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Effects of Deicers on Concrete Deterioration

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Concrete specimens were exposed to weekly cycles of wetting and drying in distilled water and in solutions of sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), and calcium magnesium acetate (CMA) with either a 6.04 molal ion concentration, equivalent in ion concentration to a 15% solution of NaCl, or a 1.06 molal ion concentration, equivalent in ion concentration to a 3% solution of NaCl, for periods of up to 95 weeks. Specimens were also exposed to air only. The effects of exposure were evaluated based on changes in the dynamic modulus of elasticity and the physical appearance of the specimens at the conclusion of the tests.

Concretes exposed to distilled water and air show, respectively, an increase and a decrease in dynamic modulus of elasticity, due principally to changes in moisture content; overall, no negative impact on the properties of these specimens is observed. At lower concentrations, NaCl and CaCl₂ have a relatively small negative impact on the properties of concrete. At high concentrations, NaCl has a greater but still relatively small negative effect. At low concentrations, MgCl₂ and CMA can cause measurable damage to concrete. At high concentrations, CaCl₂, MgCl₂, and CMA cause significant changes in concrete that result in loss of material and a reduction in stiffness and strength.

Keywords: calcium chloride; calcium magnesium acetate; chlorides; concrete; deicing salts; magnesium chloride; sodium chloride.

INTRODUCTION

The application of deicing chemicals can result in the deterioration of concrete roads and bridges by causing scaling when the concrete is subjected to cycles of freezing and thawing. Deicing chemicals can also cause concrete to deteriorate as the result of salt crystallization within the pores of both cement paste and aggregate and chemical changes to occur within the cement paste, whether or not the deicers cause significant scaling damage. Studies have demonstrated that sodium chloride (NaCl) and calcium chloride (CaCl₂), the two principle deicing chemicals, cause maximum scaling under freezing-and-thawing conditions at concentrations in water between 2 and 4% by weight, with NaCl having the greater effect.^{1,2} Concentrations outside of this range, both lower and higher, have less effect on scaling. In contrast, studies of concrete deterioration caused by cycles of wetting and drying show that deterioration increases with an increasing concentration of the solution.³ The latter observation has important implications because high concentration solutions are often used for deicing and because deicer concentrations will build up in concrete over time.

One drawback in studies of the effects of wetting and drying with deicers is that comparisons are typically made using solutions that have either an equal weight of deicing chemical or an equal molar concentration (equal number of molecules for a given volume of solution).^{3,4} The problem with this approach is that the ice melting capability of a deicer, and thus the concentration at which it is used, is more closely related to the number of ions in a given quantity of

water than to either the weight or molar concentration. Thus, at the same molar concentration, CaCl₂ will have 50% more ions in solution than NaCl. The test procedures used in this study account for the number of ions produced when a deicer goes into solution, providing a fairer measure than the other approaches in evaluating the effects of deicers on concrete.

A number of different test procedures have been used to evaluate the effects of wetting and drying. These have included cycles at room temperature, cycles at elevated temperatures, as high as 58 °C (135 °F), and wetting and drying cycles that include changes in temperature during both the wet and dry cycles. Specimens are usually evaluated based on physical changes at the macroscopic and microscopic level, as well as chemical changes that are observed using petrographic analysis, scanning electron microscopy, and X-ray microanalysis.

Previous studies indicate that deicers can affect the chemistry of hardened cement paste.³⁻⁶ Chloride solutions tend to cause the formation of calcium chloride hydrate and calcium oxychloride, whereas magnesium chloride (MgCl₂), in particular, results in the conversion of calcium silicate hydrate to noncementitious magnesium silicate hydrate. In mixtures of calcium and magnesium acetate (CMA), a deicer that does not cause corrosion of reinforcing steel, magnesium acetate has been shown to cause the most severe damage, due to the formation of magnesium silicate hydrate, with little negative effect demonstrated by calcium acetate.⁴ To the extent that crystal growth plays a role in deterioration, CaCl₂, MgCl₂, and calcium acetate, but not magnesium acetate or NaCl, are hygroscopic, forming lower density (and thus high volume) crystals when moisture is available.⁷ The greater volume of the hydrated salt crystals can increase the crystal pressure, with a simultaneous increase in the potential for physical damage.⁸

The effects of CMA on concrete have been observed in ongoing corrosion research at the University of Kansas, with molal ion concentrations (based on the number of ions for a given quantity of water) equivalent to a 15% NaCl solution causing severe damage, not only to the concrete in corrosion specimens but also to the adjacent concrete floor. CMA solutions with molal ion concentrations equivalent to a 3% NaCl solution have resulted in much less damage.

