A Study of Corrosion Properties of A New Deicer, Calcium Magnesium Acetate

CARL E. LOCKE, KEVIN J. KENNELLEY, MARK D. BOREN, AND VIRGINIA LUSTER

The Federal Highway Administration has sponsored research to develop a noncorrosive deicing chemical as one way to reduce the costly damage of bridges because of chloride-containing deicers. Calcium magnesium acetate (CMA) is under consideration as a replacement for sodium chloride and calclum chloride as a deicer as a result of that research. Corrosion of A-36, A-325, and A-588 steel, grey cast iron, and aluminum was studied in CMA, sodium chloride, calcium chloride solutions, and tap water. Exposure to these solutions was in full and half immersion, vapor space, sprays, and dip testing. The corrosion electrochemistry of these metals in CMA solutions was also studied. The effect of CMA on the corrosion behavior of reinforcing steel in portland cement concrete was investigated with steel in simulated pore solutions, mortar cylinders, and concrete slabs. CMA solutions were found to be less corrosive to steel than sodium chloride solutions by a factor of two to four, dependent upon solution concentration. Cast iron and aluminum corrode at a lower rate in CMA solutions than in sodium chloride solutions. CMA causes a substantial shift of the potential of steel in mortar, simulated pore solutions, and concrete slabs. It is possible that this shift could result in a corrosion problem for bridge decks similar to that found when sodium chloride is used as a deicer.

Deicing chemicals are widely used in the United States because of the bare roads' year-round policy existing in all the states. The public has grown accustomed to this policy and now demands that the roads, and especially bridges, be free of ice and snow at all times. As a result, the use of deicers has grown steadily since 1946. The most commonly used chemical is sodium chloride (NaCl), and 12×10^6 tons are placed on the highways and bridges in the United States annually (1). This statistic can be stated in other ways. In Wisconsin, approximately 450 pounds of salt are used for each lane-mile of highway each winter season (2). Calcium chloride is also used as a deicer but is used less because of its higher cost.

These chloride-containing salts are corrosive. Automobile corrosion is a widely known and costly problem in all developed countries faced with high use of deicing salts. It is estimated that 50 percent of the automobiles in the United States and Canada are located in areas where NaCl is used extensively (2). In addition to contributing to automobile corrosion, the use of chloride deicers leads to corrosion of bridge structural materials, for example, the corrosion of the reinforcing steel embedded in concrete.

Bridge decks designed to last 50 years are being replaced in 10 to 20 years (3). The accumulated damage on bridges located on the federal-aid system has been estimated to have a cost of repair of \$26.7 billion. Of this, \$8.8 billion is needed for bridge deck restoration. For bridges outside the federal-aid system, an additional \$7.3 billion is needed for bridge deck restoration. Annual cost for all bridge deck restoration is estimated to be \$400 million (3).

Several different approaches are used to reduce the corrosion damage caused by the chloride-containing deicing salts: (a) automobiles are now manufactured with special primers and coatings to combat the corrosion process; (b) bridge structural materials are painted and several methods are used for corrosion control of the concrete reinforcing steel; (c) epoxy-coated steel is the most commonly used corrosion preventive system for new construction; and (d) cathodic protection of reinforcing steel in existing construction seems to be a widely accepted method of halting corrosion in bridge decks.

The Federal Highway Administration (FHWA) has investigated the possibility of using a noncorrosive deicing material as another approach to reducing the cost of corrosion caused by the chloride-containing chemicals. A study commissioned by the FHWA in 1980 identified calcium magnesium acetate (CMA) as a possible alternate deicing compound (4). This initial project included an exploratory corrosion experiment the results of which indicated CMA might be a noncorrosive deicer. Based on this project the FHWA funded a relatively extensive corrosion project to determine the corrosivity of CMA to a range of bridge structural metals. This paper is a summary of that project.

