

Effects of Various Deicing Chemicals on Pavement Concrete Deterioration

HYOMIN LEE, ROBERT D. CODY, ANITA M. CODY, AND PAUL G. SPRY

The deleterious effects of deicers on concrete pavements and bridges have concerned concrete researchers for several decades. The present study experimentally investigates the effects of different deicers on concrete deterioration. Laboratory simulations of environmental conditions (wet/dry and freeze/thaw cycling) were conducted on highway concrete samples with various deicer chemicals (NaCl, CaCl₂, MgCl₂, calcium magnesium acetate (CMA) of 5 different Ca/Mg ratios, Ca-acetate, and Mg-acetate). Each deicer produced characteristic effects on the concrete samples by physically and chemically altering the dolomite coarse aggregate, the dolomite coarse aggregate-paste interface, and cement paste. Chloride solutions commonly promoted decalcification of paste and altered ettringite to chloroaluminate. Magnesium-bearing deicer solutions (e.g., CMA, Mg-acetate and MgCl₂) caused severe paste deterioration by forming brucite and non-cementitious magnesium silicate hydrate. For acetate solutions, the effects caused by Ca-acetate on concrete deterioration was much less severe than those caused by Mg-bearing acetates. For the experimental conditions utilized herein, NaCl solution was the least deleterious to the cement paste and aggregate. Key words: concrete, aggregate, deterioration, deicers, secondary minerals.

INTRODUCTION

Deterioration of concrete by deicers is related to complex processes associated with physical and chemical alteration in cement paste and aggregates. It is affected by factors such as the cation composition of the deicer, aggregate type, and aggregate reactivity. The present investigation evaluates these factors by studying the effects of different deicers on Iowa highway concrete. Cody et al. (1) determined the effects of NaCl, CaCl₂, and MgCl₂ solutions on the deterioration of concrete from Iowa highways and on Mg migration from dolomite coarse aggregate. In the present investigation, a more detailed study was conducted on the effects of NaCl, CaCl₂, MgCl₂, CMA, Ca-acetate, and Mg-acetate on the deterioration of concrete during freeze/thaw (F/T) and wet/dry (W/D) conditions. Special attention was paid to the secondary minerals that formed and the mineral changes that occurred as a direct result of deicers. Because acetates are less detrimental than chlorides to the environment and to steel reinforcement in concrete, the effects of three acetates (calcium acetate, magnesium acetate and calcium magnesium acetate) were examined to determine if one was less detrimental to concrete than the others. In addition, the effects of different ratios of Ca-acetate to Mg-acetate were examined to determine the relative aggressiveness of Ca and Mg ions.

Department of Geological and Atmospheric Sciences, Iowa State University, Ames, Iowa 50011-3212.

EXPERIMENTAL METHODS

Cores were taken from seven existing Iowa highway concretes of different service records, and small 3cm x 1.5cm x 1.5cm blocks were cut from the cores. Two blocks from each core were immersed in 100 ml of solution and sealed in cleaned polymethylpentene containers that were stored for 132 hours at 58°C in a constant temperature chamber. The solutions used were 0.75 M CaCl₂·2H₂O, MgCl₂·6H₂O, NaCl, calcium acetate Ca(CH₃COO)₂·H₂O, magnesium acetate Mg(CH₃COO)₂·4H₂O, and CMA based on a molar ratio of 3:7, i.e. 3[Ca(CH₃COO)₂·H₂O] : 7[Mg(CH₃COO)₂·4H₂O], and distilled water. Experiments were also conducted with five solutions of 0.75 M CMA with different molar ratios of Ca-acetate and Mg-acetate (5:3, 7:3, 1:1, 3:5, and 7:3). All solutions contained 0.01% sodium azide to control bacterial growth.

Wet/Dry (W/D) experiments: After being immersed in solutions at 58°C for 132 hours, blocks were removed from the solutions, dried at 58°C (≈135°F) for 24 hours, air cooled to 25°C, returned to their immersion solutions at 25°C, and again stored at 58°C for 132 hours.

Freeze/Thaw (F/T) experiments: Samples removed from the 58°C solutions after 132 hours were air cooled to 25°C and stored for 24 hours in a freezer at -4°C (25°F). The blocks were air warmed to 25°C, returned to their respective solutions at 25°C, and stored at 58°C for 132 hours.