This paper describes the results of a study in which the effects of four deicers—NaCl, CaCl₂, MgCl₂, and CMA—on concrete are compared by combining exposure procedures that were originally developed to allow deicing chemicals to rapidly penetrate concrete corrosion specimens with techniques that are used to evaluate the physical effects of cyclic

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RESEARCH SIGNIFICANCE

The negative impact of deicing chemicals on the deterioration of pavements and bridges has been of concern for a number of years, especially as deicers with potentially less impact on the corrosion of reinforcing steel or greater ice-melting capacity than NaCl have entered the marketplace. This study compares four of the most widely used deicing chemicals and describes the first application of a widely used nondestructive evaluation technique to this problem. The results provide clear evidence that, over time, three of the deicers in the study—CaCl₂, MgCl₂, and CMA—have the potential to significantly weaken concrete.

EXPERIMENTAL STUDY

Materials

In the study, the effects on concrete of cyclic wetting and drying with solutions containing NaCl, CaCl₂, MgCl₂, and CMA (4:6 molar ratio of calcium acetate to magnesium acetate) were evaluated. The study also includes control specimens that were exposed to air or to distilled water throughout the test period. Two concentrations were tested for each deicing chemical, a 6.04 molal ion concentration, equivalent in ion concentration to a 15% solution of NaCl, and a 1.06 molal ion concentration, equivalent to a 3% solution of NaCl. The compositions of the solutions are shown in Table 1.

The concrete mixture used in the study contained Type I/II portland cement and had a water-cement ratio (*w/c*) of 0.45 and an air content of 6%. Mixture proportions and aggregate properties are shown in Table 2.

Prismatic test specimens (3 x 3 x 12 in. [76 x 76 x 305 mm]) were used. The concrete was mixed and the specimens fabricated in accordance with ASTM C192.¹⁰ After casting, the specimens were covered with plastic, cured for 24 hours at room temperature, and then removed from the molds and cured in lime-saturated water at 73 ± 3 °F (23 ± 1.7 °C) for 6 days. After 6 days, the specimens were removed from the curing tank and allowed to dry at a temperature of 73 ± 3 °F (23 ± 1.7 °C) and a relative humidity of 50% ± 4% for 48 days.

The control specimens were cast separately from those exposed to deicers. To limit variations in performance that might occur due to differences in concrete properties, the specimens

exposed to the deicers were cast together, with equal numbers of specimens from each batch exposed to one of the four deicers.

Test procedure

The test procedure involves wet/dry exposure similar to that used for Southern Exposure corrosion test specimens,¹¹⁻¹³ while the effect of the cycles is evaluated by measuring changes in the dynamic modulus of elasticity in accordance to the ASTM C215,¹⁴ as used for freeze-thaw specimens in ASTM C666.¹⁵

Six specimens were used for each of the solutions shown in Table 1, along with six specimens each in air and distilled water. The specimens were submerged in the solutions (or distilled water) for 4 days at a temperature of 73 ± 4 °F (23 ± 2 °C). After 4 days, they were removed from the solution and dried in air at a temperature of 100 ± 3 °F (38 ± 1.7 °C) for 3 days. The deicer solutions and distilled water were replaced every 5 weeks. Specimens exposed to air were subjected to the temperature cycles. Cycles were repeated for up to a maximum of 95 weeks. Based on chloride concentrations obtained at a depth of 1 in. (25 mm) in the corrosion specimens^{13,16} and on bridge decks,¹⁷ exposure to cyclic wetting and drying using this regimen simulates 10 years of exposure for bridge decks within the first 30 weeks and 30 years within the 95-week maximum duration of the test.

