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Cl^-, SO_4^{2-}, and PO_4^{3-} Distribution in Concrete Slabs Ponded by Corrosion-Inhibitor-Added Deicing Salts

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Deicing chemicals are mixed with corrosion inhibitors to reduce rebar corrosion in bridge decks. The corrosion inhibitors are thought to penetrate into concrete to the depth of the rebars and form the passive film on the rebar surface. In a previous study, it was found that corrosion-inhibitor-added deicing salts interacted with 3% NaCl-added concrete and produced precipitates through chemical reactions. The amounts of precipitates produced was dependent on the type and concentration of corrosion-inhibitor-added deicing salts. In this investigation, the precipitates formed by chemical reactions between concrete and corrosion-inhibitor-added deicing salts were identified by using chemical analysis and X-ray diffraction methods. The distributions of Cl^-, SO_4^{2-}, and PO_4^{3-} in concrete slabs ponded with corrosion-inhibitor-added deicing salts were determined by chemical analyses of powder samples obtained from the slabs. The major precipitates were calcium and/or magnesium phosphates as major chemical compounds and gypsum as a minor component. High concentrations of phosphate were observed at the top portion of concrete slabs when the deicing chemicals contained phosphate inhibitors. Voids were observed at the interface of aggregate and mortar in the concrete slabs tested with the deicing salts solutions containing corrosion inhibitors. ADVANCED CEMENT BASED MATERIALS 1998, 8, 101–107. *© 1998 Elsevier Science Ltd.*

KEY WORDS: Deicing salt, Concrete, Corrosion, Corrosion inhibitor, Chemical reaction, Precipitater

The use of deicing salts causes rebar corrosion in concrete and leads to structural failures. Corrosion inhibitors mixed with deicing chemicals are used to reduce rebar corrosion in bridge decks. The corrosion inhibitors are thought to penetrate into concrete to the rebar level and form a passive film on the rebar surface for protection from corrosion. However, recent research [1–5] showed the doubtful effectiveness of corrosion-inhibitor-added deicing salts on rebar corrosion, and concrete degradation by corrosion-inhibitor-added deicing salts and salt substitutes. The corrosion-inhibitor-added deicing salts and salt substitutes interacted with concrete and produced precipitates through chemical reactions. The amounts of precipitates produced (chemical reaction products) were dependent on the type and concentration of corrosion-inhibitor-added deicing salts and salt substitutes [6].

In this investigation, the precipitates formed by chemical reactions between concrete and corrosion-inhibitor-added deicing salts were identified by using chemical analysis and X-ray diffraction analysis. The distributions of Cl^-, SO_4^{2-}, and PO_4^{3-} in concrete slabs ponded with the corrosion-inhibitor-added deicing salts solutions were determined by chemical analyses of powder samples of the slabs.

Experimental

Corrosion-Inhibitor-Added Deicing Salt Solutions

Six commercial corrosion-inhibitor-added deicing salts and NaCl were mixed with tap water and deionized water for the slab tests and the cone-shaped concrete tests, respectively, at a concentration of 3% each. Their chemical composition in simulated concrete-saturated solutions are presented in Table 1.

Concrete Slab Samples

Concrete slabs (30 cm × 30 cm × 15 cm) (Figure 1a) [6] were fabricated by using a two cubic yard mix consisting of Portland cement (313 kg) with coarse (797 kg) and fine (523 kg) aggregates. The bottom half of all slabs

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TABLE 1. Chemical composition and pH of solutions containing 6% corrosion-inhibitor-added deicing salts mixed into simulated concrete-saturated solutions [4]

Deicing Salt	Ca	Mg	P	SO_4	Cl	pH_1	pH_2
A	0.033	0.100	0.102	0.016	3.29	8.8	7.8
B	0.002	0.024	0.173	0.046	0.39	7.7	5.4
C	0.051	0.064	0.002	0.083	2.89	10.1	7.7
D	0.017	(0.00005)	0.036	0.044	3.37	10.0	7.7
E	0.008	(0.00005)	0.011	0.004	3.39	12.2	8.0
F	0.028	(0.00005)	(0.0003)	0.008	3.60	10.6	7.5
Concrete-saturated solution	0.028	(0.00005)	0.004	(0.0007)	0.02	12.5	12.5

