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Effect of Corrosion-Inhibitor-Added Deicing Salts and Salt Substitutes on Reinforcing Steels: II. Influence of Temperature and Oxygen Content

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The effect of corrosion-inhibitor-added deicing salts and salt substitutes on reinforcing steels (rebars) was investigated at various temperatures and oxygen contents using galvanic cells and optical microscopy. Temperatures and oxygen contents were varied by applying stirring, oxygen-bubbling, high temperature, freeze-thaw cycle, and dry-wet cycle conditions to simulated concrete solutions mixed with 6% corrosion-inhibitor-added deicing salts, salt substitutes, and plain sodium chloride. Corrosion of reinforcing steel varied with oxygen contents and temperatures of the corrosion-inhibitor-added deicing salt and salt substitute solutions. The reinforcing steels under the freeze-thaw cycle condition showed the least corrosion, whereas those under the dry-wet cycle condition showed the most severe corrosion. The effectiveness of corrosion-inhibitor-added deicing salts and salt substitutes was found to vary with temperatures and dissolved oxygen contents. ADVANCED CEMENT BASED MATERIALS 1995, 2, 152–160

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Deicing salts are spread on road surfaces to lower the freezing point of snow and ice, thereby providing improved driving conditions during the winter months. The most commonly used deicing salts are sodium chloride (rock salt) and calcium chloride. The deleterious effect of deicing salts on reinforcing steel (rebar) in concrete is well known [1,2]. A number of deicing salts treated with inhibitors and deicing chemical substitutes have been suggested as replacements for sodium chloride and calcium chloride. However, the treated deicing salts and the substitute chemicals sometimes show doubtful value in preventing or reducing corrosion of reinforcing steels in concrete due to complex environmental conditions [3].

The effectiveness of inhibitors can be affected by numerous conditions in the environment and the materials [4]. The effectiveness of inhibitors can be adversely influenced by increases in temperature [5]. Corrosion of reinforcing steel in concrete is affected by the rate of oxygen diffusion and the moisture content. Differences in oxygen content along rebar surfaces could establish a galvanic cell reaction, and galvanic corrosion may result. Many inhibitors are designed to counteract oxygen attack [5]. Certain chemical elements in inhibitors are beneficial, or at least not deleterious to corrosion prevention over a range of temperatures, but can become ineffective above certain temperatures and concentrations of the elements. Our previous research [6] determined the effectiveness of corrosion-inhibitor-added deicing salts and salt substitutes on reinforcing steel corrosion under three different concentrations in a simulated concrete solution by using galvanic cells and optical microscopy. It was found that there was an optimum concentration of corrosion-inhibitor-added deicing salts and salt substitutes and that chemical reactions between a concrete-saturated solution and corrosion-inhibitor-added deicing salts produced precipitates. In this research, the tests were performed after the precipitates settled to the bottom of the corrosion cells. A more detailed analysis on the nature of precipitates becomes of interest in establishing the roles played by each corrosion-inhibitor-added deicing salt or salt substitute.

Reinforcing steel in Snowbelt states such as Minnesota normally experience freeze-thaw cycles, dry-wet cycles, and high (summer) temperatures over a year's

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time. Micro- and macrocracks in concrete can generate a difference in oxygen contents around reinforcing steels. The purpose of this investigation was to determine the effect of corrosion-inhibitor-added deicing salts and salt substitutes under static (control), stirred, oxygen-bubbled, high temperature, freeze-thaw cycle, and dry-wet cycle conditions by (1) determining the percentage of rust-covered areas of test samples and (2) observing cross sections of reinforcing steels recovered from the galvanic cells used optical microscopy. The galvanic cell method was used to accelerate the corrosion process.

Experiment

Galvanic Cells

The galvanic cells used in the previous research (Figure 1 in ref 6) were modified to determine the effect of corrosion-inhibitor-added deicing salts and salt substitutes under static (control), stirred, oxygen-bubbled, high temperature, freeze-thaw cycle, and dry-wet cycle conditions.

CONTROL. Five out of the six corrosion-inhibitor-added deicing salt solutions generated different amounts of white-colored precipitates under static conditions. The precipitates settled to the bottom of the test cells within a few hours. The corrosion tests were made after the precipitates settled to the bottom.