Calcium magnesium acetate is a name used to describe the reaction product of acetic acid and dolomitic limestone. This reaction product is a mixture of calcium acetate and magnesium acetate. Bjorksten Laboratories found that CMA had deicing properties close to those of sodium chloride and that the manufacturing costs were substantially greater (4). It is thought, however, that if CMA proves to be noncorrosive, the real cost of this material, with reduced damage caused by corrosion, would be attractive.

EXPERIMENTAL PROCEDURES

The corrosion behavior of a number of different metals in CMA was studied in different environments. Direct exposure of the metals to solutions of CMA and the vapor space above

C. E. Locke, Office of the Dean, University of Kansas, 4010 Learned Hall, Lawrence, Kans. 66045-2210. K. J. Kennelley, Exxon Production Research Company, P.O. Box 2189, Houston, Tex. 77001. M. D. Boren, University of Oklahoma, Norman, Okla. 73019. V. Luster, Alcon Laboratories, 6201 S. Freeway, Fort Worth, Tex. 76134.

the solutions was accomplished in static, dip, and spray environments. For comparison purposes the metals were also exposed to solutions of sodium chloride, calcium chloride, and tap water. The effect of CMA on the corrosion of reinforcing steel in portland cement concrete was investigated. The corrosion electrochemistry of the metal solution systems was studied using several different experimental techniques. This section provides a brief description of the experimental details of this study. Complete details of the work can be found in a dissertation by Kennelley (5) and a thesis by Boren (6).

Weight-Loss Studies

Three types of weight loss tests were conducted at 25° C: static immersion tests, dip tests, and spray tests. The metals exposed to the corrosive solutions are listed in Table 1. Two duplicate samples were used for each test condition. These metals are representative of the materials used in the construction of bridge and highway structures.

The metals used met the ASTM specification for the type of metal specified. Galvanizing was done by a commercial galvanizer to a specification 0.1 g/cm2 (3.3 oz/ft2) over all surfaces of the coupon. Weathering of the galvanized and weathering steel samples was accomplished in Norman, Oklahoma, by exposing the rectangular coupons outside during a 6-month period. Some of the steel coupons, after surface cleaning as described in National Association of Corrosion Engineers (NACE) TM-01-69 (8), were painted with a three-layer linseed oil-based system consisting of a red lead primer, a red-lead intermediate coat, and an aluminum-pigmented top coat. This paint system is one used by the Oklahoma Department of Transportation for bridge structures. All samples other than the painted, weathered, and galvanized metals were surface cleaned before and after exposure using procedures specified in ASTM G1-81 (7) and NACE TM-01-69 (8). The weathering steel samples were cleaned in the same manner as other steel samples after exposure and before weighing. Weight loss deter-

TABLE 1	METALS	TESTED	IN	WEIGIIT	LOSS
EXPERIM	ENTS				

Metals	Shape	Surface
A-36 steel	Rectangular	Cleaned
	Angle iron	Cleaned
	Crevice	Cleaned
	U-bend	Cleaned
	Rectangular	Painted
	Rectangular	
	welded	Cleaned
A-36 steel galvanized	Rectangular	Cleaned
5	Rectangular	Weathered 6 months
Grey cast iron	Rectangular	Cleaned
A-325 steel	Circular	Cleaned
	Stressed bolt	Cleaned
A-588 weathering steel	Rectangular	Weathered 6 months
	Rectangular	Weathered 6 months,
		then painted
6061-T6 aluminum		
galvanic couples	Rectangular	Cleaned
A-36/galvanized	Rectangular	Cleaned
A-588/galvanized	Rectangular	Cleaned

TABLE 2 SOLUTIONS USED IN THE WEIGHT LOSS TESTS

Reagent Grade CMA (%)	Commercial Grade CMA (%)	NaCl (%)	CaCl ₂ (%)
0.50	0.50	0.30	0.28
1.00	1.00	0.60	0.57
2.00	2.00	1.20	1.14

NOTE: Solutions were made using tap water as the solvent.

minations were made by weighing before and after exposure for all but the painted samples, the U-bend samples of A-36, and the A-325 stressed samples. These three groups of samples were visually inspected for relative damage of the painted samples and any evidence of stress cracking in the stressed samples.