Note: pH_1 = initial pH of solution; pH_2 = after 240 days.

was cast from the mix as delivered. The top half was cast after adding 9 kg of NaCl to the remaining mix. The average Cl^- content at the top half was about 2500 ppm. After casting, the slabs were placed in a moist room for a period of 28 days, then dried in a chamber maintained at a temperature of 43° to 49°C for 45 days. The air content determined by the linear traverse test was 13% (spacing factor: 0.0021).

Plexiglas dams were bonded to the top surface of the slabs with silicone rubber. The concrete slabs were ponded with 3% corrosion-inhibitor-added deicing salts and NaCl solutions for 484 days. The solution levels were kept constant on each slab. The slab surfaces were examined visually for rust stains, concrete cracks, and roughness of concrete surfaces caused by the deicing salts. The details are given elsewhere [6].

Powder samples were obtained from the slabs by drilling to depths of 1.27, 2.54, 3.81, 5.08, 6.35, 7.62, and 8.89 cm from the top surface for Cl^- and PO_4^{3-} distribution in the slabs, and 3.81, 6.35, and 10.16 cm for SO_4^{2-}. The chemical analysis procedures of ASTM Standard C 114-88 were used to determine the contents of Cl^-, SO_4^{2-}, and PO_4^{3-} in the powder samples.

Three-centimeter diameter cylindrical samples from the slabs ponded with 3% NaCl, and deicing salt A and B solutions were obtained by dry coring for observation of concrete conditions. The cored samples were cross-cut by dry sawing, polished by 10-μm silicon carbide powder to smooth the surface, and visually examined to observe the physical changes in the concrete caused by corrosion-inhibitor-added deicing salts.

Cone-Shaped Concrete Samples and Precipitates

The cone-shaped concrete samples (Figure 1b) [6] were made by mixing 374-kg type III cement, 635-kg sand (Minnesota DOT Specification 3126), and 635-kg quartzite meeting CA-70 grade (Minnesota DOT Specification 3137). A paper mold was used to cast the cone-shaped concrete samples. The cone shape of the samples was chosen to provide a large surface area exposed to the corrosion-inhibitor-added deicing salt solutions and a shape that would accelerate the chemical reactions at the tip. Physical changes of concrete samples could be readily recognized at the tips. The samples were placed in a moist room for 28 days after fabrication, then air dried. The compressive strength of the cone-shaped concrete samples was 63.4 MPa. The base of the cone was cut with a water-cooled diamond saw to make samples of uniform dimensions. The samples were cleaned with a Dayton 3Z856 sand blaster and graded Ottawa Sand (ASTM C-109) under 0.4-MPa air pressure. The distance between the sand blaster nozzle and the samples was kept constant. The average dimension of the samples was 5.08-cm bottom diameter by 6.4-cm height. The initial dimension of each sample was measured using a dial caliper, and the weight was measured with a Sartorius balance. The average weight was 120 g.

Cone-shaped concrete samples were placed in the 3% corrosion-inhibitor-added deicing salt solutions. After leaving the concrete samples in the test solutions for 1 day, various amounts of precipitates were found in the test cells, depending on the type and concentration of corrosion-inhibitor-added deicing salts. The precipitates were formed by chemical reactions between the concrete and the corrosion-inhibitor-added deicing salts. Precipitates were observed on the concrete sample surfaces and/or at the bottom of the test cells. The precipitates were collected from the test cells, rinsed three times with alcohol to remove salt solution by displacement from the precipitates, then dried in an oven at 120°C.

The chemistry of the precipitates formed by chemical reactions between concrete and corrosion-inhibitor-added deicing salts was determined by: (1) a DIONEX 4000i ion chromatography for anions and a Perkin Elmer/Sciex Elan 5000 inductively coupled plasma-mass spectrometer for cations; and (2) a Siemens D-500 diffractometer in this investigation.