STIRRED. A galvanic cell with a stirring mechanism was constructed to investigate the effect of stirred precipitates on the effectiveness of the corrosion-inhibitor-added deicing salts. A T-shaped pyrex glass stirring bar was rotated in a beaker continuously at a speed of 15 rpm, which was sufficient to agitate the precipitates in the solution.

OXYGEN-BUBBLED. Corrosion of reinforcing steels in concrete will be affected by the rate of oxygen diffusion, especially through cracks. Oxygen was supplied to the solutions by continuous bubbling to investigate its effect on reinforcing steel corrosion under high oxygen concentrations. The bubbling action also provided agitation of the precipitates.

HIGH TEMPERATURE. A typical pavement temperature of bridge decks during summer in Minnesota is 45°C. A hot plate was adjusted to maintain a temperature of 45 ± 1°C during the tests. A 127-mm deep bed of sand on the hot plate provided uniform temperature distribution to all the galvanic cells. In these tests, the Bacto-Agar in the salt bridge was replaced with hydrogel because the Bacto-Agar with a low melting point could not be used at the temperature.

FREEZE-THAW CYCLE. The galvanic cells were placed in a temperature controlled freezer. Initially, the temperature was set at −17°C, which is the freezing point of a 6% NaCl solution. However, all of the 6% corrosion-inhibitor-added deicing salt solutions froze at −7°C. In view of this, the tests were performed at −7°C and 2°C for the freeze-thaw cycle. It took 6 hours to reach −7°C for the test solutions and 24 hours to reach 2°C. A cycle was set for 2 days at the freezing temperature and 3 days at the thawing temperature. A total of 23 freeze-thaw cycles were performed on the galvanic cells.

DRY-WET CYCLE. An important factor in determining the susceptibility of reinforcing steels to corrosion in concrete is the percentage of time that critical humidity for conductivity is exceeded. The intention of the dry-wet cycle tests was to make the relative comparison among corrosion-inhibitor-added deicing salts under ideal dry-wet cycle conditions. The reinforcing steel samples were removed after 17 dry-wet cycles. A cycle consisted of two reinforcing steel samples dipped in a solution for 4 days and air-dried for 3 days. The average room temperature was about 25°C during the tests.

Dissolved Oxygen in Solutions

The oxygen contents in the 3, 6, and 20% corrosion-inhibitor-added deicing salt solutions under the control conditions were measured using a Lazar model DO-166 dissolved oxygen probe. Also, the oxygen contents in the 6% solutions under stirred and oxygen-bubbled conditions were measured. Measurements of oxygen content in the 3 and 20% solutions were made only to determine the solubilities of oxygen in these solutions.

Optical Microscopy

The reinforcing steel samples were removed from the galvanic cells after 120 days and examined using an Olympus model BHSP optical microscope to determine the percentages of rust-covered areas, the pit depths, and the degrees of corrosion. For further details see ref 6.

Results

Rust-Covered Areas

The rust-covered samples were removed from the galvanic cells after a test period of 120 days and are shown in Figure 1. The extent of the rust-covered areas of the samples varied with the types of deicing salts and test conditions. Under the control condition, deicing salts A and B showed smaller rust-covered areas than NaCl. Only deicing salt B showed some rust-free areas under the stirred, oxygen-bubbled, and dry-wet cycle conditions. No deicing salt showed smaller rust-covered ar-

