

Recent Research on Alternative Deicers at Chevron

C. D. BUSCEMI, K. A. HOENKE, AND K. L. EKLUND

A calcium magnesium acetate (CMA)-based deicing product has been tested as an alternative to salt-based deicers, which are corrosive to steels used in the construction of bridges, roadways, and automobiles. The CMA-based deicer showed much lower corrosion rates than salt-based deicers in alternative immersion tests. Electrochemical testing of steels in CMA-based deicer suggests that although similar corrosion potentials to salt-based deicers occur with the CMA-based product, corrosion currents, and thus corrosion rates, are greatly reduced. Results of alternative immersion and electrochemical testing are presented.

Substantial corrosion of roadways and bridges due to the application of deicing salts has come to be recognized as a major problem. Today's road salts contain chlorides, which are responsible for the corrosion of bridge and roadway steels. Substitute deicing chemicals have been formulated and are being tested in various forums for their ability to remove snow and ice without causing further infrastructure damage.

Two classes of deicers are undergoing testing currently. One class uses small amounts of inhibiting chemicals added to plain road salt; in this case the chloride-containing road salt is still the deicer, but the chemical additions cause reduction of metal corrosion rates as long as the inhibiting chemical remains in contact with the steel.

Another class of deicer relies not on chlorides, but on low-corrosion chemicals, which are deicers themselves. These deicers have the potential to eventually allow removal of destructive chlorides entirely from the infrastructure.

CURRENT RESEARCH ON DEICERS

Research has been focused on three primary areas: corrosion of bare metal, corrosion of steel rebar in concrete, and deterioration of concrete. In all cases, solutions of varying concentration have been tested. Representative concentrations range from 3.5 percent to more dilute values, which simulate what might be encountered on a roadway following deicer spreading and melt runoff.

Bare metal testing is a straightforward way to evaluate the effects of deicing solutions on structural metals, can be done quickly and cheaply, and has provided much of the information known about deicer corrosivity. Although corrosion rates for bare metal do not necessarily indicate corrosion rates

for reinforcing steel in concrete, bare metal tests allow comparisons of the relative effects of deicing solutions on structural highway metals.

To determine the effects of deicing solutions on reinforcing steel bar in concrete, tests have been done on concrete slabs containing rebar. These tests take longer to complete, so less data are currently available on rebar in concrete.

Tests on the effects of deicing solutions on concrete have also been performed. In these tests, concrete slabs are usually cyclically ponded with deicing solutions, so that they go through wetting and drying cycles that simulate actual road conditions. Freeze-thaw cycles are a common test on concrete to determine if use of alternative deicing chemicals leads to increased cracking and pothole damage during the winter.

WHAT IS KNOWN ABOUT BARE METAL CORROSION BY CALCIUM MAGNESIUM ACETATE?

Most corrosion testing of calcium magnesium acetate (CMA) to date has been on structural steels. CMA has been found to reduce corrosion of highway steels by five to fifteen times compared with plain road salt.

Extensive coupon weight loss work by Locke and Kennelley, sponsored by FHWA, concluded that corrosion of steel in CMA is about two to five times less than in salt solution (1,2). The corrosion rate of A-36 steel in CMA was found to be only 1 mil per year (mpy) in a 2 percent CMA solution.

Another large study on the effects of CMA has been performed by the Michigan Department of Transportation (DOT) (3), which tested a variety of structural steels, including ASTM A-36 bridge steels, A-588 weathering steel rebar, and galvanized steel, along with several galvanic couples of stainless steel with carbon steel and with aluminum. Welds were also tested, as were some common aluminum alloys. Test solutions included CMA, various CMA/NaCl mixtures, NaCl with a commercially available $MgCl_2$ corrosion inhibitor, simulated acid rain, and distilled water.

Steel specimens in CMA corroded at only 1/4 to 1/15 the rate of steel specimens in NaCl (5–10 mpy for CMA versus 30–60 mpy for salt). CMA also caused less pitting. Additions of one part CMA to two parts NaCl also greatly reduced corrosion rates over plain salt. Steel welds were dramatically less corroded in CMA as well. Aluminum was attacked aggressively in neither CMA nor salt, but pitting was less in CMA. CMA was only slightly more corrosive than distilled water, and was less corrosive than simulated acid rain.

The Minnesota and Washington DOTs have also seen reduced corrosion of highway steels by CMA. Minnesota

C. D. Buscemi, Materials Unit, Chevron Research and Technology Co., 100 Chevron Way, Richmond, Calif. 94802-0627. K. A. Hoenke, Chevron Chemical Co., 6001 Bollinger Canyon Road, San Ramon, Calif. 94583-0956. K. L. Eklund, Department of Materials Science, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

reported that out of seven deicers sprayed on steel three times daily over a period of about 250 days, a 20/80 mix of CMA/salt showed the least corrosion, actually less than water alone (unpublished data). The CMA/NaCl mix corroded steel six times less than plain salt, and two times less than its closest competitor. Washington DOT reported corrosion five to seven times less in CMA solution (about 4 mpy) than in salt solution (4).

Southwest Research Institute (SwRI) reports corrosion rates for steel in pure CMA to be near zero (5). SwRI found that additions of about 20 percent CMA to NaCl solutions reduces corrosion by up to 80 percent more than plain salt.

In another comprehensive FHWA report (6), CMA was found to be less corrosive than salt to automotive steels, stainless steels, aluminum alloys, automotive and road paints, brake linings, and portland cement concrete. CMA did no damage to plastics, elastomers, ceramics, rubbers, sealants, adhesives, and asphalts.

