing chemicals, concrete mixtures containing fly ash were next best, and straight portland cement mixtures were the worst performing.
- In general sealants were effective at reducing chloride ingress at 60 days. The siloxane appeared to perform better than the silane.

RECOMMENDATIONS

SHAs should plan that the use of any deicing chemical will negatively impact the durability of concrete pavements and bridges. The mechanisms of attack differ; NaCl being known to readily induce corrosion of steel embedded in concrete, $MgCl_2$ and $CaCl_2$ have been shown to attack the hardened cement paste, and CMA appears to potentially be harmful to concrete through dissolution of the hardened cement paste.

SHAs should adopt a strategy of preparing durable concrete mixtures that resist penetration of deicing chemicals. To accomplish this the following recommendations are made:

- Include supplementary cementitious materials (SCMs) to decrease permeability, particularly include the use of GGBFS whenever possible. Fly ash is also useful for reducing permeability. SCMs also consume calcium hydroxide through the pozzolanic reaction, thereby limiting the formation of oxychloride.
- Use durable aggregates that are not reactive or susceptible to freeze-thaw.
- Establish an air-void system targeted to the severity of the environmental exposure.

Likewise, SHAs should construct well-consolidated concrete free of plastic shrinkage cracks (and other early-age cracking) and without surficial defects. To accomplish this, the following recommendations are made:

- Avoid construction under extreme weather conditions.
- Perform adequate consolidation to remove entrapped air.

- Use corrosion-resistant dowel bars or tie bars at joints and cracks.
- Ensure reinforcing steel has adequate concrete cover (2.5 inches [63.5 mm] minimum suggested).
- Ensure bleed water has disappeared before finishing, and avoid overworking surface.
- Provide adequate curing using an effective curing compound. Make sure that the proper amount is uniformly applied to the surface.
- Employ a 30-day "drying period" before applying deicing chemicals to new concrete

SHAs should adopt maintenance strategies that minimize the deleterious effects of deicing chemicals on in-service concrete structures. Steps to accomplish this goal include:

- Minimize application of deicing chemicals and maximize effectiveness of each deicing application.
- Use deicing chemicals at the lowest possible concentration levels and preferably less than the pessimum amount reported in this research (i.e. 20% for $MgCl_2$ and 22% for $CaCl_2$).
- Consider increased use of sodium chloride brines wherever possible.
- Consider surface sealers (particularly the use of siloxanes or possibly silanes) at areas of heavy deicing applications to reduce ingress of chemicals.

SHAs should consider future research regarding the effects of deicing chemicals on concrete. Focus areas for future research include the following:

- To better understand the life cycle cost impact of deicing strategies, a controlled test environment is needed, which could be a dedicated test pavement or a portion of an in-service pavement. Multiple sections should be adopted so that different deicers could be tested. The sections should be newly placed concrete, not existing sections that have already been exposed to deicers, and whose construction history is well documented. The amount and type of deicer used on each section, along with detailed records of weather events, including ice/snow accumulation, should be recorded. Periodically, the concrete sections should be sampled and examined petrographically to determine the effects of the deicers on the concrete over time. This information obtained in a controlled environment would allow for accurate determination of the effects of the maintenance strategies used. Additionally, sealants could be tested on the same sections and their effectiveness monitored to establish the necessary cycle of replacing those sealants.
- In-service pavements should be examined by coring in the wintertime to facilitate identification of the oxychloride phases in field concrete. This information would be useful to unequivocally confirm the applicability of the laboratory results reported here.
- Additional testing of CMA is required to determine long term impacts of this deicing chemical given that results from this research were mixed.
- Further testing should be performed to determine the effect of different replacement levels of SCMs on the resistance of concrete to deicers.
- The results of this study indicate that reducing the *w/c* of a concrete mixture does not improve resistance to deicer attack and in fact reducing the *w/c* appeared to make concrete mixtures

more susceptible to deicer attack. This aspect needs further study as this observation is contrary to accepted practice.

- New approaches to freezing point depression of NaCl brines, or altogether new deicing chemicals, should be investigated to allow for use of these brines at lower temperatures.