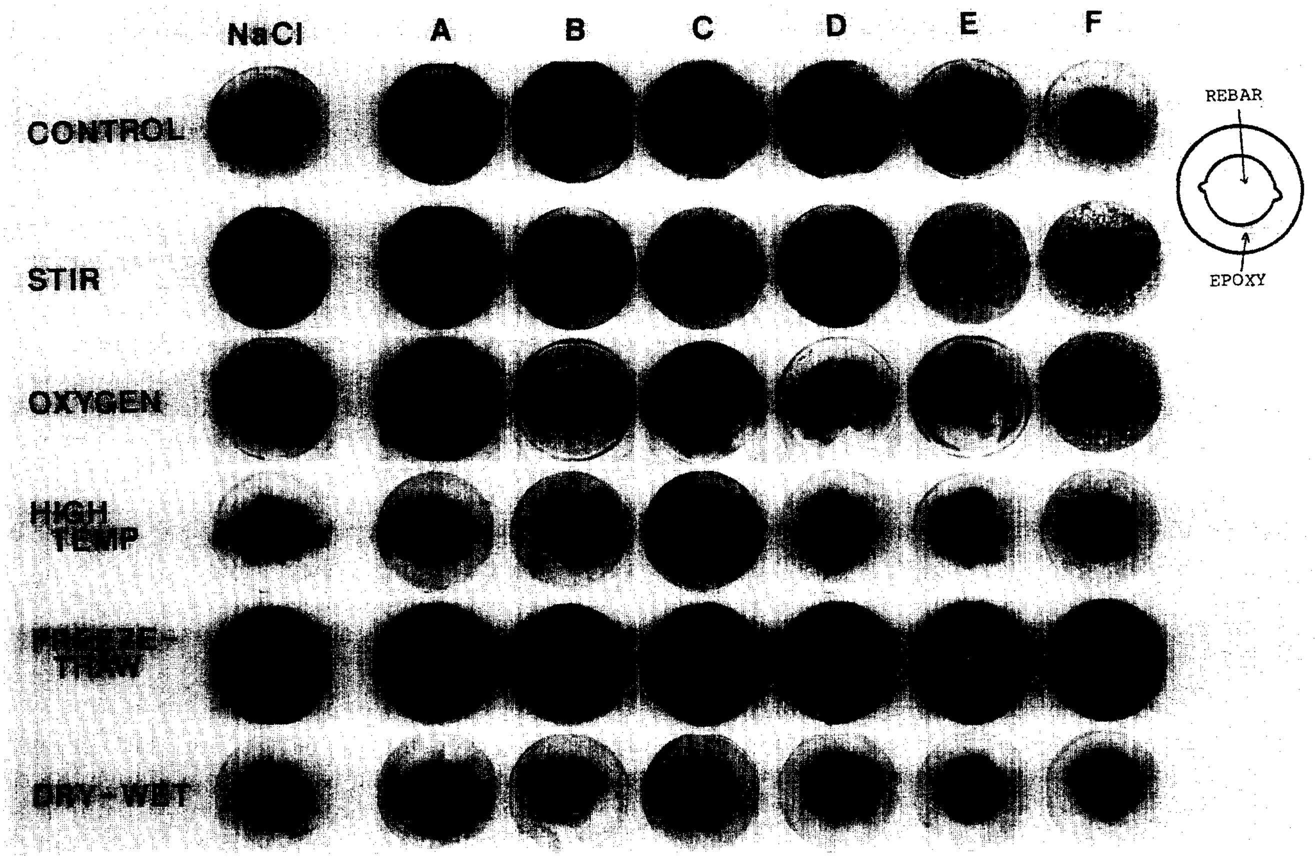

FIGURE 1. Rust-covered areas of reinforcing steels tested under control, stirred, oxygen-bubbled, high temperature, freeze-thaw cycle, and dry-wet cycle conditions for 120 days (**a** indicates rust-free areas).

eas than NaCl under the high temperature condition. Deicing salts A, B, C, and D showed larger rust-covered areas than NaCl under the freeze-thaw cycle condition.

Pits

Only deicing salts A and B showed shallower pits than NaCl under the control, stirred, and oxygen-bubbled conditions. Under the high temperature condition, only deicing salt E showed shallower pits than NaCl. Deicing salt A showed deeper pits than NaCl under the freeze-thaw cycle condition. Under the dry-wet cycle condition, deicing salts B, E, and F showed shallower pits than NaCl. In general, the pit depths ranged from 10 to 350 μm and increased in the order of freeze-thaw cycle, control, stirred, oxygen-bubbled, high temperature, and dry-wet cycle conditions.

Degrees of Corrosion

The degree of corrosion was determined by measuring the areas of the pits on the cross-sectional samples. The degrees of corrosion varied with the test conditions and the types of deicing salts. Maximum corrosion of the samples occurred under the dry-wet cycle and high temperature conditions, while the least corrosion was under the freeze-thaw cycles.

Deicing salt A showed less than 10% corrosion under freeze-thaw cycle, control, stirred, oxygen-bubbled, and high temperature conditions, but the corrosion increased to more than 300% under the dry-wet cycles. The corrosion of deicing salts B and D was the highest under the high temperature conditions, whereas the corrosion under other conditions was less than 10%. Deicing salt C showed the highest corrosion under the stirred condition, while deicing salt E showed the highest corrosion under the oxygen-bubbled condition. Deicing salt F under the control condition showed the highest corrosion of about 15%, but corrosion remained less than 15% under the other conditions.