WHAT IS KNOWN ABOUT CORROSION OF REBAR IN CONCRETE BY CMA?

Locke and Kennelley performed electrochemical measurements of corrosion potential for rebar in concrete (1,2). They concluded that although an active corrosion potential is measured for rebar in concrete exposed to CMA solutions, the actual corrosion rate is small compared with that in salt solution. Another important conclusion was that "galvanic type" corrosion cells can be set up when corrosion potential differs from one area of a reinforced concrete mat to another.

Locke and Kennelley found that CMA solutions ponded on reinforced concrete can change local corrosion potentials; however, their work did not measure corrosion current, which would have yielded a clearer picture of the amount of corrosion that was occurring. The finding that CMA causes active corrosion potentials for rebar in concrete, but that actual corrosion is small, has been reproduced by Chevron. It will be discussed in more detail in the section dealing with Chevron's electrochemistry work.

Two European studies, one by British Petroleum (7), the other sponsored by the Danish Ministry of Transport (8), have concluded that corrosion by salt solutions of steel embedded in concrete can be slowed down or terminated once the use of salt is discontinued and the concrete is exposed to CMA solution. The Danish study concluded that ponding a 50/50 CMA/salt mix "has a retarding effect on the corrosion of steel in concrete."

The most current work on rebar in concrete is being performed by Peart at FHWA. Peart's unpublished data show that ponding of either clean or chloride-contaminated concrete by CMA solutions results in minimal corrosion current and passive corrosion potentials, whereas ponding of the same slabs with salt solutions results in higher corrosion currents and active corrosion potentials.

WHAT IS KNOWN ABOUT THE EFFECTS ON CONCRETE OF CMA?

In several major studies, CMA caused the least damage to concrete of all deicers tested, including the road salt com-

monly used today. Michigan DOT found freeze-thaw damage from salt to be dramatically decreased when CMA was added to NaCl and to be eliminated by plain CMA (9). A salt-based deicer containing phosphates, tested at the same time, caused more concrete spalling as well as more corrosion to rebar than even plain salt.

A study by Nadezhdin et al. found that CMA caused less freeze-thaw damage than any of the other deicing chemicals tested, including CaCl_2 , sodium formate, urea, and NaCl (10). CMA accounted for far less spalled concrete material than plain road salt in a 100-cycle test.

Chollar and Virmani found that salt ponded on concrete slabs caused rust-filled surface cracks to develop (11). Over time, cracks grew wider and deeper. CMA, on the other hand, showed no evidence of concrete cracking. Electropotential measurements of rebars embedded in concrete showed CMA-ponded specimens lie in the passive (noncorroding) range, whereas salt-ponded specimens lie in the active (corroding) range.

An interesting side effect of spreading CMA on roadways has been the observation by several state DOTs that CMA has a residual effect on concrete. That is, once CMA is applied to a roadway, it tends to be less susceptible to being washed away, so that subsequent applications need not be as frequent. A recent thesis published at Michigan Tech explains that CMA actually is absorbed into limestone and diffuses into some types of rock, thereby creating a reservoir of deicer in the roadway surface that is available at the next snowfall (12).

CHEVRON'S CURRENT RESEARCH ON CMA

This part of the report is divided into three sections. Results of a 3-month planned interval test utilizing alternative immersion testing of plain carbon steel (ASTM A-36) in solutions of CMA and other deicers are summarized in the first section.

The second section concerns alternative immersion testing of a weathering steel commonly used for bridges (ASTM A-588). The weathering steel was subjected first to immersion in salt solutions and then to alternative deicers to determine the effect of deicers on precorroded bridge steels.

Results of subsequent electrochemical testing which was performed to further explore the corrosion phenomena observed in the immersion tests are summarized in the third section.

Alternative Immersion Testing of Plain Carbon Steels

Background

A 3-month planned interval test was used to determine steel corrosion rates after longer-term exposure to solutions of Chevron CMA-based deicer and several other deicers. The advantage of such testing is that both the liquid corrosiveness and the metal corrosivity can be measured. Not only were corrosion rates determined, but pH, solution conductivity, corrosion potential, metal surface appearance, corrosion product composition, acetate concentration, and microbiological activity of Chevron CMA-based deicer also were measured.

In a planned interval test, samples are placed in test solutions for different durations and at different times as shown in Figure 1 (13). Comparison of the corrosion rates observed in the first month (A_1) with those in the third month (B) shows changes in the corrosiveness of the liquid. Comparison of A_2 (the corrosion rate of only the final month of the 3-month immersion) with B gives information on changes in metal corrodibility with time. Metal corrodibility is affected by such factors as corrosion product formation and other changes to the metal surface.

Procedure

Six ASTM A-36 carbon steel coupons ($\frac{1}{2} \times 4 \times \frac{1}{16}$ in.) were hung from nylon rods and immersed in several different deicing solutions and distilled water at ambient temperature (Table 1) for 10 min, then raised into ambient air for 50 min. This cycle was repeated throughout the 3-month testing period using an automatic hydraulic system controlled by an electronic timer.

Corrosion potentials, conductivity, and pH of the solutions were recorded twice a week in each of the test solutions. Two samples from each solution were removed at the end of each exposure period (1, 2, and 3 months), and their corrosion rates determined. Corrosion products and scale on certain samples were analyzed.

