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Effect of Corrosion-Inhibitor-Added Deicing Salts and Salt Substitutes on Reinforcing Steels: I. Influence of Concentration

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Corrosion of reinforcing steel (rebar) samples was investigated in concrete-saturated solutions containing corrosion-inhibitor-added deicing salts and salt substitutes as well as in plain sodium chloride solutions. Galvanic cells were used to determine the effects of corrosion-inhibitor-added deicing salts and salt substitutes on rebar corrosion. The reinforcing steel samples were galvanically coupled and were recovered after 240 days. Pit depths and area percentages of corrosion were determined on the reinforcing steels with an optical microscope. Optimum concentrations were found to exist for the corrosion-inhibitor-added deicing salts and salt substitutes in reducing the rebar corrosion. Dramatic changes of pH values were noted in the concrete-saturated solutions containing corrosion-inhibitor-added deicing salts and salt substitutes. The formation of precipitates caused by chemical reactions between a concrete-saturated solution and corrosion-inhibitor-added deicing salts and salt substitutes was observed. ADVANCED CEMENT BASED MATERIALS 1995, 2, 145–151

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Corrosion inhibitors in deicing salts frequently show varied effectiveness in preventing or reducing the corrosion of reinforcing steels (rebars) in concrete due to complex regional environmental conditions. Corrosion results from field tests may not agree with laboratory results because of the unpredictability of weather, the nature of corrosion conditions, and the manner in which rebars corrode. Thus, the correlation between corrosion resistance and the use of inhibitor-added or inhibitor-free deicing chemicals is not always clear. The effectiveness of corrosion inhibitors in deicing salts for reducing rebar corrosion depends upon a complex combination of environmental conditions, concrete properties, and rebar materials [1,2].

In this investigation, a galvanic cell method was chosen for evaluating the effect of corrosion-inhibitor-added deicing salts and salt substitutes on rebar corrosion, because this technique is capable of continuously monitoring corroding rebars *in situ* over extended periods of time and of accelerating corrosion processes [3]. The effectiveness of six corrosion-inhibitor-added deicing salts and salt substitutes with respect to plain NaCl on rebar corrosion was evaluated by (1) examining the rust-covered areas of test samples and (2) observing the cross sections of rebars recovered from galvanic contacts using optical microscopy. The pH changes in test solutions were also monitored for comparison with the results of the above two methods.

Experimental

Rebar Electrode Samples

Samples of grade 60 rebar were used in this investigation, and the chemical composition of six samples are shown in Table 1. The samples were made into electrodes by attaching electrical wires to 6-mm thick sections of grade 60 rebar with silver conductive epoxy and mounting them in epoxy. After the epoxy had hardened, the bottom surfaces of the mounted rebars were ground and polished using conventional metallographic polishing techniques. Data were obtained on three samples at three different concentrations for each of seven test solutions, 63 samples in all. Cross sections of the rebars were chosen for testing rather than

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TABLE 1. Chemical composition of grade 60 rebar

	C	Mn	P	S	Si	Cu	Ni	Cr	Mo
Maximum	0.436	1.196	0.025	0.043	0.243	0.329	0.100	0.131	0.025
Minimum	0.383	0.950	0.013	0.032	0.186	0.214	0.087	0.096	0.033
Average	0.402	1.053	0.022	0.039	0.214	0.264	0.094	0.120	0.029

Spectrographic analyses were made by North Star Steel. Data is based on six samples.

longitudinal sections, because the cross-sectional area provides a better surface for controlled testing.

Galvanic Cells

A bulk test solution was prepared by equilibrating 120 L of deionized water with 10 kg of 3-mm concrete chips. The bulk concrete samples used to make the 3-mm chips were obtained from a bridge deck of Interstate Highway 94 in the Twin Cities, Minnesota. The concrete was analyzed and found to contain approximately 1,100 ppm Cl^-. Individual test solutions were made from this bulk solution by pouring 500 ml into a 600-ml beaker and adding 30 g of concrete chips to ensure saturation in each beaker. Corrosion-inhibitor-added deicing salts and salt substitutes or plain NaCl were added to the simulated concrete-saturated solution to have 3, 6, and 20% (by weight) concentrations for use in the galvanic cells (Figure 1). For further details see ref 3.