Results

Chemical Composition of Precipitates

The chemical composition by weight percentage of the precipitates determined by the chemical analysis is

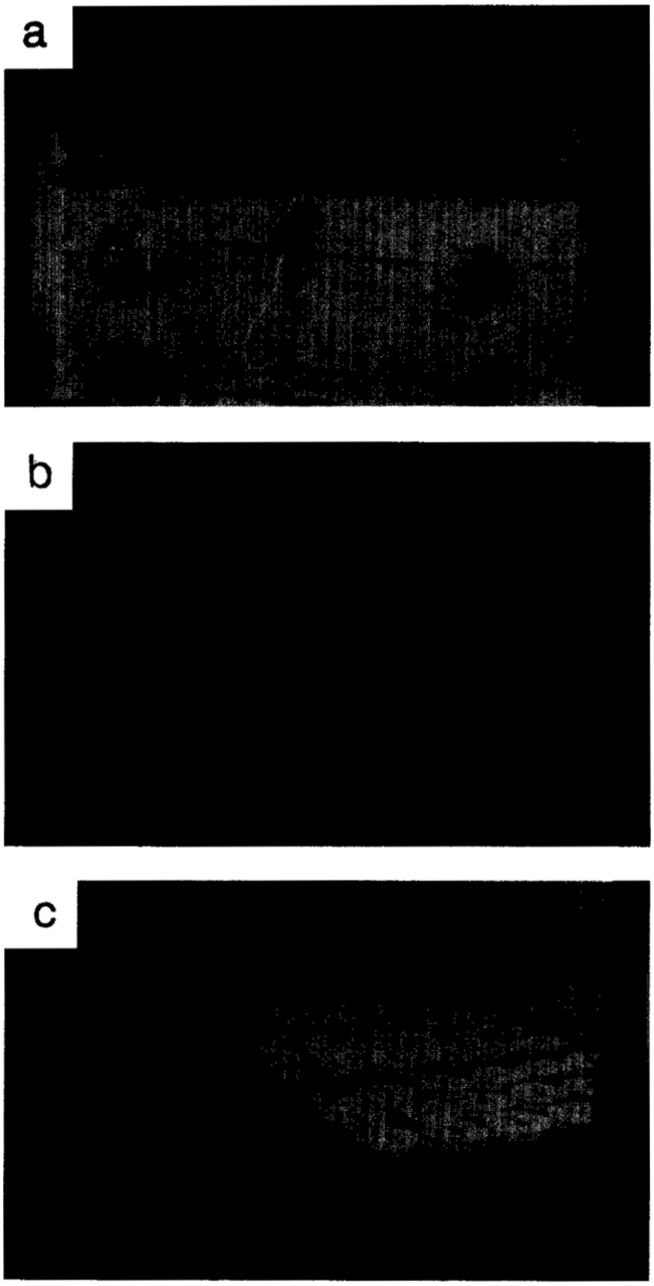

FIGURE 1. (a) A concrete slab sample and (b) a cone-shaped concrete sample in (c) the test cells for concrete degradation by corrosion-inhibitor-added deicing salts and salt substitutes [6].

TABLE 2. Chemical composition of precipitates determined by chemical analysis

Deicing Salt	Ca	Na	K	Mg	SiO_2	P	SO_4	Cl
A	4.22	6.20	0.01	8.65	0.63	4.91	1.68	10.12
B	13.60	0.12	0.01	10.58	0.61	7.79	1.50	0.03
C	13.71	2.54	0.17	0.85	0.72	0.03	1.08	1.40
D	12.63	3.26	0.01	0.48	0.60	8.17	0.06	0.49
E	22.56	2.60	0.01	0.41	1.00	7.40	3.33	0.89
F	18.61	1.10	0.03	7.10	3.90	8.26	6.00	0.41