Corrosion Rate Results

Figure 2 shows average corrosion rates after 1, 2, and 3 months for each of the test solutions. The CMA-based products, and urea, showed low corrosion rates (less than 5 mpy)—about the same as water. By far the highest corrosion rate was that of pure salt (30–60 mpy); 10 percent Chevron CMA-based deicer or CMA added to salt solutions reduced the corrosion rate to about $\frac{1}{3}$ that of NaCl alone.

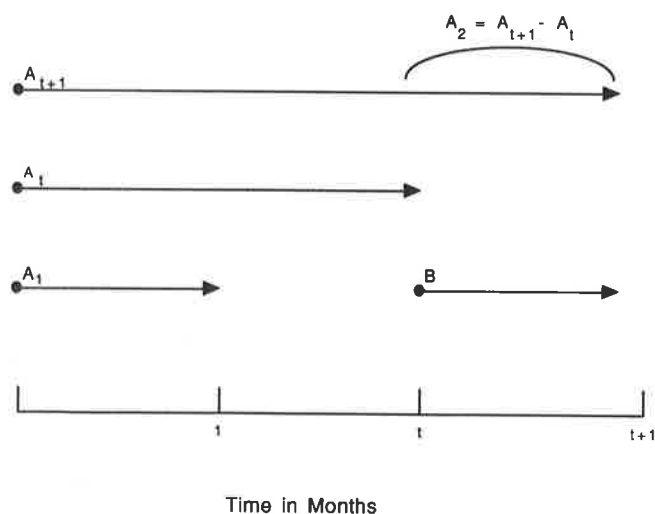


FIGURE 1 Planned interval test design. Each arrow represents immersion of corrosion coupons in solution for duration shown ($t = 2$ for 3-month test).

TABLE 1 Solution Chemistries for 3-Month Planned Interval Testing

Solution	Composition	Concentration
Water	Distilled Water	100%
NaCl	Sodium Chloride	3.5 wt%
Chevron CMA-Based Deicer	CMA-Based	3.5 wt%
NaCl/Chevron	9 g. Sodium Chloride	3.5 wt%
CMA-Based Deicer	1 g. Chevron Deicer	
Reagent Grade CMA	7 moles Mg Acetate	3.5 wt%
	3 moles Ca Acetate	
NaCl/Reagent Grade CMA	9 g. Sodium Chloride	3.5 wt%
	1 g. Reagent Grade CMA	
Urea	Chevron Chemical Urea	3.5 wt%
NaFo	Commercial Grade Sodium Formate	3.5 wt%

For the Chevron CMA-based deicer, some samples displayed a passive film with zero corrosion rate and underwent minimal active corrosion. There appear to be two stable corrosion potentials for CMA: one active with a corrosion rate of about 5 mpy, and one passive with zero corrosion. It is not statistically correct to average the corrosion rates in such cases. For this reason, only the nonzero (active) corrosion rate has been used in determining average corrosion rates. A more detailed explanation of the dual corrosion potential for CMA is given in the next section.

In most cases, average corrosion rate decreased with exposure time. Figure 2 shows that the highest corrosion rates generally occurred in the first month of testing. This could be a result of either a decrease in metal corrodibility or an increase in liquid corrosiveness. In most cases, it was found that metal corrodibility decreased over time. This is because scale formation tends to act as a barrier that decreases the availability of corrodent species at the metal surface.

A detailed analysis of metal corrodibility and solution corrosivity is beyond the scope of this paper, but interested readers can obtain more detailed information from the Chevron Materials Laboratory.

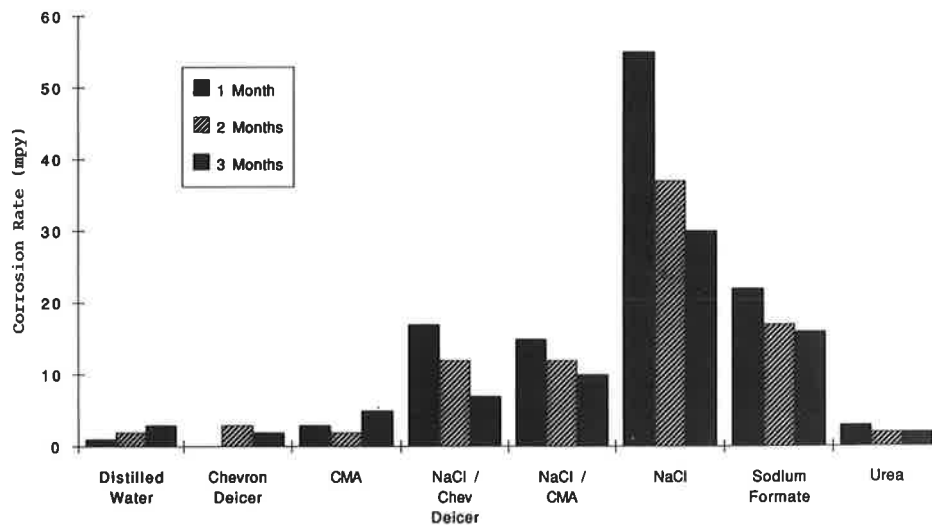


FIGURE 2 Summary of results from A-36 carbon steel alternative immersion corrosion testing.

Corrosion Coupon Surface Analysis

After a 4-week exposure, representative metal samples from each solution were cleaned per ASTM G1-88 and analyzed using a scanning electron microscope. Samples tested in NaCl were the most corroded. Chevron CMA-based deicer, CMA, and urea samples showed little surface attack. Surface appearances correlated well with the corrosion rates measured during the test.

