

The Effect of Deicing Chemicals on Reinforced Concrete

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The role played by deicing chemicals in the deterioration of reinforced concrete is addressed in this paper. Several newer and faster bench-scale methods of study and materials evaluation are described and compared to the ASTM recommended techniques. The difference in freezing temperatures between concrete pore solution and an outside deicer solution is shown to be one of the important factors in the spalling process. The importance of an anisotropic character of freezing zone is outlined. The macrocell corrosion mechanism of rebar deterioration has been studied in the laboratory environment using specially constructed mini slabs. The results were correlated with previously conducted microcell corrosion studies of small encapsulated rebar probes.

The use of rock salt as a deicing chemical has given rise in the last few years to important environmental concerns because of the potential damage to concrete pavements, to steel through corrosion, and to vegetation and soil. In 1983 Domtar Inc. launched a major R&D effort aimed at developing basic knowledge on salt's unfavorable side effects and how they could be minimized or eliminated. The major objectives were to (a) improve the understanding of the effects of rock salt and other deicing chemicals on metals, pavements, and the environment, (b) develop safer but still cost-effective deicers through additives to rock salt or new alternative products, and (c) devise methods for the evaluation of chemical deicer properties and their effect on various materials. Described in this article are several methods that were used in the laboratory to study the effects of deicer chemicals on reinforced concrete.

STUDIES OF CONCRETE SPALLING

The acceleration of freeze/thaw (f/t) deterioration of concrete as a result of the presence of deicing chemicals in solution has been known for over three decades. It has been shown in the past that scaling of the concrete surface is caused by physical processes, such as growth of crystals, rather than chemical reactions. The air entrainment in concrete formulations creates additional space for crystal growth to "cushion" the impact of physical change.

Standard methods exist for testing the performance of a given concrete formulation under f/t cycle conditions. These methods could be used for the evaluation and ranking of various deicing chemicals, as well as various road construction materials.

Effect of Deicing Chemicals on Air-Entrained Concrete: The ASTM Test

A test program was carried out to compare the effects of various deicer formulations on concrete. Equipment included a walk-in freezer in a room with controlled climate and an abrasion test rig well described by Minsk (1) (Figure 1). A large number of concrete blocks were prepared by Canada Cement Lafarge in accordance with ASTM C672-84. The concrete blocks contained a built-in stainless steel dam to contain the deicing solution on the top surface of each block. The test procedure including f/t tests without abrasion and with abrasion using a steel blade under a specified load is well described elsewhere (1). The procedure basically consisted of ponding various solutions on top of the concrete slabs which were then subjected to f/t cycles. At the end of every five cycles the deicing solutions were poured through a filter. The material that came off the concrete surface as a result of f/t damage or abrasion in the tests was collected, rinsed with distilled water, and dried in an oven. The weight of the material was then used as a measure of the damage.

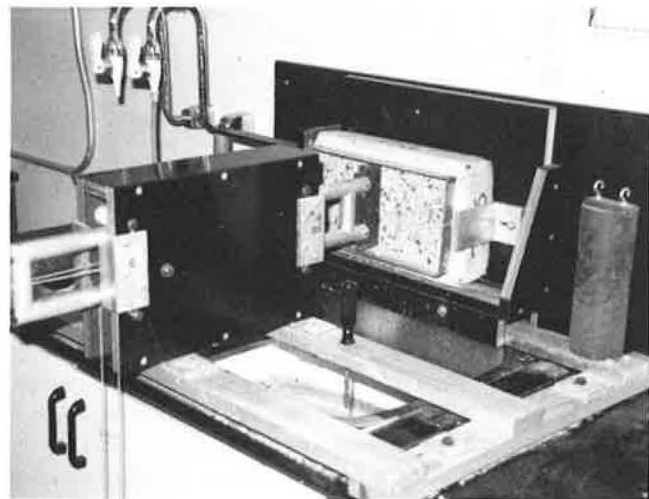


FIGURE 1 Abrasion of the concrete to supplement f/t spalling.

The rate of freezing and thawing was monitored using a thermocouple incorporated into one of the concrete blocks. A typical curve of temperature versus time during freezing is shown in Figure 2.