All experiments were continued until visual signs of deterioration were detected in samples, at which point the blocks were washed and dried. Petrographic analyses of thin sections were conducted with both transmitted and reflected light in order to identify specific areas to be studied by scanning electron microscopy (SEM) and to supplement observations of features difficult to observe with an SEM such as color changes on coarse aggregate margins. A Hitachi S 2460 reduced-vacuum scanning electron microscope was used. Back-scattered images were taken and energy dispersive analytical x-ray (EDAX) area mapping was performed for Si, Al, K, Na, O, Ca, Mg, S, Cl, and Fe. EDAX point analyses were obtained at high magnification for mineral identification. An accelerating voltage of 15 kV was generally used for imaging, whereas EDAX point analyses were obtained at 20 kV.

RESULTS AND DISCUSSION

Each deicer solution had characteristic effects on the concrete blocks under freeze/thaw and wet/dry conditions. CMA caused the most aggressive degradation of concrete in both W/D and F/T experiments. All CMA-treated samples showed deterioration after 15 cycles.

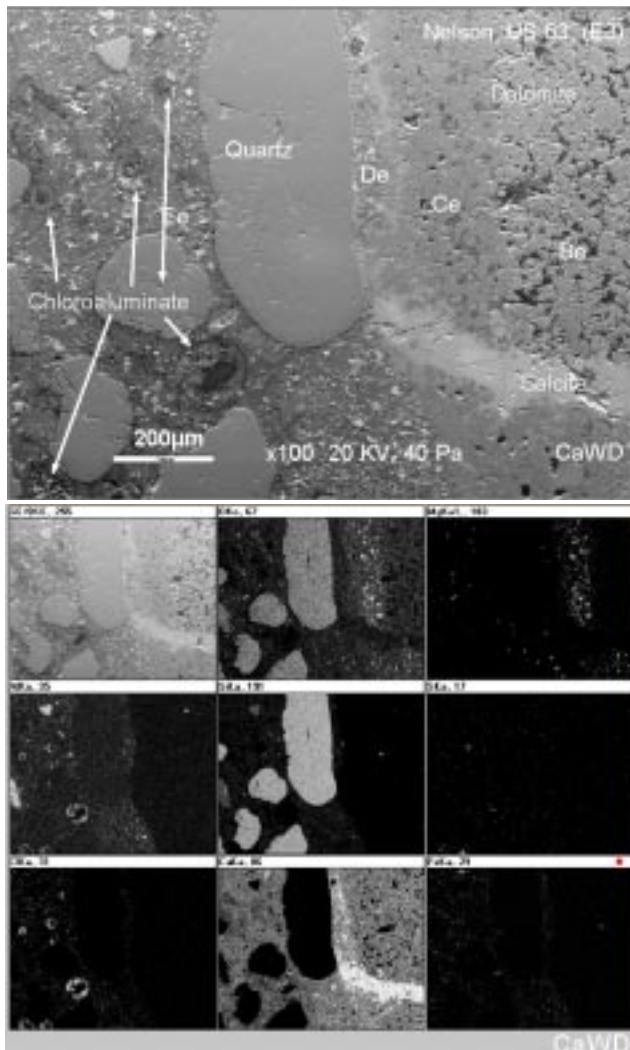


FIGURE 1 SEM micrograph and EDAX element maps showing experimentally-induced deterioration after wet/dry cycling in CaCl_2 of Nelson quarry concrete, US 63. Abundant brucite precipitated in the interstitial voids of a light-colored dolomite rim (Zone Ce). In air entrainment voids, areas rich in Ca, Al, and Cl probably are chloroaluminate. The limited S concentrations at the margins of air-entrainment voids indicate chloroaluminates have replaced ettringite that occurs abundantly in untreated concrete voids.

Magnesium chloride wet/dry experiments were ended after 23 cycles, indicating rapid deterioration, but freeze/thaw cycling was less deleterious. Longevity of the F/T treated blocks is attributed to precipitation of a protective coat of new mineral matter on the concrete surfaces. Beneath the white coating, the paste was brown-colored and crumbled, with random fractures. Calcium chloride wet/dry experiments were typically terminated between 33 and 49 cycles, indicating relatively minor deterioration, and freeze/thaw experiments were even less damaging and a shiny, blue-gray protective mineral coat formed on the concrete surfaces. Sodium chloride and distilled water were least destructive, giving similar durability in W/D experiments, but NaCl was slightly more deleterious in F/T experiments. NaCl-treated F/T blocks showed surface roughening (dissolution), edge crumbling, and a thin gray-white surface coating.