Corrosion Coupon Scale Analysis

Scales from all samples were typically iron oxide and iron hydroxide corrosion products, such as Fe_3O_4 (magnetite) and various forms of $\text{FeO}(\text{OH})$. Precipitation deposits were also found in scales. Examples of this are CaCO_3 (calcite) in Chevron CMA-based deicer and CMA-containing solutions, and NaCl in salt solutions.

How the corrosion mechanisms for CMA-based solutions are affected by scale formation is described in the second section. As mentioned previously, the presence of scales can decrease metal corrodibility.

Conclusions from Carbon Steel Tests

- CMA-based solutions cause minimal corrosion (less than 5 mpy) to A-36 carbon steel, even when tested in alternative immersion conditions, which are more severe than constant immersion because of the ample supply of oxygen. Urea also showed minimal corrosion of A-36 carbon steel.
- Addition of 10 percent CMA or Chevron CMA-based deicer to salt lowered the corrosion rate to roughly that of plain salt (10–20 mpy for the mixtures versus 30–60 mpy for plain salt).
- CMA-based solutions show corrosion behavior that can be either passive, indicating zero corrosion, or active, which

accounted for corrosion of about 5 mpy or less. Potentials can change from passive to active and back within the same test.

Alternative Immersion Testing of Weathering Steels

Introduction

For this test, ASTM A-588 weathering steel was chosen because it is commonly used on bridges because of its increased corrosion resistance.

The test was designed to simulate changes in corrosion phenomena that would occur if alternative deicers were applied to previously corroded and chloride-attacked bridge steel. Samples were thus first subjected to salt solutions and then to deicing solutions. To our knowledge, this is first time such a test program was carried out.

Procedure

The procedure for these tests was essentially the same as for those described in the previous section. Samples of weathering steel were immersed in ambient temperature solution for 10 min, followed by drying in ambient air for 50 min. The cycle was continued for the duration of the 6-week tests. For the first 2 weeks samples were immersed in salt solution; for the next 4 weeks samples were immersed in the same 10 deicing solutions and distilled water as in the previous section.

Samples were removed at various intervals, and corrosion rates were measured. Some samples were removed after just 2 weeks to determine corrosion rate in salt solution only; others were left in for 6 weeks to determine if corrosion rate was lowered after the switch from salt to alternative deicer.

A mixture of 10 percent Chevron CMA-based deicer and 90 percent NaCl was also tested following salt solution immersion to determine whether Chevron CMA-based deicer has inhibitor capabilities when added to salt on pre-corroded weathering steels.

Results of Testing on Weathering Steels

Figure 3 shows the results of tests on weathering steel. For simplification, only the final corrosion rates (those that occurred during the 4 weeks of immersion in deicing chemicals) are shown.

As anticipated, corrosion rates were highest for the samples exposed to NaCl only (about 28 mpy). As in the tests on carbon steel, CMA-based solutions (including reagent grade CMA and Chevron CMA-based deicer) performed the best, with corrosion rates dropping to 2–6 mpy.

Corrosion in urea was slightly higher in these tests (about 8 mpy), suggesting that for steel previously exposed to NaCl, urea does not slow corrosion as fast as CMA.

Corrosion rates in plain water were also significantly higher than in CMA solutions (about 9 mpy), showing that switching to alternative deicers such as CMA can limit further damage to steel previously exposed to chlorides. The corrosion rate for the 10/90 Chevron CMA-based deicer and NaCl mixture dropped to 12 mpy versus 28 mpy for the plain salt solution.

Conclusions from Weathering Steel Tests

- When applied to precorroded samples of weathering steel, CMA-based solutions reduced the corrosion rate to $\frac{1}{5}$ to $\frac{1}{10}$ that in NaCl solution after 4 weeks (3–6 mpy for the CMA-based deicers versus 28 mpy for plain salt).

- Addition of 10 percent CMA or Chevron CMA-based deicer to salt reduced corrosion by about half versus plain salt (12 mpy for the mixture versus 28 mpy for plain salt).

Electrochemical Testing

Summary

Both the tests on carbon steel discussed in the first section and those on weathering steel discussed in the second section indicated the possibility that carbon steels were passivated in the presence of CMA-based solutions, such as the Chevron CMA-based deicer. To explore the mechanisms at work behind these two product types, electrochemical tests (poten-

tiodynamic scans) were conducted on carbon steel (ASTM A-36) and weathering steel (ASTM A-588) in Chevron CMA-based deicer and in pure CMA.

Procedure

Potentiodynamic scans were run per ASTM standard G5. Test solutions of 3.5 wt percent concentration were made from pure CMA, Chevron CMA-based deicer, and salt. To ensure an oxygen concentration similar to that of the alternative immersion tests, air was bubbled through the solutions for 15 min before sample immersion. Solution temperatures were held at 30°C throughout the test using a constant temperature bath.

The working electrodes were machined from ASTM A-36 carbon steel and ASTM A-588 weathering steel. Surfaces were wet-sanded with 600 grit emery cloth, rinsed, dried, and stored in a desiccator for 1 hr before testing. Average surface area of several samples (4.55 cm²) was used for consistency in calculations. The platinum auxiliary electrodes were cleaned with hot aqua regia and electrolyzed in 10 percent sulfuric acid. A saturated calomel electrode was used for the reference electrode such that all potentials can be referred to as versus standard calomel electrode (SCE).

Each sample was degreased with trichloroethane and rinsed with distilled water immediately before immersion in the test solution. After 1 hr of exposure, the rest potential (E_{corr}) was recorded. Samples were cathodically cleaned by applying a potential of -800 mV (versus SCE) for 10 min. The potential was then swept through a range of -800 mV to 1200 mV (noble) at a rate of .6 V/hr and the corresponding currents recorded. To obtain a hysteresis effect, the scan was then run in the negative (active) direction. The potential was held at 1200 mV for 10 min, then driven from 1200 mV to -800 mV.