The samples were exposed to 13 different solutions, listed in Table 2. The reagent grade CMA [CMA(R)] was prepared from equimolar amounts of reagent grade calcium acetate and reagent grade magnesium acetate. The commercial grade CMA [CMA(C)] was furnished by the FHWA from a batch of CMA prepared from dolomitic lime and acetic acid. The solution concentrations were chosen from a series of electrochemical tests conducted by Luster (9). These test indicated that 1 percent by weight solutions of CMA could be expected to have the highest corrosion rates of any of the compositions. One concentration (0.5 percent by weight) below this and one concentration (2 percent by weight) above were also chosen. The concentrations of sodium chloride used are equiosmolal (same number of ions) to the CMA concentrations. The calcium chloride concentrations were based on the same concentration of chloride ions as those in the sodium chloride solutions. Tap water was also used for purposes of comparison.

Each type of metal sample was exposed to each of the solutions, fully immersed, half immersed, and in the vapor space (see Figure 1). The exposure time was 17 months and the solutions were changed after 8 months of exposure. Water lost by evaporation due to the bubbled air was replaced monthly.

A set of metal samples was exposed to sprays of each of the 13 solutions. Some difficulty was encountered with the initial spray apparatus based on an aspirator; the arrangement shown in Figure 2 was then developed. Test time was 14 months, which included the exposure to the original setup and the arrangement shown in Figure 2. The equipment shown in Figure 2 was used for approximately 75 percent of the time.



FIGURE 1 Experimental setup for static immersion tests.



FIGURE 2 Atomized spray test setup.

A dip apparatus was constructed to immerse each metal sample in the test solutions periodically and then remove it. The guidelines for a dip test specified for stress corrosion cracking in ASTM G-44 (7) were used in the selection of the fraction of time the samples were immersed. The metals were immersed for 10 min of each hour and suspended above the solutions for the remaining 50 min of the hour. The average duration of the test time was 16 months.

Electrochemical Tests

The procedures and apparatus used for the polarization tests were similar to those described in ASTM G-5 (7). Steel (A-36) was polarized in each of the 13 solution compositions used in the weight loss tests. In addition, steel samples were polarized in solutions of 5, 10, and 20 percent CMA.

A Princeton Applied Research Potentiostat (Model 173), Model 175 Programmer, and Model 376 Logarithmic Current Converter were used for the electrochemical experiments. The apparatus that was used to hold the solution and electrodes was similar to that described in ASTM G-5 (7). A saturated calomel reference electrode was used for all polarization experiments.

Air was bubbled through the solutions for about 1 hr before beginning each polarization experiment. The potential sweeps were conducted at 0.278 mv/sec and were started after the air was bubbled through the solutions. It was found that steel would temporarily passivate because of the oxygen saturation after the air bubbling but the steel potential would shift to the active range [-680 to -700 mv saturated calomel electrode (SCE)] if sufficient waiting time was used. In some systems it required 24 hr for the potential to shift to active.

The polarization experiments were started at the active corrosion potential and the scan direction was first begun in the anodic direction for the anodic polarization experiments. The potential was shifted to about +1,100 mv and the scan direction was then automatically reversed. The potential was then scanned to the original corrosion potential. Cathodic polarization curves were also begun at the active corrosion potential and the potential was shifted to about -1,500 mv. The potential was scanned only in the active direction with no reverse scan for the cathodic polarization. A plot of potential versus log current was generated for each experiment.

Linear polarization experiments were conducted to determine corrosion rates by scanning the potential +30 mv from the corrosion potential. The scan direction was then automatically reversed and the potential was scanned to a value -30 mv from the corrosion potential.