presented in Table 2, and Figure 2 shows the typical X-ray diffraction patterns of precipitates formed by deicing salts B, C, and E. Table 3 shows the major and the minor chemical components in precipitates determined by both the chemical analysis and the X-ray diffraction. The precipitates of deicing salts D and E contained calcium phosphate as a major components, while those of deicing salts C and F were calcite. The precipitates of deicing salts A and B contained magnesium hydroxide as a major component along with calcium or magnesium phosphate. $Ca_2Na_3(SO_4)_3$ was found as a minor component in all deicing chemicals tested in this investigation. The precipitates of deicing salts E and F contained some forms of silica as a minor

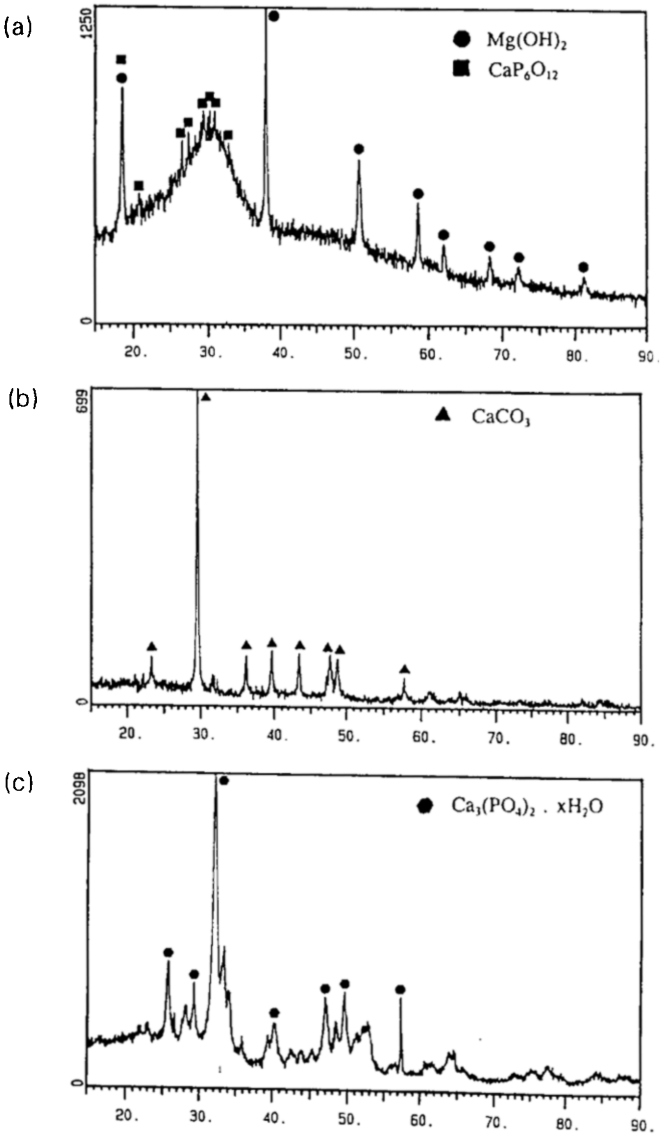

FIGURE 2. X-ray diffraction patterns of precipitates formed by chemical reactions between concrete and deicing salt (a) B, (b) C, and (c) E.

TABLE 3. Chemical compounds in precipitates formed by chemical reactions between corrosion-inhibitor-added deicing salts and concrete