The bulk solution had a pH of 12.5, and the chemical analyses of the solutions are given in Table 2. The chemical compositions of solutions containing 6% corrosion-inhibitor-added deicing salts and salt substitutes are also presented in Table 2. Most of the corrosion-inhibitor-added deicing salts tested in this investigation were basically plain sodium chloride mixed with corrosion inhibitors. The simulated concrete-saturated solutions were directly exposed to the atmosphere, and the carbonation film formed on top of the solution. Because the concrete-saturated solutions were exposed to the atmosphere, the solutions tend towards saturation with CO_2 in the atmosphere. In Table 2, however, the pH of the concrete-saturated solution shows no change in pH over the 240-day period. It may be concluded, therefore, the pH changes due to carbonation were negligible over the test period. Also, to compensate for evaporation loss, the solution levels were maintained constant by frequent additions of distilled water.

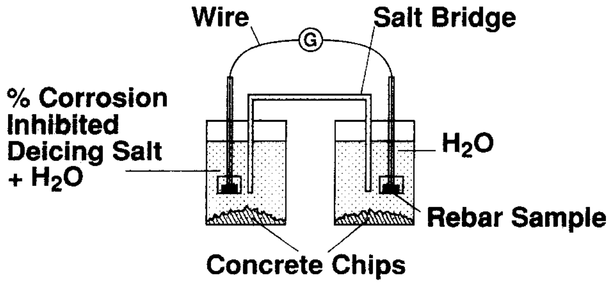

FIGURE 1. Schematic representation of experimental set-up for galvanic cells of rebars in a simulated concrete environment [3].

All of the corrosion-inhibitor-added deicing salt solutions, except plain NaCl, generated different amounts of white-colored precipitates as shown in Figure 2. The precipitates of deicing salt D could not be observed due to dark color. In all cases, the precipitates settled down to the bottom of the test cells within a few hours.

Optical Observations

RUST-COVERED AREAS. The 63 rebar samples were recovered from the galvanic cells after 240 days, and the percentage of the rust-covered area on each sample was estimated.

PIT DEPTH AND DEGREE OF CORROSION. The 63 rebar samples recovered from the galvanic cells were examined with an Olympus model BHSP optical microscope to determine the pit depths and the degrees of corrosion. The recovered rebar samples were cross-cut, mounted in an epoxy, and then polished using conventional metallographic polishing techniques.

Most cross sections of corroded areas of rebars showed an extended corrosion pit (Figure 3). The measured lengths of pits including the lip and their maximum depths were used to determine the average pit depths and the degrees of corrosion as shown in Figure 3. The average pit depths and the percentages of corrosion were calculated as defined below:

$$D_{\text{Average pit depth}},\ \mu\text{m} = \frac{\sum_{n=1}^{i} y_n}{n} \tag{1}$$

$$C_{\text{Corrosion}},\ \text{percent} = \frac{\sum_{n=1}^{i} x_n \cdot y_n}{X' \cdot Y'} \times 100 \tag{2}$$

TABLE 2. Chemical composition and pH of solutions containing 6% deicing salts mixed into simulated concrete-saturated solutions

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

pH_1 initial pH of solution; pH_2 = after 240 days.
For identification of these products, contact MN/DOT, Research Laboratory, Maplewood, MN 55109.

where x = the width of individual pits; y = individual maximum pit depth; X' = total surface width observed; Y' = depth; and n = number of pits. Equation 2 defines the percentages corrosion assuming a rectangular shape of maximum measured depth and width for each corrosion pit.

Results

Even though the galvanic currents and potentials of the cells were measured, only the results of optical observation are discussed in this manuscript; the results of electrochemical measurement will be reported in a later paper.

Rust-Covered Areas

Sixty-three samples were recovered from the galvanic cells after 240 days. Percent corrosion for each of the 21 test solutions is based on the average of three samples each. Twenty-one representative samples are shown in Figure 4. The rust-free areas (indicated by a in Figure 4) of samples varied with the types and the concentrations of deicing salts. In 3% corrosion-inhibitor-added deicing salts mixed into concrete-saturated solutions, deicing salts C, D, E, and F showed smaller rust-covered areas than that of NaCl. Deicing salts A, B, and F showed smaller rust-covered areas than that of NaCl in 6% corrosion-inhibitor-added deicing salt solutions. However, in 20% corrosion-inhibitor-added deicing salt solutions, only deicing salt B showed a smaller rust-covered area than NaCl.