Steel in Concrete

Reinforced concrete slabs were constructed to determine the effect of CMA solutions on the electrochemical potential of the reinforcing steel. Each slab contained two rebar mats that were not electrically connected in the slab, as shown in Figure 3. Slabs were made with bare steel bars in both mats, epoxy-coated bars in both mats, and epoxy-coated bars in the top mat and bare bars in the bottom mat. A standard-mix design of



FIGURE 3 Arrangement of reinforcing in concrete slabs used in ponding tests.

portland cement concrete was used for the blocks. In some of the blocks sodium chloride was added to the mix water for the portion of the concrete poured around the top mat to provide a 0.2 percent chloride ion concentration in the concrete, based on cement content. Solutions of CMA, sodium chloride, and calcium chloride were ponded on top of these slabs after a curing time of 28 days under wet curing mats. The potentials of the top and bottom mats of copper/copper-sulfate reference electrodes were recorded periodically over an 18-month period. Current flow between the top and bottom mats was taken each time after the potential measurements. The mats were not connected electrically during the time of the measurements.

The potentials of the reinforcing steel were measured in simulated pore solutions and mortar cylinders soaked in CMA solutions. The simulated pore solutions' compositions were based on work done by Farzammehr (10). CMA was added to these pore solutions to obtain 0.5, 2.0, and 10 percent by weight with chloride ion compositions up to 1.0 percent by weight.

RESULTS

Weight-Loss Tests

Corrosion rates of the metals were calculated from the weightloss tests and are reported in mils per year (mpy). The results for the steel samples (A-36, A-588, A-325), the cast iron, and the aluminum samples are reported for each of the test conditions in Tables 3-7. The results of the rectangular, the angle iron, the welded, and the crevice samples of A-36 have been averaged and reported as such. The tabulation of the complete results is available in a report on which this paper is based (11).

The corrosion rates from all the test conditions have a similar pattern of type of test solution. The sodium chloride solutions

Concentration		Steel				
(weight %)	Solution	A-36	A-588	A-325	Cast Iron	Aluminum
0.3	NaCl	8.9	7.3	5.3	6.2	1.3
0.6	NaCl	8.6	11.8	6.6	4.3	0.2
1.2	NaC1	6.6	18.3	3.9	4.1	1.3
0.29	CaCl ₂	3.0	7.1	1.9	2.2	0.0
0.57	CaCl ₂	2.3	5.2	2.5	1.6	0.0
1.14	CaCl ₂	1.8	13.6	2.7	1.8	0.1
0.5	CMA(R)	1.6	1.3	2.2	3.3	0.0
1.0	CMA(R)	1.2	1.5	2.4	1.6	0.0
2.0	CMA(R)	0.9	1.6	2.2	1.9	0.0
0.5	CMA(C)	1.8	1.5	3.0	2.2	0.0
1.0	CMA(C)	2.7	1.7	3.8	1.6	0.1
2.0	CMA(C)	2.6	2.7	2.5	2.0	0.1
Tap water		4.1	0.9	5.7	4.3	0.9

TABLE 3 CORROSION RATES OF METALS FULLY IMMERSED IN CORROSIVE SOLUTIONS (mils per year)

TABLE 4CORROSION RATES OF METALS HALF IMMERSED INCORROSIVE SOLUTIONS (mils per year)

Concentration		Steel	Steel			
(weight %)	Solution	A-36	A-588	A-325	Cast Iron	Aluminum
0.3	NaCl	10.2	10.6	9.3	5.5	0.6
0.6	NaCl	13.1	17.9	9.7	5.5	0.2
1.2	NaCl	13.9	18.4	12.7	6.5	0.8
0.29	CaCl ₂	4.1	7.9	4.9	3.5	0.0
0.57	CaCl	3.9	6.7	6.7	3.3	0.1
1.14	CaCl ₂	3.1	10.4	7.9	3.1	0.0
0.5	CMA(R)	2.5	1.9	1.9	2.9	
1.0	CMA(R)	1.9	2.0	4.0	1.7	0.0
2.0	CMA(R)	1.4	2.6	2.2	1.8	0.0
0.5	CMA(C)	2.0	2.8	4.0	2.9	0.0
1.0	CMA(C)	2.2	3.1	6.4	3.4	0.0
2.0	CMA(C)	2.4	2.7	2.8	1.6	0.5
Tap water		3.7	3.1	5.4	3.5	0.4