Deicing Salt	Major	Minor
A	$Mg(OH)_2$ $Mg_3(PO_4)_2$	$Ca_3(PO_4)_2 \cdot xH_2O$ $Ca_2Ha_3(SO_4)_3\ (OH)$
B	$Mg(OH)_2$ CaP_6O_{12}	$Ca_2Na_3(SO_4)_3\ (OH)$
C	$CaCO_3$	$Ca_2Na_3(SO_4)_3\ (OH)$ $Ca_3(PO_4)_2 \cdot xH_2O$
D	$Ca_3(PO_4)_2 \cdot xH_2O$	$Mg(OH)_2$ $Ca_2Na_3(SO_4)_3\ (OH)$
E	$Ca_3(PO_4)_2 \cdot xH_2O$	$Ca_2Na_3(SO_4)_3\ (OH)$ $Mg(OH)_2$ $CaCO_3$ SiO_2
F	$CaCO_3$	$Ca_2Na_3(SO_4)_3\ (OH)$ $Ca_3(PO_4)_2 \cdot xH_2O$ SiO_2 Ca_2SiO_4

component. In general, the chemical reactions in concrete by the corrosion-inhibitor-added deicing salts produced calcium or magnesium phosphate, magnesium hydroxide, and calcite.

Cl^-, SO_4^{2-}, and PO_4^{3-} Distributions in Concrete Slabs

Figure 3 shows the distribution of Cl^-, SO_4^{2-}, and PO_4^{3-} in the concrete slabs as a function of depth from the top surfaces. Generally, Cl^- in all of the slabs were 4000 to 5000 ppm in the top 3-cm depth, and then decreased to ~3000 ppm (Figure 3a). High Cl^- contents in the slabs tested with deicing salt B were found at the middle of slabs, which appears to indicate movement of Cl^- by elution. The sulfate contents seem to be uniform at 4000 to 5000 ppm, although the slabs tested with deicing salts A and D showed a maximum at the middle (Figure 3b). High concentrations of phosphate were observed at the top portion of slabs tested with deicing salt A, D, and E solutions (Figure 3c).

Cross-Sections of Cored Samples from Slabs

Figure 4 shows the cross-sections of cored samples from the slabs tested by 3% NaCl, deicing salt A and B solutions. The top 0.5 cm of the cross-sections indicates that the deicing chemicals may damage the interfaces between aggregates and mortar. The cross-section from the plain NaCl slab (Figure 4a) showed the least amount of voids at the interface, while that of deicing salt A (Figure 4c) showed the most.