The f/t damage was compared to the air-entrained concrete caused by several deicer chemicals during 100 f/t cycles. All

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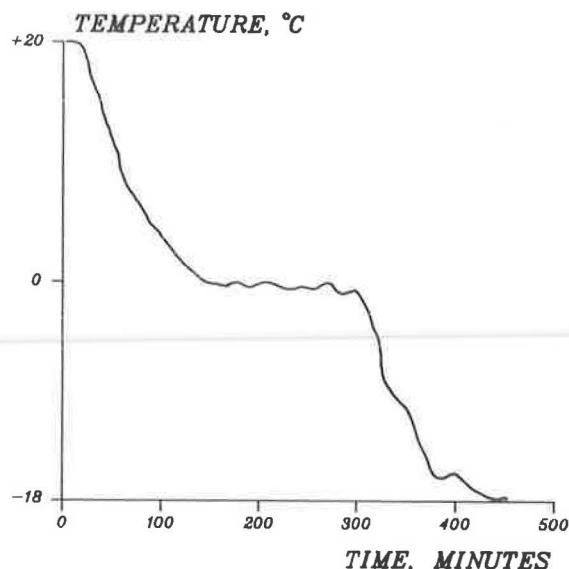


FIGURE 2 Temperature of a concrete slab in the freezer during the freezing cycle.

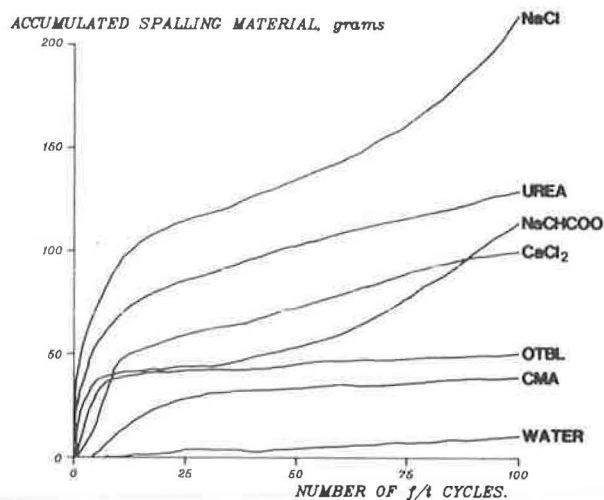


FIGURE 3 Air-entrained concrete spalling by various deicer solutions in the ASTM test. Concentration of all solutions was 4 percent. No abrasion.

subsequent concentrations are reported as w/w percent of solute. The degree of spalling without abrasion caused by 4-percent solutions of NaCl, urea, CaCl_2 , sodium formate, and CMA (calcium magnesium acetate) is shown in Figure 3. Each point corresponds to the average value given by three identical specimens. The relatively large damage caused by urea and an accelerating destruction caused by sodium formate are quite evident.

Two deicer chemicals were less destructive toward concrete than the rest of the group not only in absolute level of spalling but also because the damage appeared to be levelling off with time, unlike the case of uninhibited salt, urea, or sodium formate. One of the chemicals, CMA, is a product well known to the transportation community for at least a decade. It has been shown to be less corrosive than rock salt while providing a comparable level of ice control. The other chemical, designated OTBL, is a Domtar proprietary, nonchloride product in

early development stage. Its deicing and corrosion characteristics are comparable to those of CMA.

The relative damage caused by different chemicals with abrasion of the exposed surface using a 10-kg load on the abrading blade (1) is shown in Figure 4. The surface area of the blade was $\sim 5 \text{ cm}^2$. Although the abrasion accelerated scaling in the case of all four tested deicers, in the case of sodium formate the effect of abrasion was considerably greater than with the other tested chemicals, including NaCl.

Accelerated Tests Using Small Concrete Specimens

Although the data obtained according to ASTM 6672084, using air-entrained concrete, provide reliable information on the expected scaling action of various deicer formulations, two great disadvantages of the standard method are (a) the considerable length of time required and (b) the amount of labor involved.