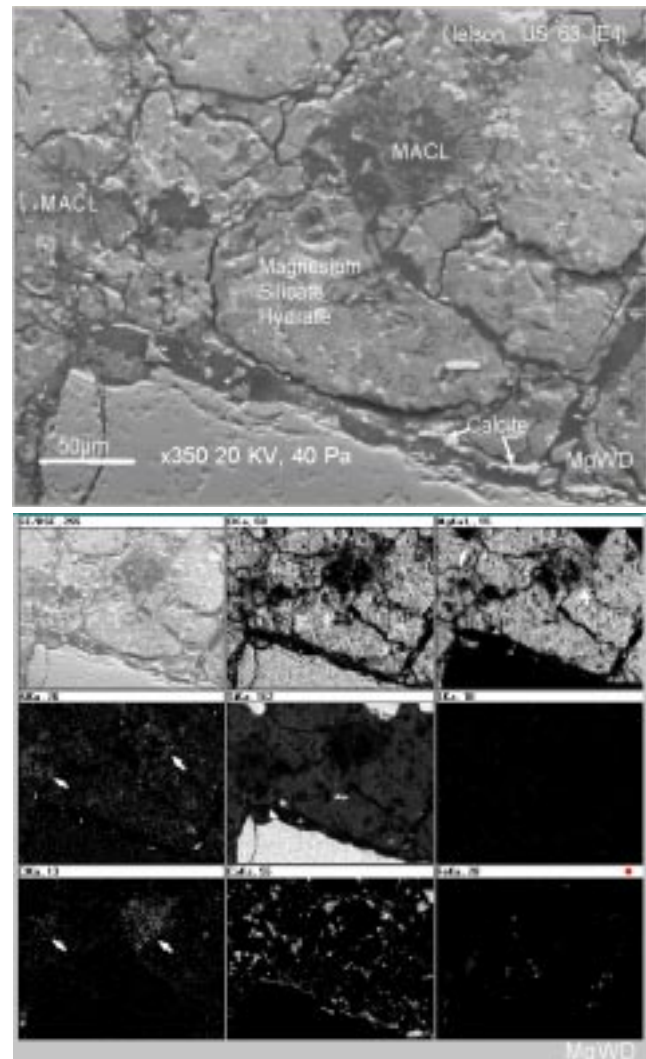


FIGURE 2 High magnification SEM and EDAX maps showing MSH features in cement paste. Abundant shrinkage cracks developed in the MSH as a result of experimental wet/dry cycling in MgCl_2 , and especially wide cracks formed at the boundary between quartz particles and cement paste. EDAX element maps and point analysis indicates that CSH in cement paste has largely changed to MSH. Calcium released by MSH formation migrated into open spaces and precipitated as calcite. Mg-, Al-, and Cl-rich material with minor Si, marked as 'MACL' formed in air voids.

Effects of Chloride Solutions

Calcium Chloride

Calcium chloride deicing salts especially affected those concretes containing reactive dolomite aggregates by enhancing dedolomitization reactions that release magnesium to form brucite and magnesium silicate hydrate (MSH). Alteration rims observed after wet/dry and freeze/thaw conditions appear similar to those seen in untreated concrete, which had resulted from reactions between the reactive dolomite aggregate and paste during highway use. Major changes occurred in an outer light-colored dolomite aggregate alteration zone (FIGURE 1). The EDAX element maps show a decrease in Ca and