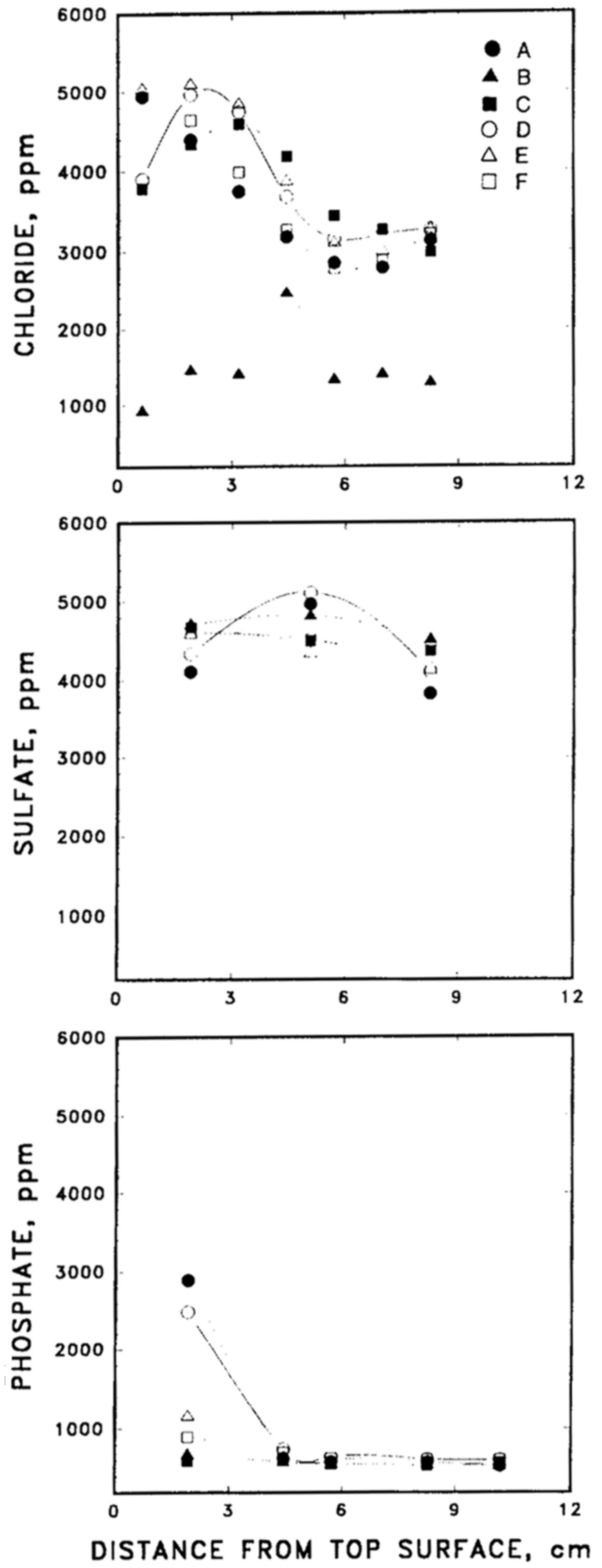

FIGURE 3. (a) Cl^-, (b) SO_4^{2-}, and (c) PO_4^{3-} distributions in concrete slabs ponded with 3% corrosion-inhibitor-added deicing salts solutions.