FIGURE 2. Different amounts of precipitates in 6% corrosion-inhibitor-added deicing salts mixed into concrete-saturated solutions.

Pit Depths

Figure 5 shows the cross sections of rebar samples tested at 3, 6, and 20% concentrations of the corrosion-inhibitor-added deicing salts and NaCl. The pit depths also varied with the types and concentrations of deicing salts. In 3% corrosion-inhibitor-added deicing salt solutions, only deicing salts D and F showed smaller pit depths than that of NaCl. Deicing salts A, B, C, and E showed smaller pit depths than that of NaCl in 6% corrosion-inhibitor-added deicing salt solutions. None of the deicing salts showed smaller pit depths than NaCl in 20% corrosion-inhibitor-added deicing salt solutions.

Degrees of Corrosion

The variation in percent corrosion calculated by eq 2 from the different deicing salt solutions is illustrated in Figure 6. Deicing salts D and F and NaCl show maximum corrosion for 6% solutions. The percent corrosion decreased for deicing salts A and B with an increase in concentration. An addition of deicing salt E decreased the corrosion initially, but it increased corrosion with an increase in concentration. In 3% solutions, deicing

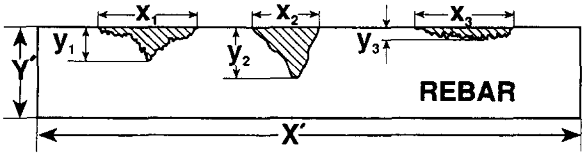

FIGURE 3. Schematic diagram of a cross section of rebar showing pits: x_i is pit width and y_i is pit depth.

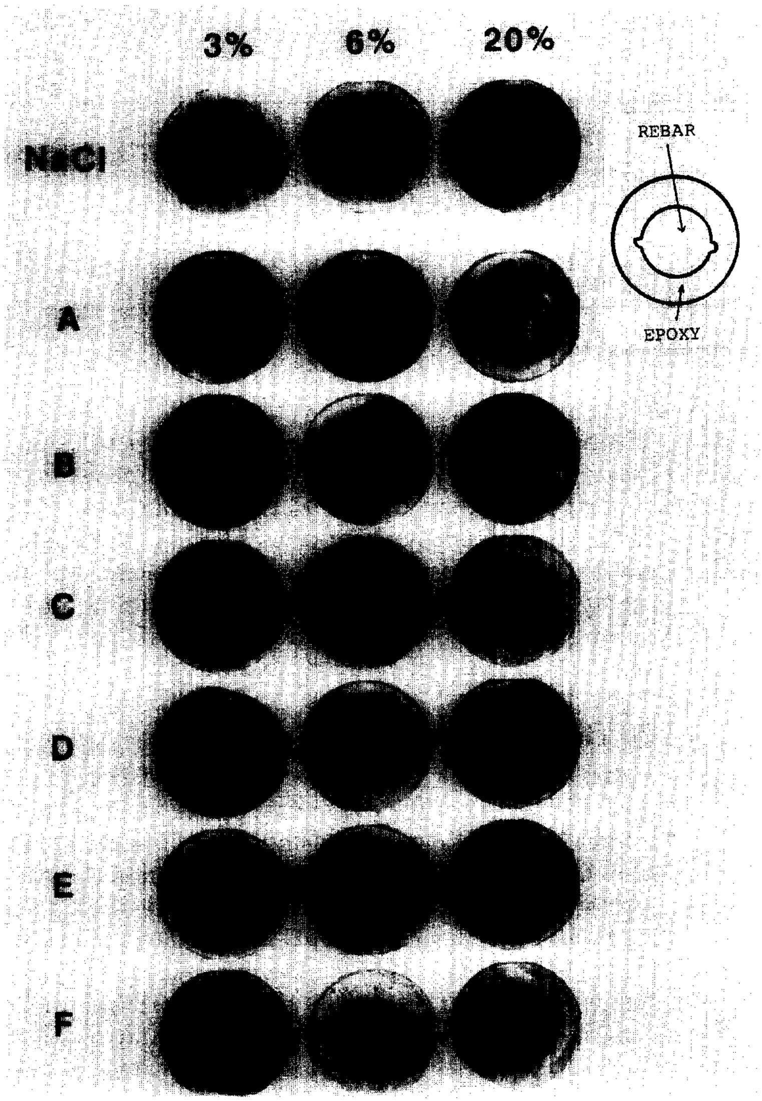

FIGURE 4. Rust-covered areas of the rebar samples tested in the galvanic cells under different concentrations of corrosion-inhibitor-added deicing salts and plain NaCl. **a** indicates a rust-free area.

salts C, D, and F showed less percent corrosion than that of NaCl. Deicing salts A, B, C, and E showed less percent corrosion than that of NaCl in 6% solutions. Only deicing salt A showed less percent corrosion than NaCl in 20% solutions.