Dissolved Oxygen in Solutions

Dissolved oxygen concentrations in the concrete-saturated solutions mixed with 3, 6, and 20% corrosion-inhibitor-added deicing salts, salt substitutes, and NaCl were measured, and the results are shown in

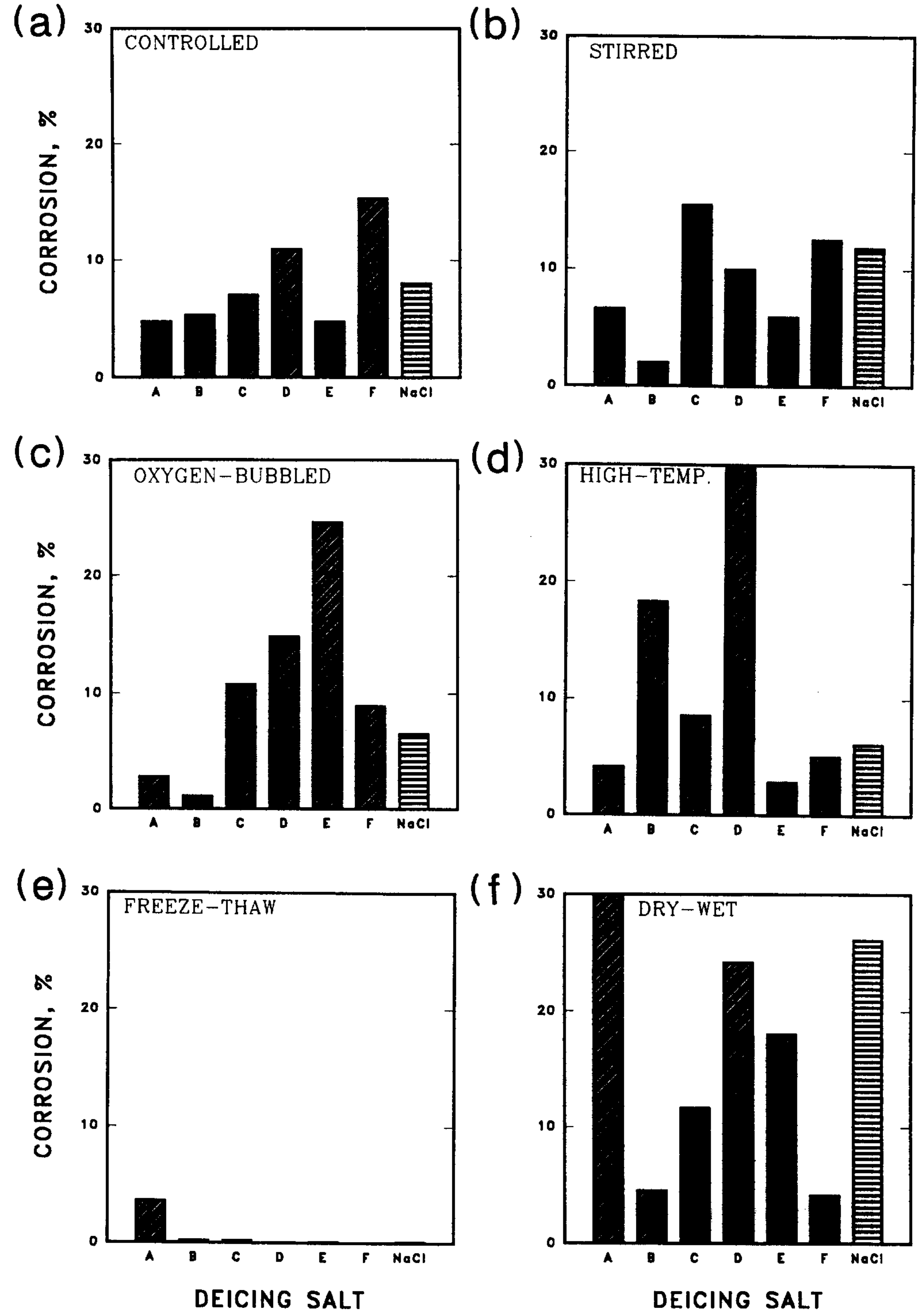

FIGURE 2. Degree of corrosion under (a) control, (b) stirred, (c) oxygen-bubbled, (d) high temperature, (e) freeze-thaw cycle, and (f) dry-wet cycle conditions. The bar filled with diagonal cross-hatch indicates the lowest corrosion.