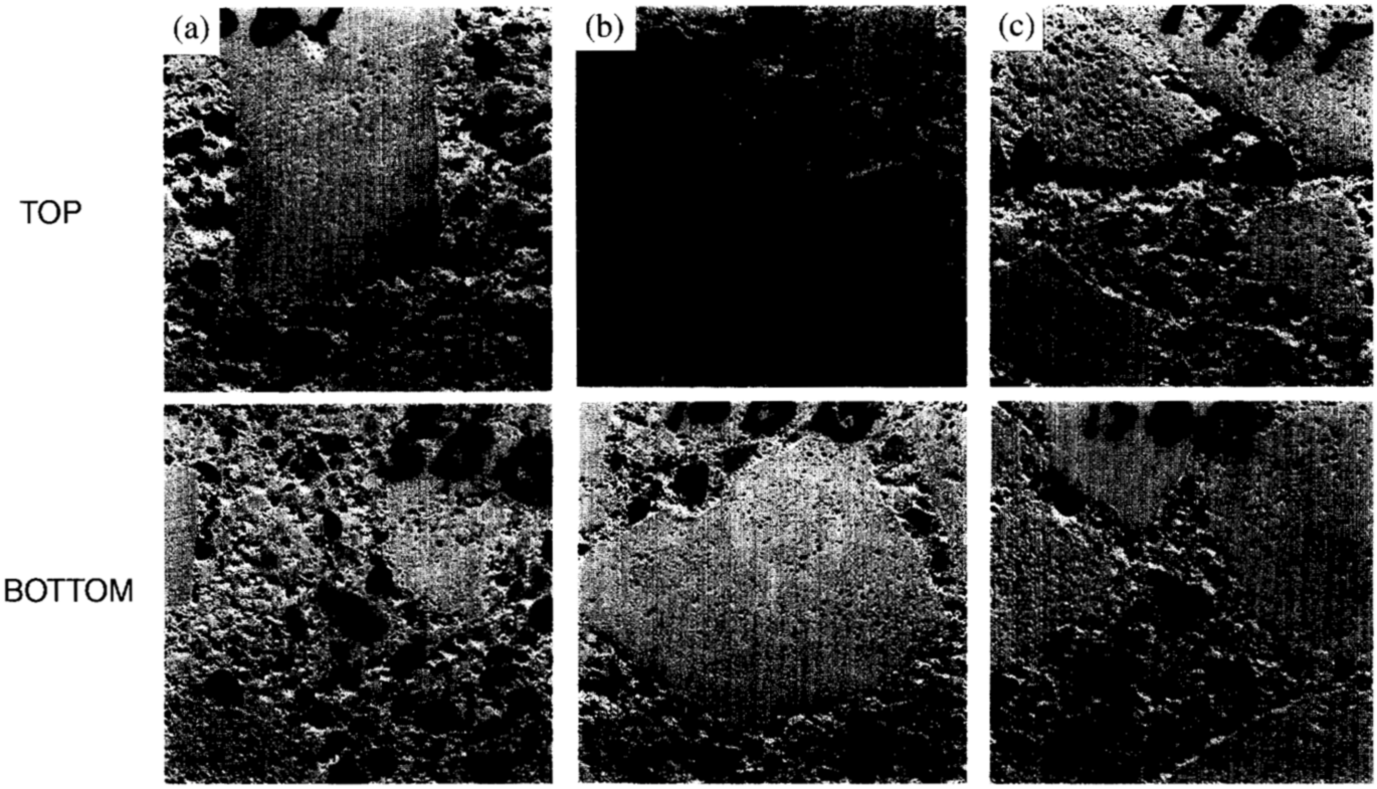

FIGURE 4. Cross-sections of cored samples from the concrete slabs ponded with 3% (a) NaCl, and (b) deicing salt B and (c) A solutions. Deicing salt A (c) shows the largest amount of voids at the interface between aggregates and mortar.

Discussion

A number of alternative chemical deicers and salt additive corrosion inhibitors have been developed in recent years. In tests conducted by the Iowa Department of Transportation [7], the steel coupons were placed in a 15% solution of a deicer and distilled water to determine which alternative deicer caused the least amount of weight loss from corrosion. The reinforced concrete blocks were ponded with a 15% solution of a deicer, and corrosion state of the steel was monitored by copper-copper sulfate half cell potential measurements. The only alternative deicer showing significant inhibition of reinforcing steel corrosion in concrete was pure CMA (among CMA, CMA + NaCl, Quicksalt + PCI, and CG-90), although all deicers were less corrosive than NaCl.

The Washington Department of Transportation [8] evaluated a number of deicers such as CG-90, FREEZGARD + PCI, Urea, CMA, Quicksalt + PCI and Ice Stop CI both in the laboratory and in the field, and found that some deicers appeared to be effective in reducing rebar corrosion. Three percent deicer solutions were used in the laboratory coupon tests.

However, the studies performed by the University of Minnesota and the Minnesota Department of Transportation [4,5] indicated that the effectiveness of corrosion-inhibitor-added deicing salts on rebar corrosion is dependent on: (1) concentration of corrosion-inhibitor-added deicing salts, and (2) environmental conditions such as temperature and oxygen content, and that most deicers were not effective on rebar corrosion protection.

Also, the corrosion-inhibitor-added deicing salts caused changes in the properties of concrete [9]. The salt interacts with concrete by chemical reactions. Some of the reactions are ettringite formation, carbonation, and penetration of chloride ions into C-S-H gels. The salt actions in concrete also affect the freeze-thaw resistance [10]. An increase in deicer impurities, such as calcium sulfate, increased damage to cement mortars [2].

In a previous investigation [6], numerous cracks and rough surfaces on concrete were found on the slabs tested with 3% deicing salt B and E solutions. The slabs tested with deicing salt B and sodium formate solutions contained cracks but did not show any yellow rust stains on the surfaces. On the other hand, the slab surfaces tested with salt (NaCl) solutions showed signs of rebar corrosion in concrete, but no cracks were observed. These observations indicate that the cracks in concrete slabs may be created by rebar corrosion or chemical reactions (or both) between corrosion-inhibitor-added deicing salts and concrete. The results indicate the need to investigate further the concrete degradation caused by chemical reactions between corrosion-inhibitor-added deicing salts and concrete. However, no precipitates were found in the test cells containing NaCl and deionized water. For deicing salts A, E, and F, the amount of precipitates increased with increasing concentrations of corrosion-inhibitor-added deicing salt. For deicing salt D, the amount of precipitates decreased with increased concentration of corrosion-inhibitor-added deicing salt. It appears that the amount of precipitates increased with time in all cases.