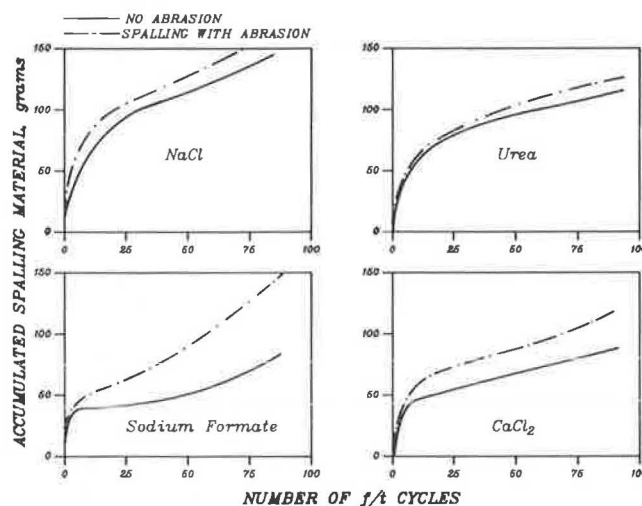


FIGURE 4 The effect of abrasion on the rate of spalling by various deicers. Four-percent solutions used in all cases. Abrasion was performed with 10-kg load on the blade (see text).

Following the example of a few researchers in recent years and, in particular, Peter Hudec of the University of Windsor (Windsor, Ontario, Canada), a quick-test method has been adopted using small concrete cubes without air entrainment. These cubes, if prepared with carefully screened aggregate and properly cured, can give reproducible data on the relative effects of deicer formulations or f/t conditions in a period of time as short as 5 days. Of course, subsequent verification of the observed effects using the standard ASTM procedure is recommended.

The specimens for the small scale tests were prepared as follows. Several kilograms of concrete mixture were made using the following composition of ingredients:

Component	Parts w/w
Portland cement, type 10	1.0
Water	0.7
Sand	2.25
Aggregate (-4 +20 mesh)	2.75

The concrete was cast into small cubes using plastic ice cube trays which were then covered with plastic sheet for 3 days. The solid cubes were subsequently cured in water for 28 days and then dried on the bench. The weight of an air dry cube was between 40 and 45 g.

Each individual test comprised four cubes placed in a shallow plastic Tupperware™ dish fitted with a lid. Prior to the beginning of f/t cycles the cubes were presoaked in a specified solution for 24 hours at room temperature (for most tests). If the presoak solution was the same as the one used for the f/t test then the cubes were simply lifted above its level in the same dish by using cellulose sponges as shown in Figure 5. When the presoak solution was different from the f/t test solution the cubes were transferred into another dish with new solution and placed on a sponge as just described. The dishes remained tightly closed with lids during the rest of the test period to prevent evaporation.

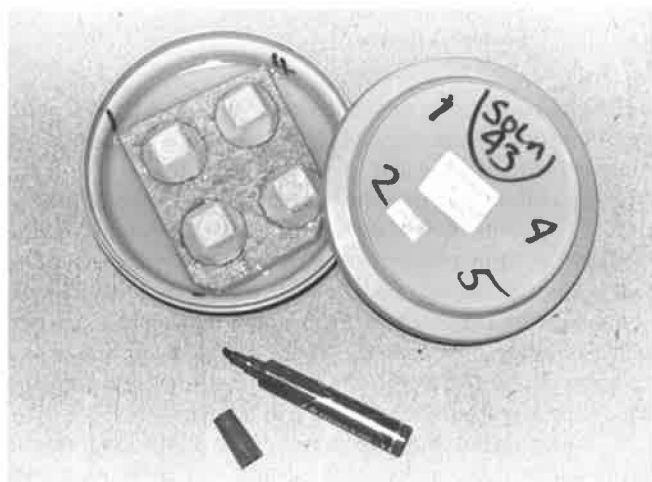


FIGURE 5 Small concrete cubes on a cellulose sponge placed in a 6-in. Tupperware™ dish.

After the predetermined number of cycles (from five to seven) the dishes were placed on the bench for complete thawing of their content, the cubes were rinsed in distilled water and all solids weakened by spalling so that they could be crushed by hand were discarded. The remaining solid pieces were dried overnight on a bench at a relative humidity of 50 percent. Each individual cube was weighed before and after the test and the dry weight loss that resulted from spalling was averaged over the four pieces per dish. It was found that the weight loss data are reproducible if all cubes are made from the same batch of concrete.

The small-scale f/t tests could at present be used only for relative ranking of various solution compositions. However, the results of recent studies have proven to be useful for the selection and refinement of antispalling additives and their combinations, which subsequently have been tested using the standard ASTM method for confirmation of the findings.