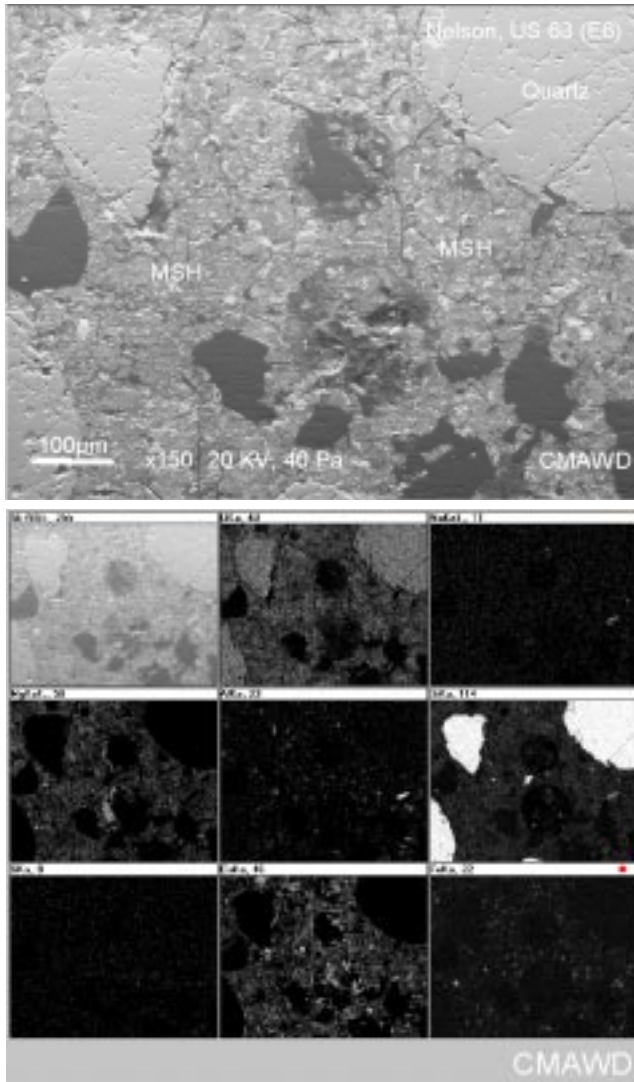


FIGURE 3 SEM micrograph and EDAX element maps showing the growth of brucite and calcite in Nelson quarry concrete from US63 after wet/dry cycling in CMA. Brucite (br) and calcite (Ca) grew in voids. Calcium silicate hydrate, CSH, in the cement has changed to magnesium silicate hydrate, MSH, with the development of abundant cracks. A wide solution channel, which appears to develop because of paste dissolution by CMA, formed between a limestone coarse aggregate particle and the surrounding cement. Note that Si-rich crystals are silicon carbide grains (Gr) from grinding powder used during thin-section preparation.

a concomitant increase in Mg in this region as a result of calcium chloride treatment. In these alteration rims, considerable volumes of calcite existed without significant quantities of brucite, but CaCl_2 produced abundant brucite and reduced the amount of calcite. An inner dark dolomite alteration zone and a light-colored cement alteration zone, both of which had developed during highway use, remained essentially the same as they were in untreated samples. In durable concrete with non-reactive dolomite aggregate, no alteration zone effects occurred during wet/dry or freeze/thaw cycling.

Calcium chloride affected the cement paste of both durable and non-durable concrete. The paste was markedly discolored. EDAX element maps show that Cl is concentrated in these areas (FIGURE 1). Chloride concentration may be due to the formation of calcium chloride hydrate ($3\text{CaO}\cdot\text{CaCl}_2\cdot 12\text{H}_2\text{O}$; $\text{CaO}\cdot\text{CaCl}_2\cdot 2\text{H}_2\text{O}$) or to