TABLE 5	CORROSION RATES OF METALS IN VAPOR SPACE ABOVE
CORROSI	/E SOLUTIONS (mils per year)

Concentration		Steel				
(weight %)	Solution	A-36	A-588	A-325	Cast Iron	Aluminum
0.3	NaCl	3.5	6.1	0.5	0.2	0.1
0.6	NaC1	5.7	7.2	8.4	0.3	0.3
1.2	NaCl	3.8	7.3	8.3	0.3	0.3
0.29	CaCl ₂	1.4	1.3	5.3	0.9	0.0
0.57	CaCl	5.1	1.2	7.7	0.7	0.1
1.14	CaCl ₂	2.6	2.0	8.9	1.0	0.2
0.5	CMA(R)	2.8	1.3	0.1	0.5	0.0
1.0	CMA(R)	2.1	1.3	0.4	1.1	0.0
2.0	CMA(R)	1.7	1.6	3.1	0.5	0.0
0.5	CMA(C)	1.4	1.6	4.6	1.2	0.0
1.0	CMA(C)	1.5	1.7	4.0	2.8	0.0
2.0	CMA(C)	1.2	2.4	2.7	1.6	0.0
Tap water		1.2	3.9	1.1	0.5	0.2

TABLE 6CORROSION RATES OF METALS EXPOSED TO CORROSIVESOLUTIONS BY DIPPING (mils per year)

Concentration		Steel	Steel				
(weight %)	Solution	A-36	A-588	A-325	Cast Iron	Aluminum	
0.3	NaCl	10.7	9.7	13.6	7.6	3.2	
0.6	NaCl	14.5	13.6	13.4	8.9	2.0	
1.2	NaCl	14.1	16.9	12.8	8.1	1.7	
0.29	CaCl ₂	7.3	7.1	5.7	5.8	0.1	
0.57	CaCl	8.9	8.2	5.6	6.8	0.1	
1.14	CaCl ₂	12.8	9.3	6.8	8.0	0.1	
0.5	CMA(R)	2.7	1.3	2.6	4.0	0.0	
1.0	CMA(R)	1.3	2.3	2.5	3.5	0.0	
2.0	CMA(R)	1.4	4.8	2.4	3.5	0.0	
0.5	CMA(C)	2.4	4.1	3.1	3.7	0.0	
1.0	CMA(C)	2.4	2.3	2.7	4.1	0.4	
2.0	CMA(C)	2.7	0.9	3.1	4.5	0.0	
Tap water		4.7	1.5	4.0	6.5	0.1	

 TABLE 7
 CORROSION RATES OF METALS EXPOSED TO SPRAYS OF

 CORROSIVE SOLUTIONS (mils per year)

Concentration		Steel	Steel				
(weight %)	Solution	A-36	A-588	A-325	Cast Iron	Aluminum	
0.3	NaCl	6.4	10.9	7.6	6.3	3.2	
0.6	NaCl	8.9	22.6	11.3	11.6	2.0	
1.2	NaCl	16.6	30.6	17.2	15.2	1.7	
0.29	CaCl ₂	6.8	7.1	7.0	5.7	0.1	
0.57	CaCl ₂	7.7	7.5	7.5	6.9	0.1	
1.14	CaCl ₂	10.2	7.8	8.1	11.2	0.1	
0.5	CMA(R)	3.2	2.9	3.3	5.2	0.0	
1.0	CMA(R)	2.8	3.8	4.5	6.7	0.0	
2.0	CMA(R)	1.9	4.0	5.4	7.8	0.0	
0.5	CMA(C)	3.2	3.3	5.0	5.5	0.0	
1.0	CMA(C)	3.3	4.4	4.2	8.0	0.0	
2.0	CMA(C)	5.5	5.3	6.1	7.5	0.0	
Tap water		2.6	1.3	2.5	2.6	0.1	

are the most corrosive. Calcium chloride solutions are less corrosive than sodium chloride solutions. The CMA solutions are less corrosive than either of the chloride-containing solutions with corrosion rates that are at least two to five times less than those found for the sodium chloride solutions.