All data were collected and plotted using EG&G PARC Model 332 Softcorr Corrosion software. Calculations of corrosion rates by the Polarization Resistance and Tafel Extrapolation methods were also completed by the computer.

Potentiodynamic Testing

Potentiodynamic testing can be used to determine the behavior of metal in a corrosive solution. As it corrodes, the metal (anode) transfers electrons to the cathode. This reaction, being electrochemical, occurs at a given potential (E). The amount of corrosion is directly related to the number of electrons transferred. This, in turn, sets the corrosion current (i).

Metal in solution can be forced to change potential by supplying an additional current to the sample. When this process is done progressively, a graph of E versus i results (a potentiodynamic scan). The behavior of the metal during such a test typically takes one of two forms, as shown in Figure 4 (14).

In Curve A the corrosion current, and thus the corrosion rate, increases for every increase in potential. Such behavior is active, with corrosion of steel by NaCl being an example. Curve B, however, shows an increase in corrosion with an increase in potential up to a critical point, where the corrosion

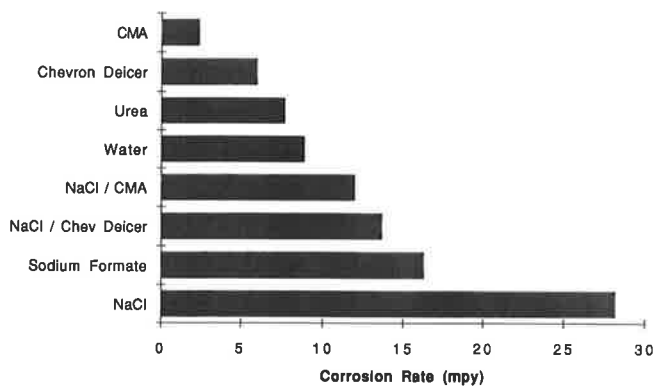


FIGURE 3 Summary of results from A-588 weathering steel alternative immersion corrosion testing.

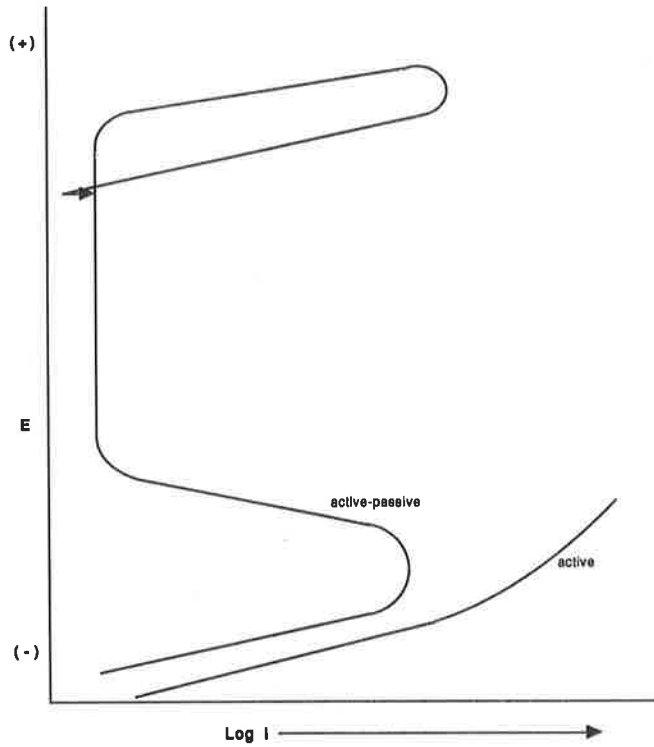


FIGURE 4 Anodic polarization curves.

rate drops dramatically to a passive state. As E is further raised, i eventually increases again in a transpassive region.

Figure 5 shows a summary of the behaviors possible for a metal/solution combination that displays active-passive behavior (14). Active-passive behavior is typical of stainless steels that passivate by forming an adherent, protective chromium oxide scale that prevents future corrosion of the metal beneath.

Just as there is an anodic curve for the corroding metal anode, there is a corresponding cathodic curve for the cathodic metal area to which electrons are flowing. Figures 6 and 7 show some typical cathodic curves and the effect they have on the corrosion behavior of the metal (14).

In Figures 6 and 7, the curves on the left are true polarization curves. These curves represent the actual relationship of potential to current for the anode and for the cathode, if they could be separated. In the laboratory, potentiodynamic tests yield the experimental curves shown on the right. These curves measure net current only; wherever the cathodic and anodic curves intersect, the measured net current is zero because their signs (+/-) are opposite. True corrosion current is determined by extrapolating the slopes of the anodic and cathodic portions of the experimental curve in the vicinity of the intersect point. The true corrosion current for any of the experimental curves is denoted by the bull's-eyes in Figures 6 and 7. A bull's-eye also denotes the true corrosion potential for any curve—the potential at which the magnitude of the anodic current equals that of the cathodic current, and the net experimental current becomes zero.

The complete shapes of the true polarization curves on the left can be surmised by analyzing the experimental polarization curves on the right. Figures 6 and 7 will be discussed later when actual tests with deicing products are evaluated.