Discussion

Effectiveness of Corrosion-Inhibitor-Added Deicing Salts

The effectiveness of corrosion-inhibitor-added deicing salts and salt substitutes on rebar corrosion with respect to NaCl on rebar corrosion may be estimated as follows:

$$\%E_{\mathrm{corr,A}} = \frac{C_{\mathrm{NaCl}} - C_{\mathrm{A}}}{C_{\mathrm{NaCl}}} \times 100 \tag{3}$$

where $\%E_{\mathrm{corr,A}}$ is the effectiveness of deicing salt A on rebar corrosion; C_{NaCl} is percent corrosion of NaCl (from eq 2); and C_{A} is percent corrosion of deicing salt A under various concentrations. Figure 7 shows that the corrosion of rebars by the corrosion-inhibitor-added deicing salts and salt substitutes is generally at most only 50% less than the corrosion by plain NaCl solutions, except for deicing salt A (~75%). The negative signs indicate their effectiveness is inferior to NaCl. The negative effectiveness $> -300\%$ was found for 20% deicing salt F solutions.

The degree of effectiveness of corrosion-inhibitor-added deicing salts and salt substitutes with respect to NaCl varied with their types and concentrations. Corrosion rates are influenced not only by the concentration of deicing salts, but also by the amount of dissolved oxygen [4]. Some deicing salts may release more aggressive ions than others and also affect the solution pH, whereas the dissolved O_2 will decrease at higher concentrations of dissolved salts [4]. It follows that an increase in the concentration of deicing salts