The fundamental transverse resonance frequency of each specimen was measured and the dynamic modulus of elasticity (Dynamic *E*) calculated based on the fundamental frequency, mass, and dimensions of the specimen at the initiation of the tests and every 5 weeks thereafter (after the 3-day drying period) using the procedures described in ASTM C215.¹⁴ Changes in concrete properties were evaluated based on the ratio of the Dynamic *E* at the given number of cycles to the Dynamic *E* at the initiation of the wet/dry cycles. This ratio is referred to as the *relative dynamic modulus of elasticity (wet-dry)*, or $P_{w/d}$, to distinguish it from the value of *P* obtained

Table 1—Deicer solutions

6.04 molal ion concentration solutions	
NaCl	850 g water,* 150 g NaCl (100% solids)
MgCl ₂	612.5 g water, 579.2 g MgCl ₂ (33.1% solution)
CaCl ₂	1000 g water, 223.5 g CaCl ₂ (92.36% solids)
CMA	1000 g water, 309.3 g CMA (96% solids)
1.06 molal ion concentration solutions	
NaCl	970 g water, 30 g NaCl (100% solids)
MgCl ₂	932.1 g water, 101.5 g MgCl ₂ (33.1% solution)
CaCl ₂	1000 g water, 42.4 g CaCl ₂ (92.36% solids)
CMA	1000 g water, 54 g CMA (96% solids)

*Distilled water used for all solutions.

Table 2—Concrete mixture proportions (SSD basis)

Cement, lb/yd ³ (kg/m ³)	Water, lb/yd ³ (kg/m ³)	Fine aggregate, lb/yd ³ (kg/m ³)	Coarse aggregate, lb/yd ³ (kg/m ³)	Vinsol resin, gal./yd ³ (mL/m ³)
598 (355)	270 (160)	1436 (852)	1473 (874)	0.024 (90)

Notes: Concrete properties: *w/c* = 0.45, 6 ± 1% entrained air, and 3 ± 0.5 in. (76 ± 13 mm) slump; cement: Type I/II portland cement; fine aggregate: sand with bulk specific gravity (SSD) of 2.62, absorption of 0.78%, and fineness modulus of 2.51; and coarse aggregate: crushed limestone 3/4 in. (19 mm) nominal maximum size, bulk specific gravity (SSD) of 2.58, absorption of 2.27%, and unit weight of 95.9 lb/ft³ (1536 kg/m³).

using ASTM C666 for specimens subjected to cycles of freezing and thawing. Wet/dry cycles continued for a total of 95 weeks or until $P_{w/d}$ drops below 0.9, at which point the tests were terminated. This value for $P_{w/d}$ was used to terminate the tests because it signals very rapid deterioration of the specimens.

TEST RESULTS

The average values and coefficients of variation (COV) of the dynamic moduli of elasticity (for six specimens of each type) at 5-week intervals are presented in Tables 3, 4, and 5, covering, respectively, specimens subjected to cycles in air and distilled water, cycles in the 6.04 molal ion concentration deicer solutions, and cycles in the 1.06 molal ion concentration deicer solutions. The initial (zero-cycle) average Dynamic E

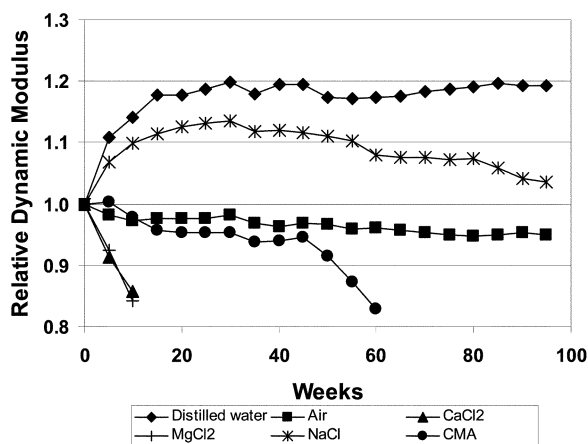


Fig. 1—Relative dynamic modulus of elasticity (wet-dry) $P_{w/d}$ versus number of weekly wet-dry cycles for specimens exposed to 6.04 molal ion concentration deicer solutions.