Discussion of Accelerated Test Results

The results of the small-cube tests can be related to the data obtained using air-entrained concrete. In Table 1 the percent of

TABLE 1 WEIGHT LOSS OF SMALL CONCRETE CUBES AFTER FIVE F/T CYCLES IN 4-PERCENT DEICER SOLUTION

Deicer Material ^a	Weight Loss (%)
NaCl	40 ± 3
Sodium formate	37 ± 2
Urea	27 ± 2
CaCl ₂	26 ± 1
OTBL	0.6 ± 0.3
CMA	0.1 ± 0.1

^a4-percent solution.

small-cube weight loss is shown after five f/t cycles with 4-percent solutions of the same deicers as in the standard ASTM tests illustrated in Figure 3. It is apparent that the relative ranking of the deicer chemicals with respect to spalling is similar for both series of tests. Another comparison of the two methods is shown in Figure 6, in which the effect of NaCl concentration in solution on the rate of f/t damage is shown for (a) standard tests with entrained concrete (200 f/t cycles) (2) and (b) small cube tests (5 f/t cycles). In both cases the degree of spalling versus the percentage of NaCl in solution passes through a maximum in the 3- to 4-percent interval.

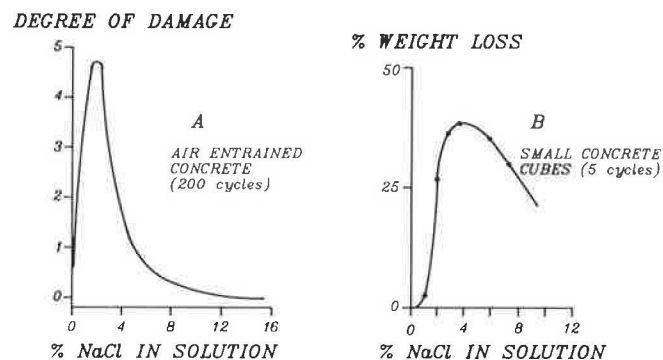


FIGURE 6 The effect of salt concentration on the degree of spalling: air entrained concrete, 200 cycles (A) (2); small concrete cubes (no air entrainment), 5 cycles (B).

With that degree of confidence in the fast method, work could cautiously proceed on the preliminary selection of anti-spalling compounds in order to reduce damage to concrete associated with the use of rock salt. It was found that a number of chemicals when added to salt solution would considerably reduce the degree of spalling as, for example, is shown in Figure 7. The weight loss sustained by concrete cubes immersed in a pure salt solution (curve 1) and into salt solution containing an additive (curve 2) is plotted versus the number of f/t cycles. The additive in that case was a soluble salt of phosphoric acid added at the level of 5 percent on the basis of total dry solids. It is hoped that the research conducted in this area will result in the early development of a cost-effective and environmentally acceptable additive that could greatly reduce f/t spalling of concrete structures where rock salt is used for ice control.

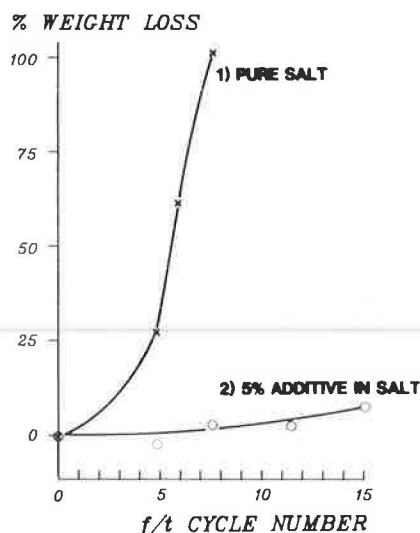


FIGURE 7 The effect of antispalling additive in 4-percent NaCl solution on the f/t resistance of small concrete cubes: 1, no additive, 2, antispalling agent added to salt solution.

In addition to the practically oriented additive selection work, a more fundamental study on the salt-assisted spalling mechanism has recently been initiated. In all previously mentioned small-cube tests the concrete specimens were presoaked and tested in f/t cycles using the same solution composition. The question was posed as to what would happen if the presoak and f/t test solution were of different concentrations or different compositions in general.