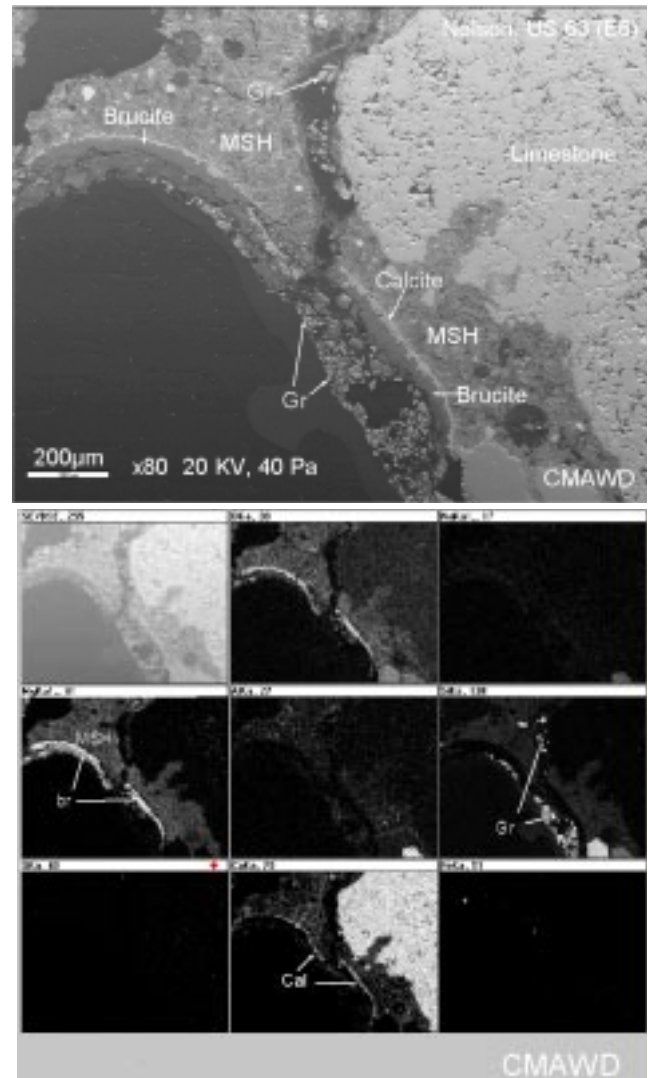


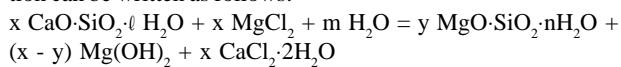
FIGURE 4 High magnification SEM and EDAX maps showing MSH features and void-filling minerals in cement paste. The cement paste has altered to MSH and abundant shrinkage cracks have developed as a result of CMA treatment. Calcium released by MSH formation migrated to tiny open spaces where it precipitated as calcite. Void-filling minerals show various compositions.

adsorption of Cl^- by calcium silicate hydrate (CSH). Discoloration may be the result of iron released from calcium aluminoferrite hydrate (2).

Magnesium Chloride

Magnesium chloride produced distinctive alteration rims at the margins of reactive dolomite aggregate. Much brucite formed in an outer light-colored dolomite rim, a feature not seen in the corresponding alteration rims of untreated material. New brucite occurred in concrete subjected to wet/dry and freeze/thaw conditions and is morphologically very similar to brucite observed in CaCl_2 -treated concrete.

Magnesium chloride produced significant concrete crumbling because of widespread replacement of CSH by non-cementitious MSH resulting from reactions between Mg^{2+} and the CSH cement phase (FIGURE 2). Abundant shrinkage cracks developed in the MSH. Using a modification of Bonen's (3) equation, the general reaction for the formation of MSH from CSH in Mg-chloride solution can be written as follows:



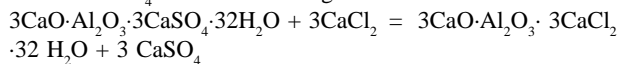
$$\text{where } l + m = n + 3x - y$$

This reaction suggests that displaced Ca^{2+} leaches out into cement paste because CaCl_2 is highly soluble and forms portlandite, $\text{Ca}(\text{OH})_2$, or calcite/aragonite, CaCO_3 . Calcite associated with brucite in air voids or in cracks in some samples supports this conclusion. Needles of calcium carbonate and brucite precipitated on the surface of a MgCl_2 -treated sample.

Sodium Chloride

Sodium chloride produced no enhanced or new alteration rim zones in either dolomite aggregate or cement paste in non-durable concrete. No reaction rims were observed in durable concrete. Brucite in the cement paste appears to be stable in NaCl -treated concrete.

All chloride solutions produced chloroaluminate. Its morphology and occurrence in air-entrainment voids suggest that it is trichloroaluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaCl}_2 \cdot 32\text{H}_2\text{O}$, resulting from the replacement of pre-existing ettringite (FIGURE 1) in which Cl^- substitutes for SO_4^{2-} ions in the ettringite structure:



Traces of gypsum detected in a surface coating of the sample block may have resulted during the above reaction. All chloride solutions also appear to cause paste deterioration by decalcification. The release of Ca^{2+} from the paste is documented by the precipitation of calcite crystals in the solutions and by a surface calcite coating on blocks treated with chloride solutions. It is known that chlorides promote the leaching of $\text{Ca}(\text{OH})_2$ and promote the formation of porous CSH, but the reactions involved are complex (4). Pre-existing brucite crystals in the cement paste are stable in chloride-treated concrete.