Table 3—Average Dynamic E (ksi) and coefficients of variation for specimens in air and distilled water

Time, weeks	Air		Distilled water	
	Average	COV	Average	COV
0	4247	0.031	4549	0.031
5	4173	0.029	5045	0.022
10	4132	0.028	5194	0.022
15	4144	0.028	5357	0.019
20	4143	0.030	5357	0.021
25	4148	0.026	5398	0.024
30	4173	0.032	5452	0.019
35	4116	0.039	5363	0.026
40	4093	0.040	5431	0.023
45	4111	0.039	5433	0.023
50	4105	0.043	5334	0.023
55	4077	0.042	5327	0.018
60	4081	0.035	5336	0.023
65	4067	0.034	5345	0.021
70	4052	0.034	5378	0.023
75	4032	0.031	5400	0.023
80	4021	0.031	5418	0.023
85	4033	0.036	5440	0.024
90	4047	0.037	5422	0.026
95	4033	0.032	5424	0.025

Note: 1000 ksi = 6.895 GPa.

value at zero cycles is lowest for the specimens cycled in air (4247 ksi [29.3 GPa]), followed by the value for specimens cycled in distilled water (4549 ksi [31.4 GPa]), which, as described previously, were cast in batches separate from those cycled in deicer solutions. The initial moduli for the specimens subjected to the 6.04 and 1.06 molal ion concentration solutions average approximately 4900 and 5000 ksi (33.8 and 34.5 GPa), respectively. The average values at 5-week intervals were used to calculate $P_{w/d}$. The consistency of the testing procedure is supported by the low COV, which are generally at or below 4%, except for specimens undergoing significant damage. The latter specimens exhibit COV between 7.5 and 10% for values of $P_{w/d}$ below 0.9. The average relative dynamic modulus of elasticity (wet-dry) $P_{w/d}$ are presented in Fig. 1 and 2, which show the values for specimens exposed to the 6.04 and 1.06 molal ion concentration deicer solutions, respectively. The figures also include the results for the specimens subjected to wet/dry temperature cycles in distilled water and temperature cycles in air.

Control specimens

$P_{w/d}$ for the specimens subjected to wet/dry cycles with distilled water increased from 1.0 at the beginning of the test to approximately 1.1 at week 5, increased again to 1.2 at week 35, and then remained approximately constant through week 95. The increase in the Dynamic E may be attributed in part to an increase in the degree of hydration, but most likely resulted from the absorption of water. The specimens subjected to the temperature variations, but otherwise stored in air, exhibited a small but consistent drop in the Dynamic E throughout the test due to the loss in water (with accompanying microcracking), reaching a $P_{w/d}$ of 0.95 at 95 weeks.

Table 4—Average Dynamic E (ksi) and coefficients of variation for specimens in 6.04 molal ion concentration solutions of deicers

Time, weeks	NaCl		CaCl ₂		MgCl ₂		CMA	
	Average	COV	Average	COV	Average	COV	Average	COV
0	4867	0.044	4879	0.053	4978	0.042	4881	0.036
5	5197	0.055	4454	0.043	4605	0.030	4894	0.026
10	5347	0.041	4180	0.085	4191	0.085	4779	0.031
15	5424	0.046	—	—	—	—	4675	0.020
20	5481	0.031	—	—	—	—	4653	0.030
25	5502	0.037	—	—	—	—	4651	0.019
30	5526	0.025	—	—	—	—	4656	0.030
35	5445	0.033	—	—	—	—	4578	0.027
40	5451	0.033	—	—	—	—	4587	0.040
45	5436	0.029	—	—	—	—	4620	0.046
50	5406	0.028	—	—	—	—	4464	0.051
55	5371	0.036	—	—	—	—	4258	0.051
60	5256	0.048	—	—	—	—	4045	0.050
65	5232	0.039	—	—	—	—	—	—
70	5240	0.041	—	—	—	—	—	—
75	5221	0.037	—	—	—	—	—	—
80	5225	0.035	—	—	—	—	—	—
85	5152	0.049	—	—	—	—	—	—
90	5071	0.046	—	—	—	—	—	—
95	5040	0.041	—	—	—	—	—	—

Note: 1000 ksi = 6.895 GPa.