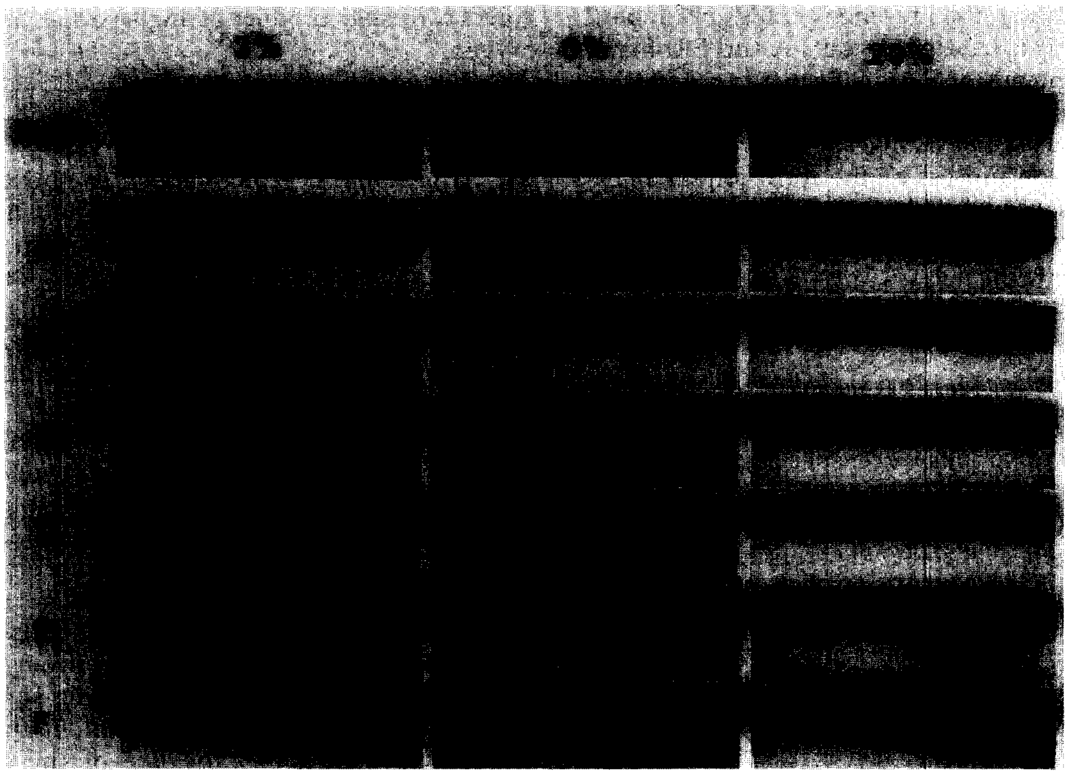

FIGURE 5. Pits of cross-sectional rebars tested in the galvanic cells under different concentrations of corrosion-inhibitor-added deicing salts and plain NaCl.

may increase corrosion to a maximum at a certain concentration and then decrease corrosion possibly due to a decrease in dissolved O_2 in the solution. In addition, the concentration of the deicing salts and dissolved O_2 reaching the rebar surface may be affected by the conditions of concrete such as cracks and porosity and by accumulation of the deicing salts in concrete. HPO_4^{2-} ions have been found to be effective in inhibiting pitting on carbon steel [5]. The pitting potential shifts to

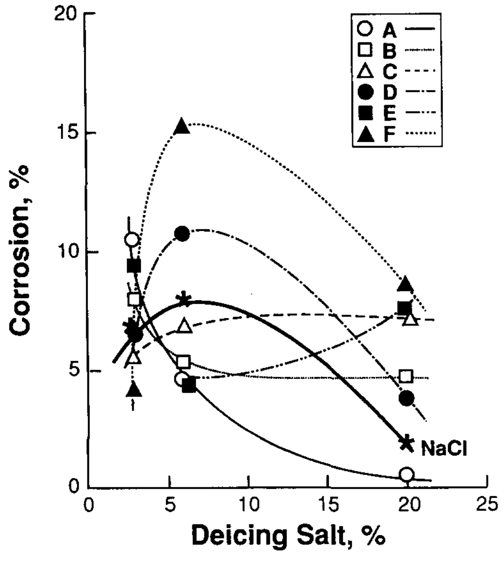

FIGURE 6. Percent corrosion as a function of amount of corrosion-inhibitor-added deicing salts.

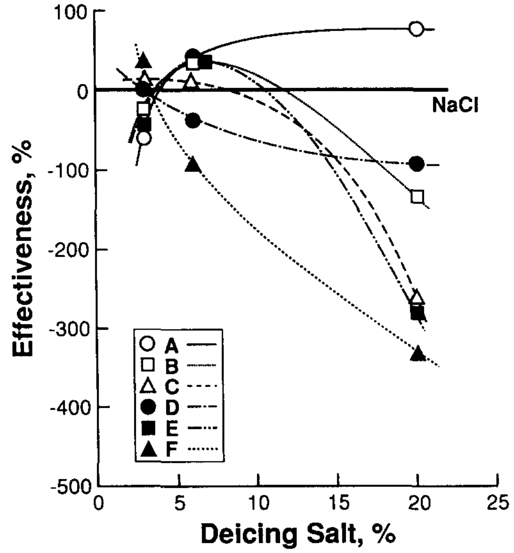

FIGURE 7. Effectiveness of corrosion-inhibitor-added deicing salts with respect to NaCl on the degree of corrosion as a function of concentration.

more noble values in the presence of HPO_4^{2-}. Table 2 and Figure 7 show that deicing salts A and B containing high percentages of P are effective in preventing rebar corrosion at concentrations greater than 6%.

The method used in this investigation was to accelerate the corrosion process by the corrosion-inhibitor-added deicing salts in the concrete-saturated solutions. Separate research is in progress to determine whether all chemical elements of corrosion inhibitors penetrated to the surface of rebars by using slab tests using similar solutions.

Rust on Rebar Sample Surfaces

The occurrence of various oxide species is dependent on pH, oxygen availability, various corrosive chemical elements in solution, and the composition of the steel. However, oxygen availability determines the nature and layering of the end-products. The actual nature of the oxide rust is important because FeO and FeOOH seem to be more adherent than Fe_3O_4 and Fe_2O_3, and, therefore, more likely to slow the corrosive attack. Also the higher oxides and oxy-hydroxides are more prone to spall [5].