The effect of NaCl concentration in the presoak solution on the f/t spalling caused by 4-percent NaCl solution is shown in Figure 8. The series of graphs in Figure 9 represents the spalling effect of NaCl solutions at various concentrations, from 0 to 8 percent at a given presoak solution concentration. Both figures clearly demonstrate that there is a sharp reduction in the f/t damage when the presoak solution concentration equals or exceeds the deicing solution concentration. It should be noted that the specimen presoaked in salt solution was not damaged by f/t action of pure water. The conclusion was drawn from these observations that it was not the salt per se but the

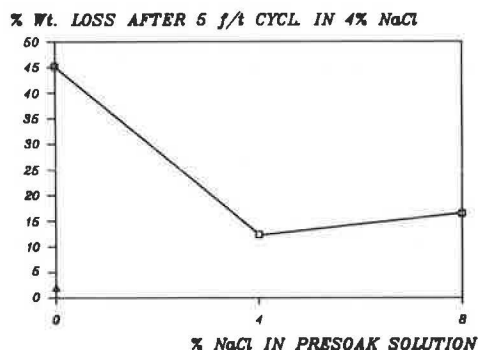


FIGURE 8 The effect of salt concentration in the presoak solution on the f/t spalling of small cubes in 4-percent NaCl solution.

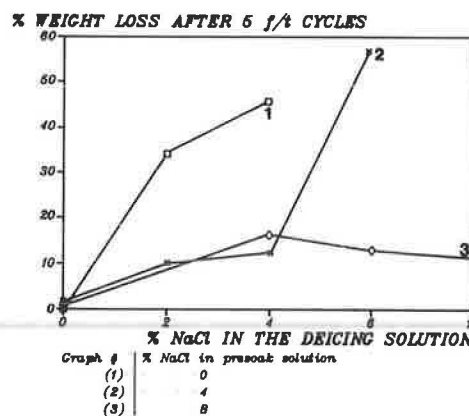


FIGURE 9 The percentage of weight loss of small cubes after five f/t cycles versus NaCl concentration in the deicing solution at three different levels of NaCl in the presoak solution.

difference between the salt concentrations in the concrete pores and those in the outside deicing solution that was primarily responsible for accelerated spalling in these tests.

It is possible to go one step further and relate the difference in NaCl concentrations to the subsequent difference in freezing temperatures of liquids under and on concrete surface. In other words the working hypothesis could be formulated as follows: if the freezing temperature of the solution inside the concrete pores is lower than or equal to the freezing temperature of solution on the surface of concrete, the f/t damage generally should be less than when the reverse is true.

The next series of tests represented in Table 2 appears to confirm that observation. In these tests the cubes were presoaked in various deicing solutions—such as 5 percent sodium acetate, 7 percent calcium nitrate, and 7 percent ethylene glycol—and 4 percent NaCl and subsequently subjected to f/t action in 4 percent NaCl. The concentrations of the deicer components in presoak solution were chosen to give the same reduction in freezing temperature of water as does 4 percent NaCl. The data in Table 2 show that all tested presoak solutions with a notable exception of calcium nitrate have considerably reduced the subsequent f/t spalling as compared to the control test with deionized water used for presoaking.

TABLE 2 EFFECT OF PRESOAK SOLUTION COMPOSITION ON THE F/T CONCRETE SPALLING CAUSED BY SALT SOLUTION

Presoak Solution Composition	Weight Loss (%)
Distilled water	30
4 percent NaCl	17
5 percent sodium acetate	14
7 percent ethylene glycol	13
7 percent $\text{Ca}(\text{NO}_3)_2$	22

NOTES: Used small cubes and five f/t cycles, with presoaking for 24 hours before freezing. Freeze/thaw test was conducted using 4 percent NaCl solution in all cases.

At this point the results obtained with the small cubes should be considered preliminary because the experimental techniques are still being refined.

It has been noted in the past [see e.g., (2), (3)] that the essentially anisotropic character of freezing in concrete-deicer solution systems is a major factor in the *f/t* spalling process. The data described here indicate the same thing. A properly designed experiment should take into account the mutual orientation of heat flow versus gradients of solution concentration and moisture content of concrete. This is one of the areas where more work is anticipated.