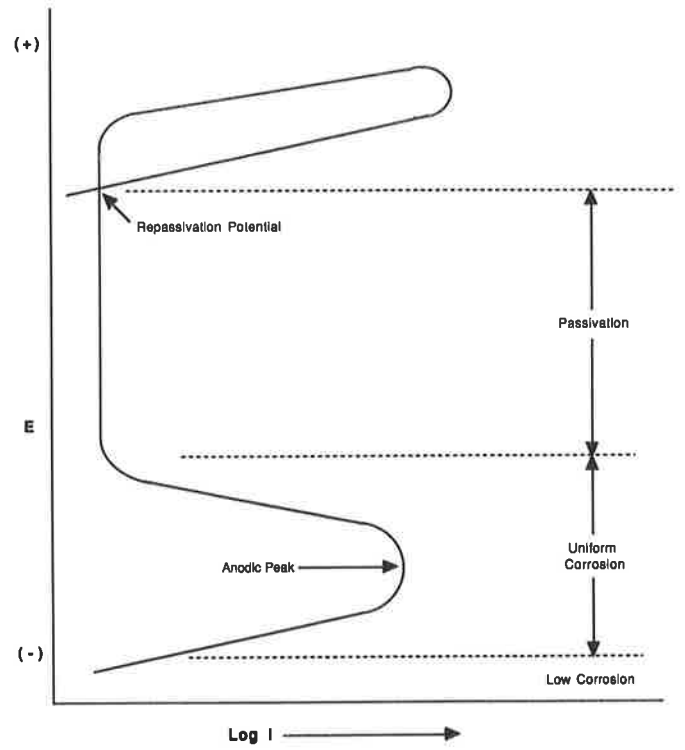


FIGURE 5 Typical active-passive polarization curve, showing regions of varying corrosion rate and type.

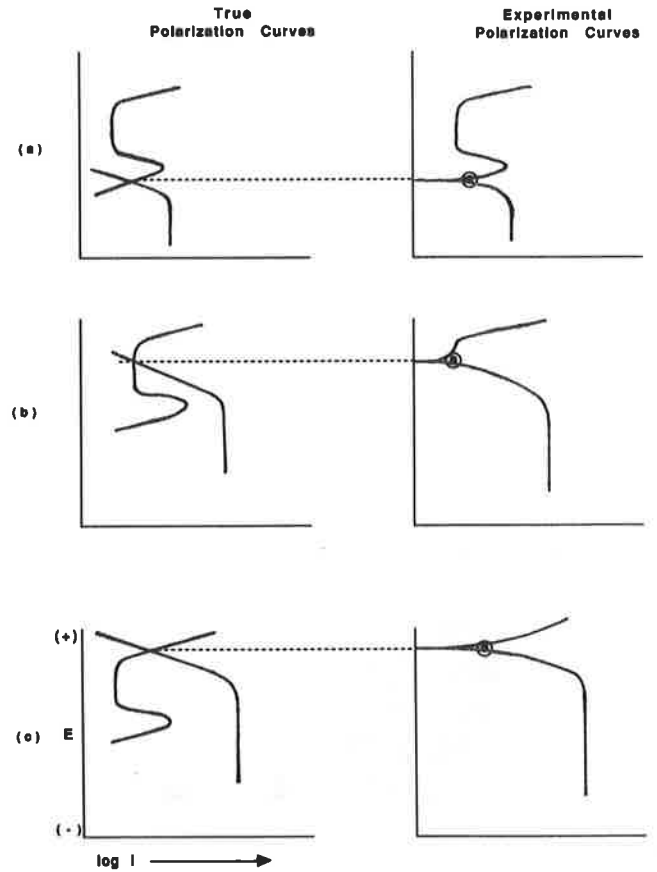


FIGURE 6 Various shapes of experimental polarization curves caused by changing locations of anodic and cathodic curves.

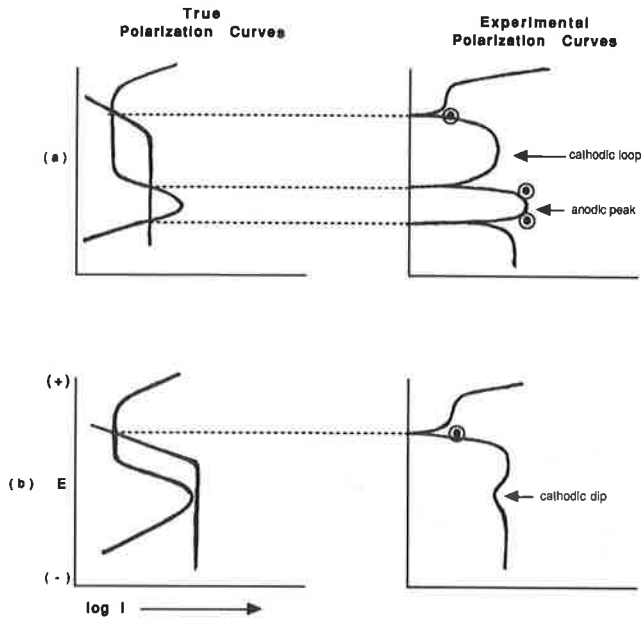


FIGURE 7 When the anodic and cathodic portions of the true polarization curves intersect (or nearly intersect) in more than one location, the experimental curve is subject to so-called double loop behavior (a). This phenomenon has been seen for steel in Chevron CMA-based deicer.

Electrochemistry Results on CMA and Chevron CMA-Based Deicer Solutions

All of the CMA-based products showed active-passive behavior (Table 2). The solid-line scan in Figure 8 is a forward potentiodynamic scan performed with A-36 steel in a 3.5 percent CMA solution, which shows active-passive behavior. The dashed line is a reverse scan showing three distinct stable (one metastable) corrosion potentials. This behavior has been referred to previously as double-loop behavior (2). The phenomenon is well known, as noted in Figure 7a, and is indicative of an unstable passive film (14).