Effects of Acetate Solutions

Calcium magnesium acetate solutions were the most damaging of all solutions tested. Both wet/dry and freeze/thaw cycling in CMA produced widespread and severe damage. Alteration rims that formed at the interface between reactive dolomite aggregate and cement paste in CMA-treated concrete were almost identical to those found in MgCl_2 -treated concrete. Both durable and non-durable concrete showed severe paste deterioration. The main causes of cement paste deterioration by CMA solutions probably are non-cementitious MSH resulting from the replacement of CSH and the formation of potentially expansive brucite. Brucite commonly formed in air voids and at paste-fine aggregate interfaces (FIGURES 3 and 4). Abundant shrinkage cracks developed in the MSH, especially under wet/dry conditions. Calcium ions displaced by the MSH-forming reaction precipitated as thin layers of calcite on the walls of open spaces such as

air voids and between the aggregate and cement paste where brucite also precipitated (FIGURE 3).

Another aggressive feature of CMA treatment was debonding of fine aggregate particles. As shown in FIGURE 3, CMA solutions penetrate the cement paste, especially along the boundaries between the fine aggregate and the cement paste where they react with the CSH at the paste/fine aggregate interface and form a thin layer of non-cementitious MSH. This MSH layer resulted in debonding of fine aggregate from the paste. Secondary brucite was then precipitated in the large voids created by loss of fine aggregate. As a result of the newly created voids, a series of new minerals were observed frequently in those open spaces.

Coarse dolomite aggregate was generally not subject to debonding. In regions of the paste in which calcite had precipitated during highway use, the CSH does not appear to change to MSH, possibly because calcite precipitation during highway use conditions reduced paste permeability to CMA solutions. As in MgCl_2 -treated concretes, major amounts of new brucite formed in air entrainment voids where ettringite only was seen previously, and the ettringite in the voids was reduced in abundance (FIGURES 2 and 4). According to Taylor (5), ettringite may be decomposed by magnesium ions because brucite formation consumes OH^- ions in pore solution that lowers $\text{pH} < 10.5$; such conditions are outside the ettringite stability region. With CMA treatment, the destruction of pre-existing ettringite appears to be even more complete than that resulting from magnesium chloride solutions. Calcium acetate treated samples that contained abundant ettringite before treatment showed no loss of ettringite, thus confirming that decomposition of ettringite occurs due to the pH decrease caused by the formation of brucite rather than dissolution by acetate solutions. The reason for the greater deterioration by CMA compared to magnesium chloride is not clear.

Experiments with CMA solutions containing different molar ratios of Ca acetate to Mg acetate (5:3, 7:3, 1:1, 3:5, and 7:3) emphasized the role that the cation Mg^{2+} has in concrete deterioration by CMA solutions. In these experiments, only concrete containing non-reactive Sundheim quarry dolomite coarse aggregate was used in order to reduce reactive aggregate effects.

Magnesium Acetate

Paste deterioration by Mg-acetate solution was similar to that occurring with CMA in which MSH and brucite formed at the interface between fine aggregate and paste and caused debonding of the two components. Brucite with thin calcite layers formed in air entrainment voids under both wet/dry and freeze/thaw condition. Non-cementitious MSH formed in the cement paste.

Calcium Acetate

Ca acetate solutions produced much less paste deterioration than CMA and Mg acetate. No new minerals formed in air entrainment voids, and the fine aggregates were present in their pre-treatment condition. The only observed change in the cement paste was that calcium increased in the paste adjacent to coarse dolomite aggregate during freeze/thaw experiments. Calcium increase was probably due to calcite precipitation.