The concentration dependence varies somewhat with solution composition and test condition. The corrosion rates of the metals exposed to the CMA (reagent grade) [CMA(R)] and CMA (Commercial grade) [CMA(C)] solutions did not vary widely in concentration. The variation is so slight in most of the test conditions that it is hard to make any such determination.

Exposure conditions greatly affect the corrosion rates. The dip test and the half-immersed test conditions resulted in the highest corrosion rates. The vapor space exposure resulted in the lowest corrosion rates of all the test conditions used.

Stressed Samples

The A-325 stressed bolts were tested in the fully immersed and vapor space immersion tests. None of the bolts broke and no cracks were observed on any of the bottles. The threaded regions of the bolts fully immersed in NaCl and CaCl₂ solutions corroded to a greater extent than the bolts in CMA(R), CMA(C), and tap water, as observed visually.

None of the A-36 stressed U-bend steel coupons broke, nor were any cracks found after exposure in the dip, spray, or immersion tests. Severe thinning of the U-bend sample in the stressed region of the coupon was visually observed on the samples exposed to the NaCl, CaCl₂, and tap water solutions. Coupons exposed to CMA(R) and CMA(C) were not as corroded as much as those in the other solutions.

Painted Samples

The effect of the solutions on the painted samples was determined visually for all samples. The paint coating on the A-36 steel samples exposed to NaCl solutions was blistered in nearly all the test conditions. The painted samples exposed in the vapor space above the NaCl solutions were in good condition. All other solutions (CaCl₂, CMA, and tap water) had no or little effect on the paint coatings.

The effect of the solutions on the painted weathering steel samples was somewhat more severe. The NaCl solutions were the most damaging of all the solutions to the painted coatings. Most were blistered and in some instances the paint flaked off the metal. The CMA solutions did not harm the paint except in two of the tests using CMA(C). Some flakes of paint were removed from the samples during exposure to 0.5 percent CMA(C) and a few blisters were found in the paint on samples exposed to 1.0 percent CMA(C). All other samples were in good condition after exposure, which was for approximately 12 months.

Galvanized Samples

It was not possible to make quantitative determination of the corrosion rates of the galvanized coupons because of problems in removal of the corrosion product without also removing the galvanized layer. Several different acidic solutions were used in an attempt to accomplish the removal. The solutions either did not adequately remove the corrosion product layer resulting in an apparent weight gain or did not remove all of the galvanized layer totally. Only visual observations are therefore reported for these samples.

Sodium chloride solutions appeared to be the most corrosive of all the solutions. Tap water was the least corrosive of all solutions to the galvanized layer.

The same difficulty was encountered in determining the effect of the solutions on corrosion of the galvanic couples. For all the samples immersed in the corrosive solutions, the steel coupon was cathodically protected by the galvanized coupon. Corrosion rates for steel were reduced in all solutions to less than 1 mpy. The galvanic coupling had little effect on the samples exposed to the vapor space, dip test, and spray test. This was a result of the lack of a continuous electrolyte to conduct current between the metals in those tests.

Electrochemical Tests

Results from polarization experiments conducted by Kennelley (5) and Luster (9) indicated that steel in CMA solutions behaved as an active-passive metal. Figure 4 illustrates the anodic polarization behavior of A-36 steel in a 1.0 percent CMA(R) solution, and Figure 5 illustrates comparable behavior in a 1 percent CMA(C) solution. The directions of the arrows indicate the direction of the potential scan. The curves are typical of active-passive behavior. The A-36 steel was at a potential of about -700 mv in relation to the calomel reference electrode before the scan, which is in an active condition. Luster (9) found that steel in most of the CMA solutions was at a potential







FIGURE 5 Anodic polarization with reverse scan for A-36 steel in 1.0 percent commercial grade CMA.

of about -150 to -200 mv in relation to the calomel, which is in the passive range displayed in the polarization curves. Kennelley (5) found that air must be bubbled through the solutions at a very high rate to maintain the steel at the passive potentials. He found that with a low rate of bubbled air or in stagnant conditions the steel would initially be at a passive potential and then with time (2 to 20 hours) the potential would spontaneously shift to an active value.