Figure 3. The dissolved oxygen decreased from 4 to 2.5 ppm with increasing concentrations of NaCl. Except for deicing salts B, D, and F in the concrete-saturated solutions, the dissolved oxygen concentration was lower than in the NaCl solutions. Deicing salt C showed the lowest dissolved oxygen in the solutions, whereas deicing salt B showed the highest dissolved oxygen. It appears that the corrosion inhibitors in the deicing salts decreased the dissolved oxygen relative to NaCl.

The dissolved oxygen content in 6% solutions changed under stirred and oxygen-bubbled condi-

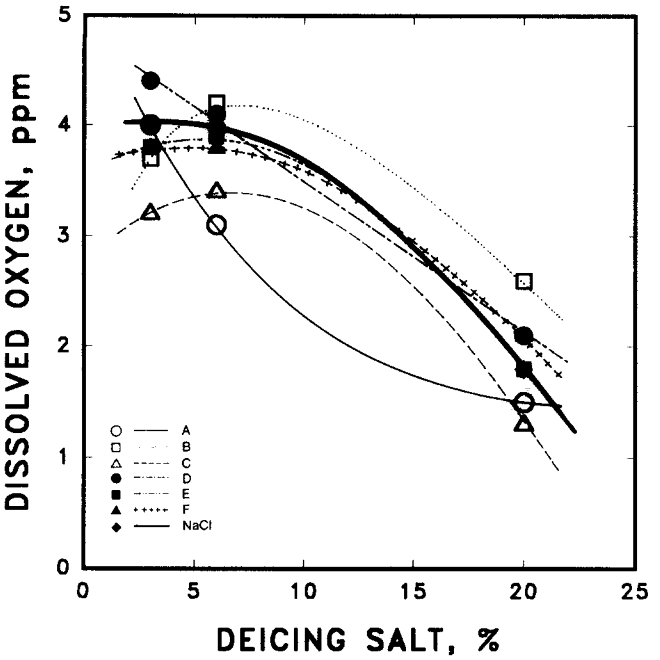

FIGURE 3. Dissolved oxygen contents in a concrete-saturated solution as a function of concentration in the corrosion-inhibitor-added deicing salts and salt substitutes.

tions. Table 1 shows the dissolved oxygen contents in the solutions under the control, stirred, and oxygen-bubbled conditions. The dissolved oxygen was 3 ~ 4 ppm under the controlled conditions, ~6 ppm under the stirred conditions, and 9 ~ 13 ppm under the oxygen-bubbled conditions.

Discussion

Effectiveness of Corrosion-Inhibitor-Added Deicing Salts

Many laboratory test results show that inhibitors produce a substantial reduction in corrosion, but field test results are less conclusive. The results of this investigation suggest that corrosion results from field exposure were inconclusive because of the unpredictability of the weather and the nature of the corrosion conditions and the effect of concrete micro- or macrocracks on the effectiveness of corrosion inhibitors.

TABLE 1. Dissolved oxygen conent in solutions containing 6% corrosion-inhibitor-added deicing salts and salt substitutes under control, stirred, and oxygen-bubbled conditions

Deicing Salt	Dissolved Oxygen, ppm		
	Control	Stirred	Oxygen-bubbled
A	3.1	6.9	11.2
B	4.2	6.8	12.4
C	3.4	6.0	9.4
D	4.1	6.6	12.2
E	3.9	6.2	11.2
F	3.8	6.1	12.0
NaCl	4.0	6.2	13.0

For identification of these products, contact MN/DOT, Research Laboratory, Maplewood, MN 55109.