From thermodynamic considerations using the Pourbaix diagram [6], the following oxidation reactions can be given for steel embedded in concrete with its pH ranging from 10 to 13:

$$Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^- \tag{4}$$

$$3Fe(OH)_2 + 2OH^- \rightarrow Fe_3O_4 + 4H_2O + 2e^- \tag{5}$$

$$3Fe_3O_4 + 2OH^- \rightarrow 3Fe_2O_3 + H_2O + 2e^- \tag{6}$$

The two possible cathodic reactions are:

$$2H^+ + 2e^- \rightarrow H_2 \tag{7}$$

$$\tfrac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^- \tag{8}$$

The mechanism of corrosion is primarily governed by the chemical environment prevailing at the interface, influenced by the ionic species from the deicing salts. Black and yellow rusts were found in this investigation. Figure 4 shows that both the amount and proportions of black and yellow rust varied depending on the type of deicing salts. X-ray diffraction analyses of the rust indicated that the black-colored rust consisted of Fe_2O_3, Fe_3O_4, and $MgO{\cdot}Fe_2O_3$, and the yellow-colored rust consisted of FeOOH along with Fe_3O_4. From eq 4–8, the black-colored rust would be the favored corrosion product at high partial pressures of oxygen.

Precipitates and pH

Even though the effectiveness of the corrosion-inhibitor-added deicing salts and salt substitutes were determined by using optical microscopy in this investigation, it is still premature to draw any definite conclusions, because the pH changes and precipitate formed in the corrosion-inhibitor-added deicing salts-mixed concrete solutions have not been fully identified.

Changes in pH were monitored, because the pH may affect both rebar corrosion and concrete degradation [7]. The initial pH of the concrete-saturated solution before mixing the deicing salts was 12.5, but the pH decreased dramatically with the addition of some corrosion-inhibitor-added deicing salts and salt substitutes into the concrete-saturated solutions (Table 2). The reasons for the dramatic decrease (from 12.5 to 5.4) in the pH value of solutions containing some deicing salts are still not clearly understood. If the low pH degrades the concrete, the use of the corrosion-inhibitor-added deicing salts and salt substitutes cannot be justified. Its use, as the pH changes, may cause the degradation of concrete properties such as bonding strength and then create or propagate concrete cracks over a period of time [8].

It was also noted that the corrosion-inhibitor-added deicing salts and salt substitutes generate different amounts of precipitates in a concrete-saturated solution (Figure 2). The reason for the pH changes may be due to the chemical reactions (precipitation) between the concrete-saturated solution and the corrosion-inhibitor-added deicing salts. An increase in the concentrations of some corrosion-inhibitor-added deicing salts increased the amount of precipitates. A scanning electron microscope with energy dispersive X-ray spectrometer and X-ray diffraction as well as chemical analyses are being used to identify the precipitates formed by the chemical reactions. The chemical elements of precipitates have been identified, and the effort is being made to identify the nature of the precipitates. The characteristics of compounds and their effect on concrete durability are being investigated and will be reported in the near future. Similar phenomena were reported by Locke and Boren [9] who found that the deicing salt CMA (calcium magnesium and acetate) changed the chemical composition of the pore solution.

A more detailed analysis on the nature of precipitates is of interest in determining the mechanism of inhibition by each corrosion-inhibitor-added deicing salt and salt substitute. The formation of precipitates in concrete cracks may act as a barrier to the penetration of salt solutions, thereby acting as an inhibitor. Alternatively, some of the precipitates in microcracks and pores of concrete may exert stresses and propagate the cracks. If certain ions in the corrosion-inhibitor-added deicing salts and salt substitutes that function as inhibitors are lost by precipitation, the effectiveness of corrosion-inhibitor-added deicing salts and salt substitutes in the field may drop significantly.

Conclusions

1. A quick and simple laboratory method for evaluating deicing chemicals was developed. The method eliminated potential difficulties in that the inhibitors actually were able to migrate into concrete.
2. There is an optimum concentration of the corrosion-inhibitor-added deicing salts and salt substitutes for effective reduction of rebar corrosion.
3. Rebar corrosion due to corrosion-inhibitor-added deicing salts and salt substitutes is generally less than 50% of that resulting from plain NaCl solutions.
4. Corrosion-inhibitor-added deicing salts and salt substitutes change the values of pH in concrete-saturated solutions.
5. Chemical reactions between a concrete-saturated solution and deicing chemicals produce precipitates.

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