High concentration of deicers

As shown in Fig. 1, the specimens exposed to the 6.04 molal ion concentrations of CaCl₂ and MgCl₂ deteriorated rapidly, with $P_{w/d}$ dropping below 0.9 by week 10. The specimens exposed to CMA deteriorated more slowly, with $P_{w/d}$ dropping below 0.9 by week 55; the wet/dry cycles for these specimens were continued for another 5 weeks. The concrete subjected to the 6.04 molal ion concentration NaCl solution exhibited a rise in $P_{w/d}$ through week 30 to 1.14, likely due to the absorption of water and perhaps the formation of salt crystals, which filled some of the pore space within the cement paste, followed by a gradual drop to a value of 1.04 at week 95, indicating damage, also likely due to salt crystal formation (refer to the Visual evaluation section).

Low concentration of deicers

As shown in Fig. 2, the use of lower concentrations of deicers reduced the negative effects of all four deicers compared with that observed at the high concentration, in some cases significantly. During the early weeks of the tests, all specimens submerged in the 1.06 molal ion concentration deicer solutions exhibited an increase in $P_{w/d}$, as described for the specimens exposed to distilled water. The specimens exposed to CaCl₂ and NaCl exhibited the greatest increase, with peak values of $P_{w/d}$ of 1.11. After week 45, $P_{w/d}$ for these specimens began to drop very slowly, indicating some damage, reaching a value of 1.07 at week 95. This value (1.07) is higher than that observed for the higher concentration solutions (0.86 at week 10 for CaCl₂ and 1.04 at week 95 for NaCl). The peak value of $P_{w/d}$ for the high concentration NaCl specimens (1.14) was slightly higher than the value observed at the lower concentration (1.11). The difference may be due to the effects of increased crystallization

Table 5—Average Dynamic E (ksi) and coefficients of variation for specimens in 1.06 molal ion concentration solutions of deicers

Time, weeks	NaCl		CaCl ₂		MgCl ₂		CMA	
	Average	COV	Average	COV	Average	COV	Average	COV
0	5005	0.013	5072	0.022	5050	0.012	5085	0.048
5	5160	0.020	5334	0.023	5322	0.018	5302	0.045
10	5399	0.016	5553	0.011	5486	0.015	5346	0.051
15	5389	0.015	5568	0.019	5426	0.004	5342	0.049
20	5486	0.017	5630	0.013	5469	0.013	5399	0.050
25	5513	0.023	5632	0.005	5374	0.024	5388	0.049
30	5544	0.016	5667	0.013	5487	0.010	5413	0.042
35	5483	0.013	5543	0.023	5355	0.022	5235	0.055
40	5539	0.016	5634	0.014	5348	0.015	5193	0.053
45	5512	0.014	5643	0.018	5418	0.014	5295	0.055
50	5286	0.021	5492	0.022	5058	0.031	4871	0.040
55	5381	0.020	5543	0.017	5045	0.024	4803	0.043
60	5420	0.021	5539	0.029	4889	0.018	4796	0.052
65	5403	0.023	5479	0.020	4836	0.033	4779	0.048
70	5390	0.026	5496	0.018	4785	0.049	4760	0.050
75	5420	0.015	5493	0.016	4578	0.073	4826	0.057
80	5431	0.018	5516	0.016	4371	0.099	4764	0.055
85	5431	0.019	5475	0.019	—	—	4759	0.054
90	5467	0.010	5475	0.017	—	—	4758	0.052
95	5369	0.023	5452	0.022	—	—	4624	0.059

Note: 1000 ksi = 6.895 GPa.

within the pores for the specimens exposed to the higher concentration solution.