STUDY OF A MACROCELL REBAR CORROSION ON A MINI SCALE

Concrete, a porous material containing a pore solution, the chemical composition of which depends on the concrete parameters, the surrounding environment, and exposure time (4), normally provides reinforcing steel with excellent corrosion protection. This is a result of the formation, in the presence of sufficient O_2 , of a stable passive layer of gamma Fe_2O_3 on the steel surface in the high-pH (12 to 13) concrete environment. The corrosion of steel in concrete, shown in Figure 10, is a naturally occurring phenomenon driven by the tendency of iron to seek the lowest possible energy state, which is the oxide (rust) form.

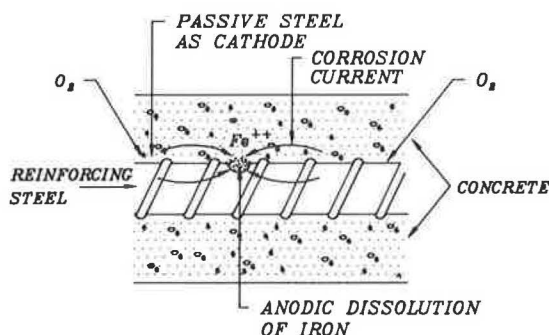


FIGURE 10 Schematic illustration of the corrosion of reinforcement steel in concrete (5).

Initially the passive film inhibits the corrosion process. However, once this film is damaged or removed, the steel continues to corrode. As the steel rusts (formation of Fe_2O_3), its oxidation products build up in the concrete and, because of their greater volume, exert tensile stress on the concrete (up to 10,000 psi) (6). This rapidly exceeds the low tensile strength of the concrete (500 psi) resulting in stress cracks which in turn allow for more rapid diffusion of corrosion-accelerating substances such as CO_2 , leading to further deterioration of the structure.

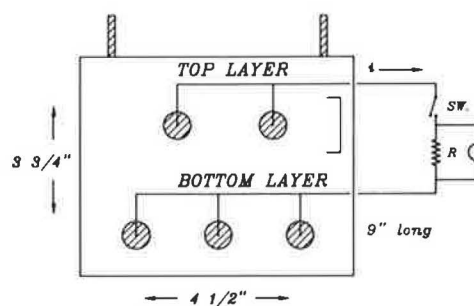
An inhibitor is a substance that, when added in small concentrations to an environment, effectively decreases the corrosion rate. The evaluation of the effectiveness of any inhibited NaCl mixture, as compared to salt alone, follows a natural procession of tests. Preliminary screening methods, such as weight-loss corrosion-rate determinations via total coupon-immersion (various metals) tests or aqueous (simulated concrete pore water) electrochemical investigations of steel probes using such techniques as linear polarization or a.c. impedance,

allow for the initial selection of suitable chemicals. The next stage in any good evaluation program involves a closer simulation of the actual concrete environment through the construction of rebar concrete probes. This yields a greater wealth of information concerning such system characteristics as the corrosion resistance (R_p) (proportional to the inverse of the corrosion rate), the double layer capacitance, film resistance, and so on. Finally, the construction of small (laboratory-controlled environment) and large (subjected to external exposure) reinforced concrete slabs allows for evaluation of inhibitor performance under macrocell current conditions. The focus of the remainder of this section of the paper is on the small-scale laboratory slabs.

In existing reinforced-concrete structures exposed to deicing salts, a macrocell corrosion effect is believed to be of major importance in the structure deterioration process. Macrocell corrosion is indicated where significantly different environments (chloride, O_2 , moisture levels, pH, etc.) exist at various sites on the rebar mat. Areas of adjacent concrete having higher levels of chloride become anodic (iron oxidation), whereas areas with low chloride or high O_2 levels become cathodic (oxygen reduction). Anodic and cathodic sites may be widely separated in real life, but generally steel close to concrete upper surfaces will be primarily anodic and steel in lower mats or shielded from chloride will be cathodic.

Based on research performed by FHWA and other agencies (7), small-scale reinforced concrete prisms were designed, fabricated, and treated in order to enhance a macrocell effect, and the macrocell corrosion current was measured as a function of deicer/inhibitor application. The present test design is also being considered by ASTM as a standard method for admixed corrosion inhibitor evaluation in reinforced concrete.

Figure 11 is a schematic of the prism used in the lab scale macrocell tests. Two mats or rebars were cast in concrete prisms using average quality air-entrained concrete. Various levels of sodium chloride were admixed into several of the top mat layers to accelerate corrosion and simulate the environment present in old bridge decks. A dam was placed on top of each slab and 6-percent NaCl/inhibitor solutions of deicer product ponded to a depth of $3/4$ in. Solutions were replenished every 2 weeks.