In such cases, the metal may either be passive or actively corroding, corresponding to the highest and lowest intersection points where the anodic and cathodic curves meet. This explains the fact that some CMA-based samples tested in the past have shown no corrosion (passive), whereas identical samples in the same test container have shown corrosion of 2–5 mpy (active). This theory is supported by the fact that CMA showed a dual corrosion potential in electrochemistry tests. Measurements typically fell either between 0 and –200 mV, or between –500 and –700 mV.

Figure 9 shows how corrosion potential for CMA can be nearly equivalent to that for plain salt, whereas corrosion rate is an order of magnitude less. In Figure 9, E_{NaCl} is about –650 mV, whereas E_{CMA} is about –610 mV. These are representative of active potentials found in this study, which have been duplicated in other studies.

It is a fact that the corrosion rate for CMA is less than that for NaCl. This is because the corrosion current of CMA (i_{CMA}) is less than that of NaCl (i_{NaCl}). In Figure 9, for example, the corrosion current for CMA is about 5 $\mu A/cm^2$, whereas that for the salt solution is 10–50 $\mu A/cm^2$. This explains how

TABLE 2 Results of Potentiodynamic Scans, 3.5 wt Percent Unstirred Solutions

Sol'n/Sample	Rest* Potential	Corr. E corr**	Corr. Rate	I cc, $\mu A/cm^2$	E cc	Pass'n?
Chevron CMA- Based Deicer/ A588	192 mV	-554 mV	2.7 mpy	Note 1	Note 1	yes
		-550 mV	2.7 mpy			
CMA 7:3/ A588	-513 mV	-676 mV	6.9 mpy	1837	-430	yes
		-666 mV	6.6 mpy			
Chevron CMA- Based Deicer/ A588	-75 mV	-322 mV	0.86 mpy	2.03	Note 1	yes
		-326 mV	0.16 mpy	Note 1		
CMA 7:3/ A36	-700 mV	-705 mV	6.0 mpy	2378	-480	yes
		-696 mV	4.3 mpy			

* Rest potential after one hour in solution.

** Potential where i_{corr} equals zero (by computer).

Upper value calculated by Tafel Extrapolation method.

Lower value calculated by Linear Polarization method.

Note 1: Full passivation (anodic nose does not exist).

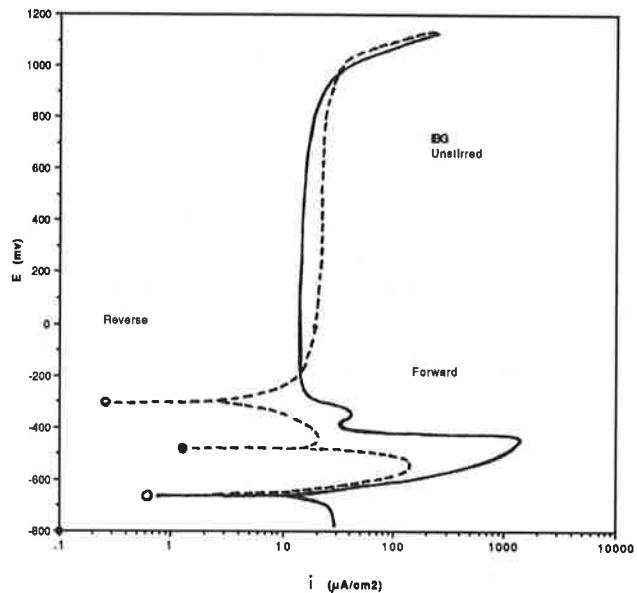


FIGURE 8 Active-passive behavior observed in CMA solution with A-36 steel, typical of behavior exhibited by all CMA-based deicers on both A-36 and A-588 steels. The dashed-line reverse scan showing one metastable (●) and two stable (○) corrosion potentials is shown in Figure 7a and results from an unstable passive film.

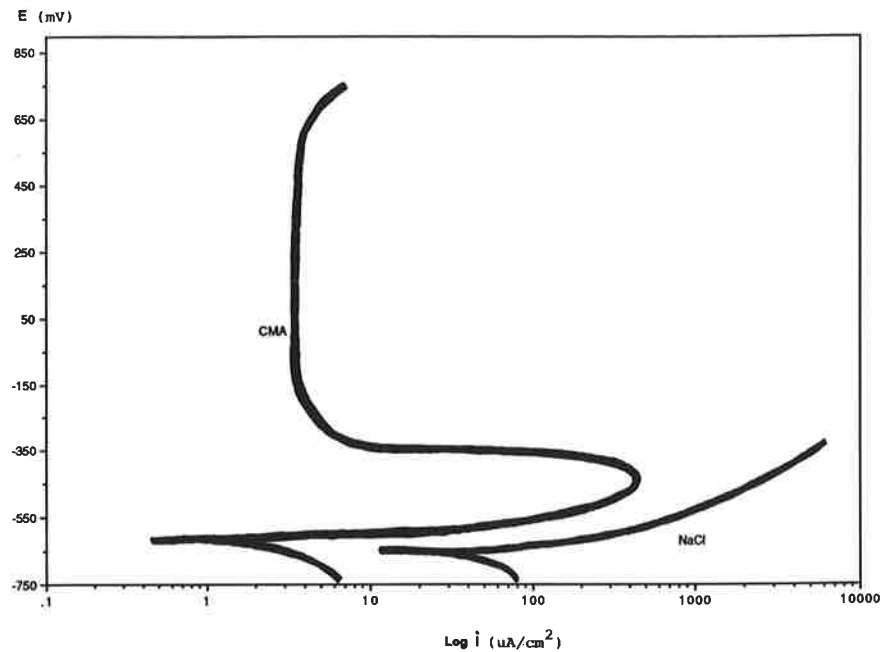


FIGURE 9 Representative E versus i curves for CMA and salt solutions. Corrosion potential is similar, but corrosion current is significantly greater for salt solution. Both curves were generated using mild steel.

measured corrosion rates for CMA-based solutions can be less than 5 mpy, whereas those for plain salt reach about 20–60 mpy.