$P_{w/d}$ for specimens exposed to the 1.06 molal ion concentration CMA and MgCl₂ solutions reached values as high as 1.07 and 1.09, respectively, remaining nearly constant through week 45 and then dropping thereafter. $P_{w/d}$ for the CMA specimens dropped below 1.0 at week 50, reaching a value of 0.91 at week 95. The MgCl₂ specimens, which initially exhibited a slightly higher value of $P_{w/d}$ than the CMA specimens and maintained $P_{w/d}$ above 1.0 until week 55, exhibited a more rapid drop in dynamic modulus after week 70, reaching a value of $P_{w/d}$ below 0.9 by week 80.

Visual evaluation

The specimens were evaluated for physical damage and photographs were taken at the conclusion of the tests. The appearance of the specimens is largely in agreement with the performance represented in Fig. 1 and 2.

Specimens subjected to temperature cycles in air (not shown) and wet-dry cycles in distilled water or in 1.06 molal ion concentration NaCl and CaCl₂ solutions (Fig. 3, 4, and 5, respectively) showed few signs of damage. The only apparent change was a slight discoloration of the CaCl₂

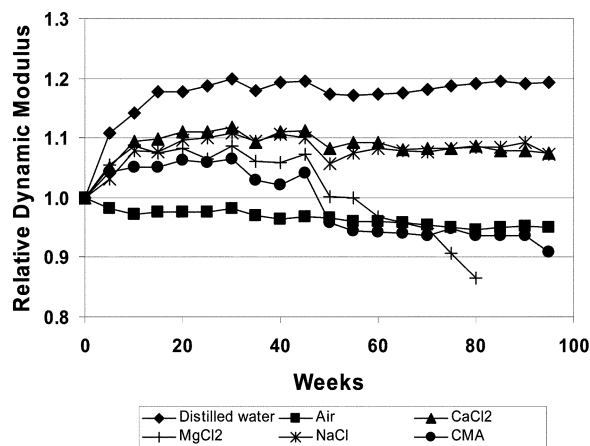


Fig. 2—Relative dynamic modulus of elasticity (wet-dry) $P_{w/d}$ versus number of weekly wet-dry cycles for specimens exposed to 1.06 molal ion concentration deicer solutions.



Fig. 3—Specimen subjected to 95 weeks of exposure to distilled water.

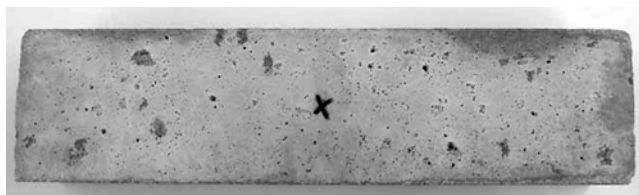


Fig. 4—Specimen subjected to 95 weeks of exposure to 1.06 molal ion concentration solution of NaCl.

specimens (Fig. 5). In contrast to the NaCl and CaCl₂ specimens, the specimens subjected to MgCl₂ and CMA exhibit signs of damage, as shown in Fig. 6 and 7, respectively. The MgCl₂ specimens (Fig. 6) were subjected to wet-dry cycles for 80 weeks, after which the test was terminated because the modulus of elasticity had dropped below 90% of its initial value. The CMA specimen (Fig. 7) completed 95 weeks of wet-dry cycling.

All of the specimens subjected to the 6.04 molal ion concentration solutions exhibited damage at the conclusion of the test. Of these specimens, only the specimens in the NaCl solution lasted for the full 95 weeks. As shown in Fig. 8, the NaCl specimens exhibited some surface scaling, likely the result of crystal growth in the concrete pores. The specimens subjected to 6.04 molal ion concentrations of CaCl₂ and MgCl₂ (Fig. 9 and 10) exhibited the greatest degree of damage, with a loss of material from the ends and edges of the specimens, as well as some delamination. This



Fig. 5—Specimen subjected to 95 weeks of exposure to 1.06 molal ion concentration solution of CaCl₂.