The chemical changes of the test solutions as well as the physical changes of the concrete samples are being monitored as a function of time. The impact of the chemical reactions on concrete degradation may be unraveled by determining the chemical and mineralogical changes of the concrete caused by the corrosion-inhibitor-added deicing salts.

Figure 3 and Table 3 suggest that the phosphate in deicing salts A, D, and E formed calcium or magnesium phosphate precipitates by chemical reactions with concrete at the top of concrete slabs. High concentrations of phosphates were observed in the top portion (1.5 cm) of concrete (Figure 3c) when the corrosion-inhibitor-added deicing salts or salts substitutes contained phosphates as inhibitors. This is coincident with the phosphate components precipitates of deicing salts A, D, and E as shown in Table 3. Thus, Figure 3 and Table 3 indicate that the phosphates added in deicing chemicals as corrosion-inhibitors might not penetrate into concrete to prevent rebar corrosion because of the chemical reactions.

Sodium phosphate is an anodic inhibitor effective in the presence of oxygen, and its protective properties toward steel are a function of pH [11]. Whether phosphate ion can act as an accelerator or as an inhibitor for steel corrosion depends on its concentration. At low concentrations, PO_4^{3-} will develop pits on the surface of the metal. Higher concentrations of 15 to 20 mg/L reverse this role, and the ion contributes to the stabilization of gamma-Fe_2O_3 [12,13].

If PO_4^{3-} in the corrosion-inhibitor-added deicing salts is lost by precipitation, the effectiveness of the corrosion-inhibitor-added deicing salts on rebar corrosion could drop significantly. On the other hand, the formation of precipitates in cracks may act as a barrier to the penetration of the salt solutions, thereby acting as an inhibitor. Alternatively, some of the precipitates may form in microcracks or pores of concrete, and facilitate propagation of cracks. Figure 4 indicates that the precipitates may generate voids at the interfaces between aggregates and mortar. Further investigation is necessary to determine the cause of voids at the interfaces. The solubility of $Ca_3(PO_4)_2$ decreases with increasing pH. Because of the low solubility of $Ca_3(PO_4)_2$ in concrete at pH 12 to 13, the precipitates remain in the air voids in concrete or microcracks [14].

The effect of sulfate ions on the potentiodynamic polarization behavior of 1020 steel (mild steel) in saturated $Ca(OH)_2$ at 22°C was investigated, and the corrosion potential was found to become more negative with increasing sulfate concentration. This implies that greater amounts of sulfate ions increase the corrosion rate of 1020 steel in saturated $Ca(OH)_2$ solution [15].

The calcite precipitates formed by deicing salts C and F may decrease the concrete pH. CaO is the dominant substance in cement. As a result, large quantities of $Ca(OH)_2$ are crystallized in pores. The impermeability of concrete, the reserve of hydroxide, and the low CO_2 concentrations that occur in air are the primary reasons why the carbonation process proceeds slowly in concrete [16]. The carbonation entails:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

The reaction gives rise to neutralization of the pore solution to pH values <9. The neutralization takes place in stages and several intermediate reactions occur [16]. One of the final products is $CaCO_3$. However, the effect of pH changes on concrete is not well understood at this time. The effect of precipitates found in this investigation on concrete durability is yet to be determined by research in progress.

Conclusions

1. Precipitates formed by chemical reactions between corrosion-inhibitor-added deicing salts and concrete were identified by using chemical analysis and X-ray diffraction analysis. Precipitates were calcium and/or magnesium phosphates as a major component, and gypsum as minor.
2. High concentrations of phosphates in concrete slabs subsequent to application of certain corrosion-inhibitor-added deicing salts were observed in the top 3 cm in depth from surface, where the precipitates were calcium and/or magnesium phosphate components.
3. Voids were observed at the interfaces of aggregates and cement matrix in the slabs tested under certain corrosion-inhibitor-added deicing salt solutions. Further investigation is necessary to determine the causes of voids at the interfaces.

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