The effectiveness of corrosion-inhibitor-added deicing salts and salt substitutes was determined under the control, stirred, oxygen-bubbled, high temperature, freeze-thaw cycle, and dry-wet cycle conditions in simulated concrete-saturated solutions at a 6% (by weight) concentration, using galvanic cells and optical microscopy (Figures 1–3). An "average" effectiveness of the corrosion-inhibitor-added deicing salts relative to NaCl on reinforcing steel corrosion may be calculated with the following formula:

$$\%E_A = \frac{I_{NaCl} - I_A}{I_{NaCl}} \times 100 \qquad (1)$$

where I_{NaCl} = percent corrosion of NaCl, and I_A = average percent corrosion of deicing salt A under the control, stirred, oxygen-bubbled, high temperature, freeze-thaw cycle, and dry-wet cycle conditions. These values were calculated by summing the data in Figure 2 and dividing by 6. $\%E_A$ may then be a convenient way to estimate the average overall effectiveness of deicing chemical A. The averaged results shown in Figure 2 are probably of interest when a given condition, for example, dry-wet or freeze-thaw cycle, dominates the environment in which the deicing salts is used.

Figure 4 shows the overall average effectiveness of

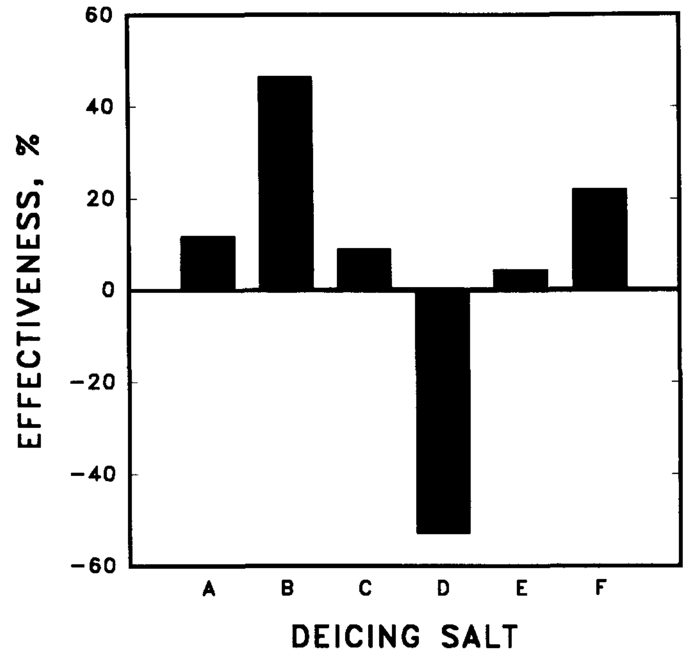

FIGURE 4. Average effectiveness of 6% corrosion-inhibitor-added deicing salts and salt substitutes on rebar corrosion under various environmental conditions. See text for explanation.

the corrosion-inhibitor-added deicing salts under six different conditions at a 6% concentration. All of the deicing salts except deicing salt D were shown to be effective, but the effectiveness was mostly less than 50%. In a previous investigation [6], the degree of effectiveness of corrosion-inhibitor-added deicing salts relative to NaCl varied with the types and the concentrations of the corrosion-inhibitor-added deicing salts. Corrosion rates were influenced not only by the concentrations of deicing salts but also by the test conditions. In this investigation, only temperatures and dissolved oxygen contents in the test solutions were varied.

Possible mechanisms of corrosion inhibition may involve (1) an interaction of a chemical substance with the outer surface of the interface, (2) a change of the chemical nature of the interface, or (3) the formation of a new interface [7]. However, inhibition action may be lost in the presence of so-called aggressive ions when they are above a certain concentration [8]. Once corrosion is initiated, deliquescent corrosion products may aggravate a local attack. A certain critical concentration of inhibitors is required in the aqueous environment, and the critical concentration depends on the nature of the inhibitor and the chemical composition of the concrete [6,9]. This study shows that factors affecting the behavior of corrosion inhibitors in deicing salt solutions include the chemical composition of the deicing chemicals, the temperature, and the oxygen content in the system.

Effect of Temperature on Inhibitors

The temperature factor is always important because the kinetics of chemical reactions are dependent on temperature. The temperatures of the freeze-thaw cycles, control, and high temperature conditions in this investigation were −7°C, 24°C, and 45°C, respectively. Figure 5 shows the effect of temperature on the degree of corrosion. The corrosion of deicing salts B, C, and D increased with increasing temperature. Deicing salts E and F, as well as NaCl, showed maximum corrosion at 24°C and then decreased. Deicing salt A showed an increase in corrosion up to 25°C and then remained constant beyond. The decrease in corrosion above 25°C was related to a decrease in the oxygen solubility in solutions as the temperature was raised [10], and this effect eventually overshadowed the accelerating effect of temperature on corrosion alone [11]. In a closed system, oxygen cannot escape and the corrosion is expected to increase with temperature until all the oxygen is consumed.