The polarization curves contained several steps during the anodic portion of the scan. These are thought to be due to changes in the nature of the passive layer on the steel.

The reverse scans initiated at about +1,100 mv in relation to the saturated calomel electrode were typical of those expected of metals susceptible to localized corrosion. The hysteresis loop found in these reverse scans is like that found with systems known to display pitting corrosion. Localized corrosion can propagate at potentials more noble than the point at which the return loop intersects the forward scan. This point is discussed in ASTM Standard G-61 (7). The reverse scans for steel in CMA solutions of higher concentrations (up to 20 percent by weight) indicated a very unusual behavior. At potentials of about -200 mv, the direction of current flow to the metal shifted from anodic to cathodic, which peaked then decreased to zero at about -500 to -600 mv. At that potential, the current again changed direction and once again was anodic. The anodic currents also peaked and decreased to zero with a subsequent shift to the cathodic direction. The potential of the steel was being shifted at a uniform rate of 0.278 mv/sec in the

		Active Corro	sion Potential	Passive Corrosion Potential	
Solution	Concentration (%)	Potential (mv)	Corrosion Rate (mils/yr)	Pontential (mv)	Corrosion Rate (mils/yr)
CMA(R)	0.5	698	9.2 ^a	-171	0.04
CMA(C)		708	5.4 ^a	-183	0.04
CMA(R)	1.0	-700	7.7 ^a	-181	0.03
CMA(C)		-690	3.5 ^a	-198	0.10
CMA(R)	2.0	-682	5.8ª	-233	0.08
CMA(C)		-647	1.7ª	-200	0.11
CMA(R)	5.0	-725	4.2	-143	0.01
CMA(C)		-729	2.9	-322	0.05
CMA(R)	10.0	721	4.6	-182	0.20
CMA(C)		748	2.2	-379	0.16
CMA(R)	20.0	711	2.6	246	0.01
CMA(C)		659	0.5	345	0.06

TABLE 8	CORROSION	RATES	FROM	LINEAR	POLARIZ	LATION	EXPERIMENTS,	A-36	STEEL
IN CMA S	OLUTIONS								

^aData from Luster (9); other data from Kennelley (5).

cathodic direction during this interesting current behavior. The full description and explanation of this current loop behavior is beyond the scope of this paper and will be published in subsequent papers.

The active-passive behavior has been shown in other studies to lead to widely different corrosion rates dependent on the potential of the metal. Linear polarization experiments for steel in CMA solutions exhibit this type of behavior (see Table 8). The corrosion rates for the steel at passive potentials were about two to three orders of magnitude less than the corrosion rates of the steel at an active potential in the same solution. The corrosion rates of the steel at active potentials, as determined by linear polarization, were higher than the rates determined by weight loss but were of the same order of magnitude.

These different rates are probably due to different surface conditions as a consequence of exposure times. The weight loss samples were exposed to the solutions for 17 months, and substantial amounts of protective corrosion products accumulated on the surface. The samples used in linear polarization experiments were exposed with a clean surface and initial corrosion rates were therefore measured. The initial rates can be expected to be higher than those measured with protective corrosion product layers in place.