Fig. 6—Specimen subjected to 80 weeks of exposure to 1.06 molal ion concentration solution of MgCl₂.



Fig. 7—Specimen subjected to 95 weeks of exposure to 1.06 molal ion concentration solution of CMA.



Fig. 8—Specimen subjected to 95 weeks of exposure to 6.04 molal ion concentration solution of NaCl.

high level of damage is consistent with both crystal formation in the concrete pores and chemical changes in the cement paste, as suggested in previous studies.³⁻⁶ The CaCl₂ and MgCl₂ specimens also exhibited the greatest reduction in modulus of elasticity, with the tests terminating at 10 weeks, as shown in Fig. 1. The specimens subjected to the 6.04 molal ion concentration CMA solution (Fig. 11) exhibited a nearly uniform loss of material on all exposed surfaces—a change that is in concert with previous observations of chemical changes in the cement paste,⁴ as well as some effects of crystal growth. The relative dynamic modulus of these specimens dropped below 0.9 at week 55 (Fig. 1).

Overall, the results of this study, as represented by the measured changes in modulus of elasticity and observable damage to the test specimens, indicate that CaCl₂, MgCl₂, and CMA have a negative impact on the long-term durability of concrete subjected to cyclic wetting and drying. As shown in Fig. 2, 6, and 7, the effects of MgCl₂ and CMA should become apparent at an earlier age than the effects of CaCl₂ (Fig. 5). In the longer term, all three deicers will significantly weaken concrete (Fig. 1 and 9 to 11). NaCl, the most widely used deicer in U.S. practice, has a more benign impact due to the effects of cyclic wetting and drying in both the short and long term than do the other deicers in the study.

SUMMARY AND CONCLUSIONS

Concrete specimens were exposed to weekly Southern Exposure-type cycles of wetting and drying in distilled water and in solutions of NaCl, CaCl₂, MgCl₂, and CMA with



Fig. 9—Specimen subjected to 10 weeks of exposure to 6.04 molal ion concentration solution of CaCl₂.



Fig. 10—Specimen subjected to 10 weeks of exposure to 6.04 molal ion concentration solution of MgCl₂.

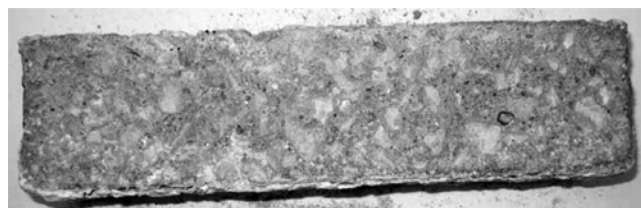


Fig. 11—Specimen subjected to 60 weeks of exposure to 6.04 molal ion concentration solution of CMA.

either a 6.04 molal ion concentration, equivalent in ion concentration to a 15% solution of NaCl, or a 1.06 molal ion concentration, equivalent in ion concentration to a 3% solution of NaCl, for periods of up to 95 weeks. Specimens were also exposed to air only. The effects of exposure were evaluated based on changes in the dynamic modulus of elasticity and the physical appearance of the specimens at the conclusion of the tests.

The following conclusions are based on the test results and analyses presented in this paper.

1. Concretes exposed to distilled water and air show, respectively, an increase and a decrease in dynamic modulus of elasticity, due principally to changes in moisture content. Overall, no negative impact on concrete properties was observed;

2. At lower concentrations, NaCl and CaCl₂ have a relatively small negative impact on the properties of concrete. At high concentrations, NaCl has a greater but still relatively small negative effect;

3. At low concentrations, MgCl₂ and CMA can cause measurable damage to concrete;

4. At high concentrations, CaCl₂, MgCl₂, and CMA cause significant changes in concrete that result in loss of material and a reduction in stiffness and strength; and

5. The application of significant quantities of CaCl₂, MgCl₂, and CMA over the life of a structure or pavement will negatively impact the long-term durability of concrete.

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