Effect of O_2 on Inhibitors

Steels can be protected from corrosion in a neutral aqueous solution by increasing the supply of oxygen to the metal surface. This is due to a shift in the balance between dissolution of the passive film by aggressive ions and repair by incorporating oxide ions [12]. Elements in this balance include (1) the action of adsorbed aggressive anions, such as chloride or sulfate in the case of mild steel, in solubilizing the oxide film at adsorption sites; (2) adsorption of inhibitor anions that block adsorption sites; and (3) incorporation of oxygen into the film. The last process will thicken the film and repair the damage.

Some deicing salts may release more aggressive ions than others and also may affect the solution pH, whereas the dissolved oxygen decreases at high con-

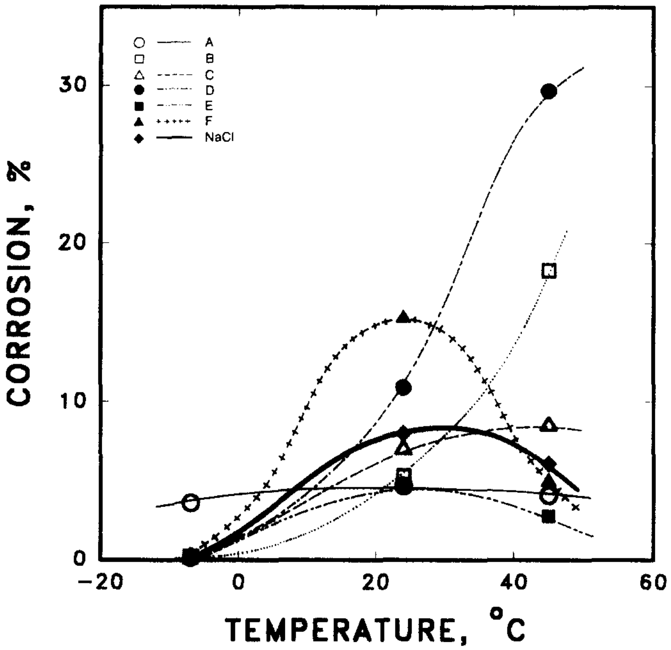

FIGURE 5. Degree of corrosion as a function of temperature for 6% corrosion-inhibitor-added deicing salt and salt substitute solutions. Data from Figure 2.

centrations of dissolved salts [13]. Under the control condition, the dissolved oxygen content decreased from 4.5 to 1.5 ppm as the amount of deicing salts in the concrete-saturated solution increased from 3 to 20%. In addition, the concentration of the deicing salts and the dissolved O_2 reaching the reinforcing steel surface may be affected by the properties of concrete. Because the diffusion rate for chemical reactions at steady state is proportional to oxygen concentration, the corrosion rate of reinforcing steel should be proportional to oxygen concentration [14]. As shown in Figure 6 our data show a general increase in corrosion with increasing O_2 content up to ~5 ppm. In the absence of dissolved oxygen, the corrosion rate at room temperature is expected to be negligible for reinforcing steels in concrete.

Different oxygen contents in the 6% solutions were obtained by stirring motion, oxygen bubbling, and the control condition in the test solutions (Table 1). Figure 7 shows the effect of dissolved oxygen at higher con-