SMALL SCALE SLABS

Portland Cement	1.0
Water	0.53
Sand	1.76
Aggregate	2.36

FIGURE 11 Schematic of small-scale prism.

The top and bottom sets of rebars were electrically connected and a momentary off/on switch in series with a 1.0-ohm resistor installed between the two mats. Initially the corrosion current ($I = E/R$) was determined from the voltage drop across the resistor. Later a direct corrosion current was obtained by using a zero-resistance (Hokuto Denko Corp.) ammeter. Measurements were taken at weekly or biweekly intervals and plotted versus time of exposure in days.

The macrocell current data, followed over a period of 231 days, for one of the proprietary inhibitor formulations (patent pending) of salt and water, are shown in Figures 12–15. The slabs contained 0, 5, 10, and 15 lb/yd³ sodium chloride mixed into the top layer. These conditions were chosen to simulate both fresh uncontaminated concrete and existing contaminated bridge surfaces.

Several conclusions can be reached. First, as might be expected, water does not initiate corrosion, suggesting that other factors (availability of O₂, differences in rebar potential, pH, etc.) are responsible. As can be seen from Figures 12–15, the inhibited salt mixture not only passivates the steel surface but appears to be nonaggressive to rebar in fresh concrete. It can be speculated that the inhibitor is diffusing through the concrete

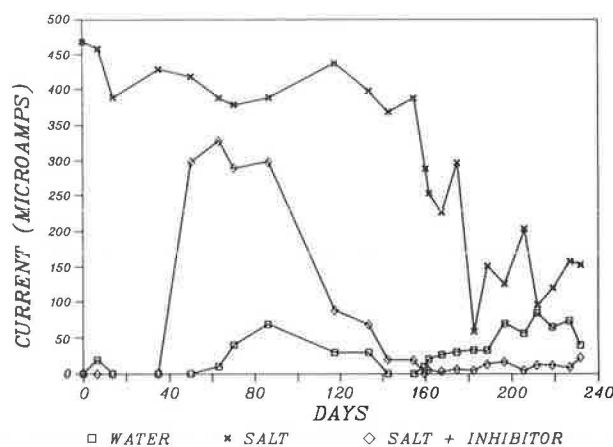


FIGURE 12 Macrocell current data: 0 lb/yd³ chloride top layer.

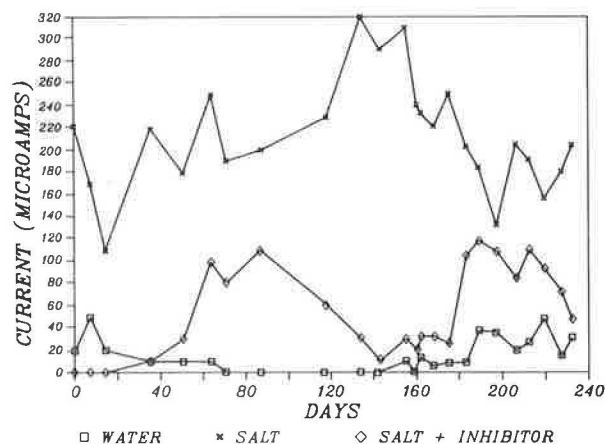


FIGURE 13 Macrocell current data: 5 lb/yd³ chloride top layer.

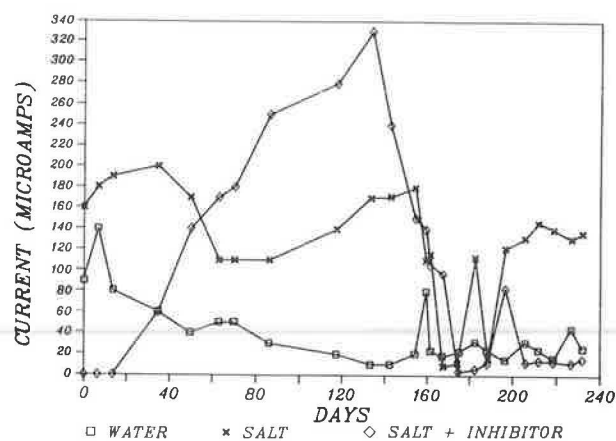


FIGURE 14 Macrocell current data: 10 lb/yd³ chloride top layer.