For any solution it is the corrosion current (i), not the potential (E), that indicates corrosion rate. Because corrosion involves the transfer of ions and electrons from metal to solution, the amount of current generated is directly related to the amount of corrosion that is occurring. For alternative deicers, therefore, it is imperative that corrosion current be measured along with corrosion potential. Erroneous conclusions can be reached if corrosion potential alone is considered as a measure of corrosion rate.

As discussed earlier, Chevron CMA-based deicer can also display both passive and active corrosion behavior. Even in the active potential range, however, corrosion rates are exceedingly low. Table 2 presents corrosion currents for Chevron CMA-based deicer that are in the neighborhood of -300 to -700 mV. Although such a low potential indicates active corrosion, in the case of the Chevron CMA-based deicer, that active corrosion is occurring at the rate of only about 3 mpy—much less than the 20–60 mpy that has been typically measured for salt.

Conclusions From Electrochemistry Testing

- CMA-based products (including Chevron CMA-based deicer) exhibit an active/passive behavior, causing identical samples in the same corrosive environments to show either passive corrosion or active corrosion with low corrosion rates.

- In CMA-based solutions passive behavior occurs at a corrosion potential of 0 to -200 mV with essentially no corrosion. Active behavior occurs at a corrosion potential of -500 to -700 mV and with corrosion rates of 2–5 mpy.

- Active and passive corrosion behavior can occur on identical samples in the same environment; this mechanism is understood and documented in the literature.

- Tests of alternative deicers should include measurement of both corrosion currents and potentials because it has been shown that corrosion potentials for CMA-based solutions can be similar to those for salt solutions, whereas measured corrosion currents and corrosion rates are markedly different.

REFERENCES

1. C. E. Locke, and K. J. Kennelley. *Corrosion of Highway and Bridge Structural Metals by CMA*. Report FHWA-RD-86-064. FHWA, U.S. Department of Transportation, June 1986.
2. K. J. Kennelley, and C. E. Locke, Jr. Electrochemical Behavior of Steel in Calcium Magnesium Acetate. *Corrosion*, Vol. 46, No. 11, Nov. 1990, pp. 888–895.
3. R. L. McCrum. Corrosion Evaluation of Calcium Magnesium Acetate (CMA), Salt (NaCl), and CMA/Salt Solutions. NACE Corrosion '89, Paper 127, New Orleans, April 17–21, 1989.
4. T. Wieman, D. Komac, and S. Bigler. *Statewide Experiments with Chemical Deicers*. Washington State Department of Transportation, 1989.
5. W. J. Machowski, and F. F. Lyle, Jr. *Comparative Evaluation of Deicer Corrosion*. Project 06-2033-001. Southwest Research Institute, San Antonio, Tex., March 18, 1988.
6. D. S. Slick. *Effects of Calcium Magnesium Acetate (CMA) on Pavements and Motor Vehicles*. Report FHWA-RD-87-037. FHWA, U.S. Department of Transportation, April 1987.
7. M. C. M. Man, m.L. KB. Hazell, and KR. P. Smith. On-Line Measurement of Simulated Reinforcement Corrosion in Concrete Under Action of De-Icers. In *Third International Symposium on Corrosion of Reinforcement in Concrete Construction*, Society of Chemical Industry, Elsevier Applied Science, New York, N.Y., May 1990.
8. Danish Corrosion Centre. *Effect of CMA on Corrosion Properties of Rebars in Concrete* (English translation). National Agency of

- Environmental Protection, Copenhagen Airports, Ministry of Transport, Road Directorate. Copenhagen, Denmark, Dec. 1990.
9. R. L. McCrum and J. V. Heffernan. *Evaluation of United Salt's Corrosion Inhibitor Intended for Use with Sodium Chloride Deicing Salt*. Project 89 G-271. Michigan Transportation Commission, Lansing, June 1991.
 10. A. Nadezhdin et al. The Effects of Deicing Chemicals on Reinforced Concrete. In *Transportation Research Record 1157*, TRB, National Research Council, Washington, D.C., 1988.
 11. B. H. Chollar and Y. P. Virmani. Effects of Calcium Magnesium Acetate on Reinforced Steel Concrete. *Public Roads*, Vol. 51, No. 4, March 1988, pp. 113-115.
 12. R. Valverde. *A Comparative Study of the Influence of CMA with Other Deicing Chemicals on Pavement Aggregates*. M.S. thesis. Michigan Technological University, April 1991.
 13. M. G. Fontana *Corrosion Engineering* (3rd ed.). McGraw-Hill Book Co., New York, N.Y., 1986, pp. 163, 445-480.
 14. E. L. Liening. *Electrochemical Corrosion Testing Techniques*. Dow Chemical Co., Midland, Mich., pp. 88-96.
-

Publication of this paper sponsored by Committee on Corrosion.