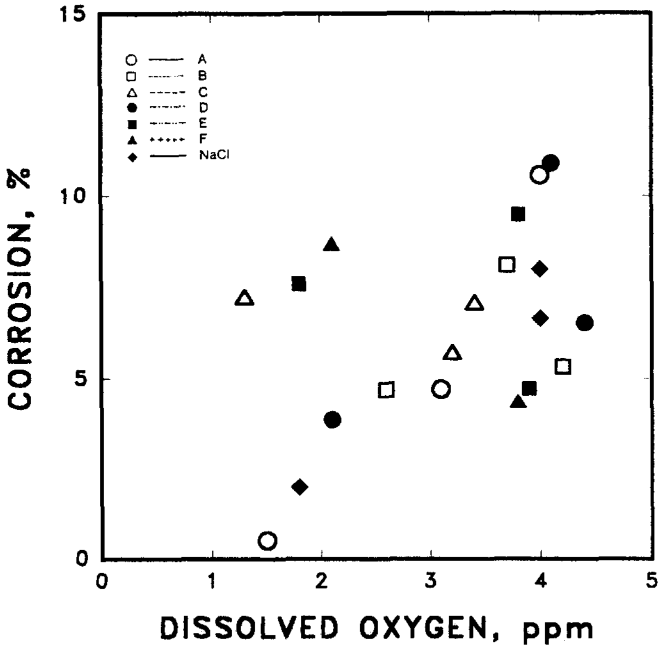

FIGURE 6. Degree of corrosion as a function of dissolved oxygen content below 5 ppm. Percent corrosion data from Figure 6 in ref 6. Dissolved oxygen data from Figure 3.

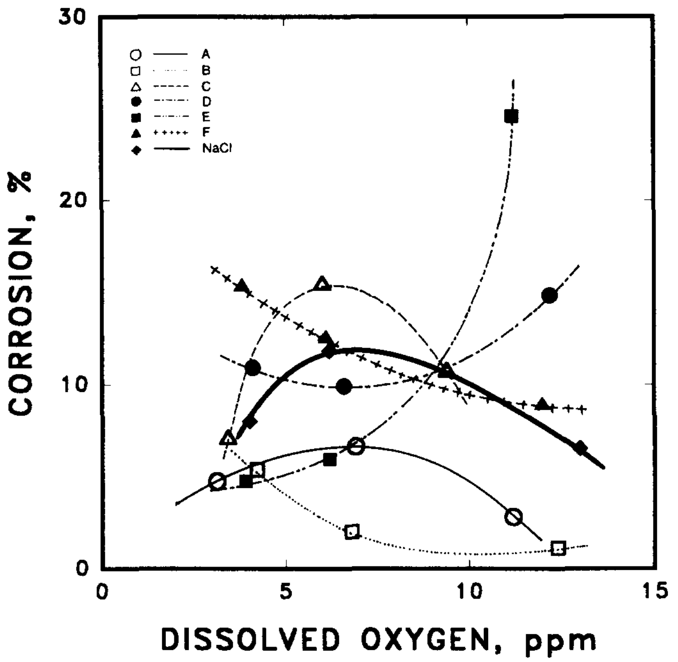

FIGURE 7. Degree of corrosion as a function of dissolved oxygen content from 0 to 15 ppm for 6% corrosion-inhibitor-added deicing salt and salt substitute solutions. Dissolved oxygen data from Table 1. Percent corrosion data from Figure 2.

centrations on the degree of corrosion. An increase in the oxygen concentration above ~5 ppm may increase corrosion to maximum at a certain concentration and then decrease due to an increase in excess O_2 in the solution. The decrease in the corrosion rate might be caused by passivation of reinforcing steel by oxygen. At higher oxygen concentrations, more oxygen reaches the metal surface than could be reduced by the corrosion reaction, and the excess oxygen, therefore, would be available to form a passive film. The excess oxygen either oxidized the ferrous oxide film to more protective oxides that may act as a diffusion barrier or was available to chemisorb on the steel surface forming an adsorbed passive film [14]. Only deicing salts D and E showed an increase in corrosion with increased oxygen content above ~6 ppm oxygen. The increases in corrosion of deicing salts D and E with increased oxygen contents suggest that other factors such as temperature and certain chemical elements in addition to the amount of oxygen in the solution may play an important role. The dry-wet cycle could provide a saturated oxygen condition on the surfaces of the samples. The most severe corrosion was found on the samples under the dry-wet cycle conditions in this investigation.

Conclusions

1. A test method was developed to determine the relative effectiveness of corrosion-inhibitor-added deicing salts under various conditions within half a year.
2. Corrosion of reinforcing steel in corrosion-inhibitor-added deicing salt solutions varied with oxygen content and temperature.
3. Effectiveness varied with the type of corrosion-inhibitor-added deicing salts and salt substitutes under various temperatures and dissolved oxygen contents, and was mostly less than 50% reduction of rebar corrosion with respect to NaCl.
4. Oxygen contents in solutions under the control condition decreased as the amount of corrosion-inhibitor-added deicing salts and NaCl increased.
5. Reinforcing samples under the freeze-thaw cycle condition showed the least corrosion, whereas samples under the dry-wet cycle condition showed the most severe corrosion.

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