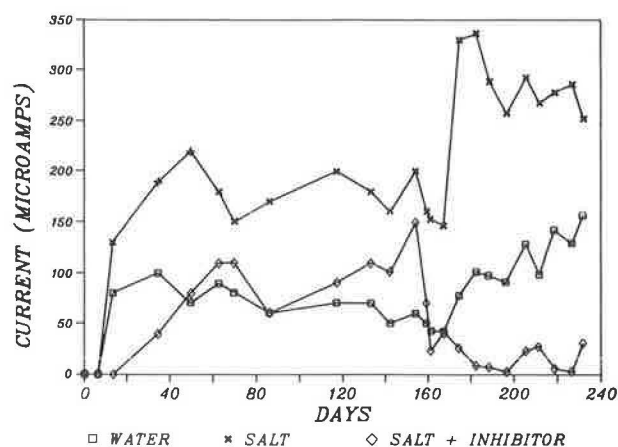


FIGURE 15 Macrocell current data: 15 lb/yd³ chloride top layer.

and forming a passivating film on the steel surface. Verification of these encouraging preliminary results under conditions that more closely approximate existing bridge decks and surfaces is in progress using larger (6- × 14½- × 24-in.) slabs under environmental exposure.

The search for an inhibitor to add to salt that would preserve the effectiveness of the deicer without damaging the environment covered a wide array of known inhibitor classes. An extensive list of chemicals was reduced to a select few using techniques previously listed. The data obtained from macrocell current measurements correlate fairly well with data obtained from the more reliable screening and rebar probe tests. A comparison of the performance of the inhibited salt with salt alone in immersion tests and through studies on a steel probe is shown in Table 3. Experiments on rebar concrete probes, which attempt to measure inhibitor performance under microcell conditions, confirm that the inhibitor functions well in this environment. This can be seen in Figure 16, which illustrates the time dependence of R_p (inversely proportional to the corrosion rate) which was obtained from a.c. impedance measurements. However, rebar probes can only simulate and provide information on microcell corrosion; problems associated with variations in the environment found within macrocells, which better

TABLE 3 COMPARISON OF CORROSION RATES OBTAINED IN SALT AND INHIBITED SALT SOLUTIONS

	214.5-hr Immersion Tests Rate of Corrosion (mpy)		Linear Polarization Rate of Corrosion ^a (mpy)	ac Impedance Corrosion Rates of Steel Electrodes ^b
	Mild Steel C1010	Galvanized Steel		
NaCl	2.32	0.98	2.0	8.01
NaCl + inhibitor	0.56 ^c	0.11 ^c	0.849	2.09

^aAs measured in 10 percent NaCl and 10 percent NaCl + 0.33 percent inhibitor solution saturated with Ca(OH)₂.

^bAs measured in 1 m NaCl; pH 8.2; C1018 steel.

^c4 percent solution of 95:5 salt:inhibitor mixture.

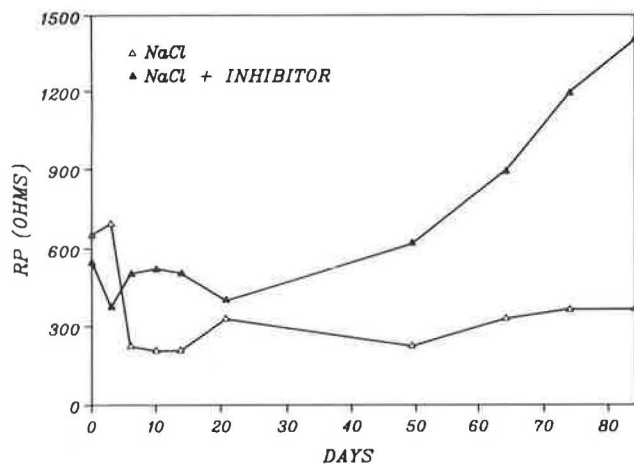


FIGURE 16 ac Impedance time dependence.

approximate real life, are not addressed. The construction of small-scale slabs is an attempt to simulate macrocell conditions (in the controlled laboratory environment) currently found in bridge decks. The results indicate that the inhibitive salt mixture continues to perform well confirming earlier observations.

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