Different Ca/Mg Ratios in CMA

These experiments showed that the Mg in CMA clearly is responsible for concrete damage. The rate of deterioration depended on the percentage of magnesium in the mixtures. Ca acetate produced little deterioration. For acetate solutions containing both Ca and Mg, the Ca/Mg ratio of 7:3 had the least effect on the concrete. In these solutions, the concrete blocks developed a brown coloration and showed slight paste deterioration with minor surface roughness and edge crumbling of the blocks. A Ca/Mg ratio of $\leq 3:5$ was very detrimental to concrete. The concrete blocks underwent major degradation by edge and surface crumbling, and loss of paste and fine aggregate. Freeze/thaw degradation was less pronounced than that in wet/dry conditions but still significant.

According to Dunn and Schenk (6), a higher ratio of magnesium to calcium should be beneficial for deicing use because of higher solubility and lower freezing point depression of magnesium acetate. However, the present study suggests that higher Mg:Ca ratios may be more destructive and may produce premature concrete deterioration.

CONCLUSIONS

In our experiments, concrete samples were exposed to freeze/thaw and wet/dry cycling in solutions containing different chloride and acetate salts. These salts are currently used as deicers or have been proposed as alternatives to those currently used. Our study observed that magnesium in any form was very damaging to the concrete. Magnesium chloride produced significant concrete crumbling because of widespread replacement of CSH by non-cementitious MSH. Calcium magnesium acetate solutions were the most damaging of all solutions tested. Wet/dry and freeze/thaw cycling in CMA produced widespread and severe damage with scaling from replacement of calcium silicate hydrate with non-cementitious magnesium silicate hydrate. Magnesium acetate produced similar damage and calcium acetate solutions produced much less alteration. On the basis of our experiments, the use of CMA with a high Ca:Mg ratio seems advisable to reduce potential premature magnesium-induced deterioration.

Calcium chloride deicing salts caused characteristic deterioration in concrete containing reactive dolomite coarse aggregate by enhancing dedolomitization reactions that release magnesium to form destructive brucite and MSH. Sodium chloride solutions were the

least deleterious to concrete under our experimental conditions. All the chloride solutions produced chloroaluminate, apparently chiefly from replacement of pre-existing ettringite.

We must point out that the validity of extrapolating the results obtained in our experimental conditions to those occurring under road use conditions is uncertain, and that our results and conclusions should be taken as cautionary only. Long-term SEM/EDAX studies comparing highway concrete treated under road use conditions with CMA or other magnesium deicers with similar concrete treated only with NaCl conditions should be performed in order to evaluate the long-term safety of magnesium deicers. We also should emphasize that we obtained our CMA from mixtures of calcium acetate and magnesium acetate. Extrapolation of results obtained with our mixtures to those that might result from the use of proprietary CMA may not be valid.

ACKNOWLEDGMENTS

This project was funded by the Iowa Department of Transportation, Project No. HR-384. This support is gratefully acknowledged. We particularly want to thank Vernon Marks, Jim Myers, and Wendell Dubberke as well as Dr. Ken Bergeson for their advice, suggestions, and support of this project. Without their help this project would not have been possible. We also thank Drs. Jerry Amenson, Scott Schlorholtz, and Warren Strazheim of the ISU Materials Research Laboratory for their assistance with SEM analyses.

REFERENCES

1. Cody, R.D., P.G. Spry, A.M. Cody, and G. Gan. *The Role of Magnesium in Concrete Deterioration*. Final Report HR-355, Iowa Department of Transportation, 1994.
2. Kosmatka S.H. and W.C. Panarese. *Design and Control of Concrete Mixtures*. Portland Cement Association, Skokie, Illinois, 13th edition, 1988.
3. Bonen, D. Composition and Appearance of Magnesium Silicate Hydrate and Its Relation to Deterioration of Cement-Based Materials. *Journal of the American Ceramic Society*, Vol. 75, No. 10, 1992, pp. 2904-2906.
4. Ftikos, C. and G. Parissakis. The Combined Action of Mg^{2+} and Cl^- Ions in Cement Paste. *Cement and Concrete Research*, Vol. 15, No. 4, 1985, pp. 593-599.
5. Taylor, H.F.W. *Cement Chemistry*: Academic Press Ltd., London, 1990.
6. Dunn, S.A., and R.U. Schenk. Alternatives to Sodium Chloride for Highway Deicing. In *Transportation Research Record 776*, TRB, National Research Council, Washington, D.C., 1980, pp. 12-15.