TABLE 9 POTENTIALS OF REBAR IN SIMULATED PORE SOLUTIONS AS A FUNCTION OF CI⁻ AND CMA CONCENTRATION

CI ⁻ Content in	CMA Concentration, Weight (%)					
Mortar Sample (%)	0.0 (mv)	0.5 (mv)	2.0 (mv)	10.0 (mv)		
0.0	-178	-312	-292	-601		
0.036	-179	-300	-340	-671		
0.18	-249	-301	-319	-667		
0.4	-235	-393	-336	-648		
0.6	-328	-406	-480	-619		
1.0	-557	-450	-486	-651		

NOTE: Potentials versus saturated calomel electrode (SCE).

Steel in Concrete

Potentials of steel samples made from reinforcing steel immersed in simulated pore solutions are given in Table 9. The potentials of the solutions containing no CMA are in the passive region except for the ones containing chloride ions in an amount equivalent to 0.6 and 1.0 percent by weight in a mortar sample. The accepted value of the active-passive difference for steel in concrete is -275 mv with the saturated calomel electrode (-350 mv with the copper-copper sulfate). All samples containing CMA were at an active condition. The potentials shown in Table 9 were taken after several months' exposure in the solutions.

Table 10 contains the potential of reinforcing steel in mortar samples that had been soaked in a CMA solution for several months. All potentials were in the same range as the potentials of the pore solutions containing 10 percent CMA, which indi-

TABLE 10 POTENTIALS OF REBAR IN MORTAR CYLINDERS SOAKED IN A CMA SOLUTION

C ⁻ Content in Mortar Cylinder (%)	Potential (mv) Versus Cu/CuSO ₄			
0.0	-701 -697			
0.036	693 680			
0.18	669 704			
0.4	672 697			
0.6	694 671			
1.0	760 636			

Locke et al.

cated the CMA had reached the rebar surface. All potentials were in the active range.

Table 11 contains the potential and corrosion current data taken from the concrete slabs on which different solutions were ponded. These data are quite scattered and varied. They do indicate that the amount of corrosion current is dependent upon two main factors: (a) the potential difference between the top and bottom mats of steel and (b) the presence or absence of the epoxy-coated bars. In all slabs on which CMA was ponded except three, it appears that the CMA had not reached the top mat of steel. In one slab with both mats bare and salt in the top portion of the concrete, the potential of the top mat was in the same range as that found for the mortar samples. Similar results were found in both slabs with the top mat of epoxy-coated bars and salt in the top portion of the slab. In several of the slabs on which chloride-containing solutions were ponded, similar shifts were also found.

In a few slabs the bottom mat potential was shifted into the active range with the top mat remaining in the passive range. This result can be explained by channels that were left in these slabs during preparation. The solutions could then reach the bottom mats in preference to the top mat, which would produce the observed results.

CONCLUSIONS

Steel exposed to CMA solutions behaves like an active-passive metal. If it were possible to maintain the steel in a passive condition, CMA would be an inhibitor. The conditions under

		Тор	Bottom	Potential	Corrosion
Potential vs	Ponding	mat	mat	difference	current
Cu/CuSO ₄	Solution	(mV)	(mV)	(mV)	(mA)
Тор ероху	CMA	-254	-21	233	0.007
Bottom epoxy		-13	-12	1	0.0002
Top bare	CMA	-136	-17	119	0.033
Bottom bare		-208	-151	57	0.027
Тор ероху	CMA	-27	-24	3	0.0002
Bottom bare		-19	-20	-1	-0.0003
Top epoxy-salt top	CMA	-28	-25	3	0.0003
Bottom epoxy		-51	-23	28	0.0008
Top bare-salt top	CMA	-51	-105	-54	-0.0065
Bottom bare		-677	-46	631	1.50
Top epoxy-salt top	CMA	-740	-96	644	0.70
Bottom bare		-656	-24	632	0.97
Тор ероху	NaC1	-547	-344	213	0.008
Bottom epoxy		-505	-158	347	0.083
Top bare	NaCl	-185	-327	-142	-0.238
Bottom bare		-401	-102	299	0.325
Тор ероху	NaCl	-266	-80	186	0.036
Bottom bare		-514	-147	367	0.70
Тор ероху	CaCl ₂	-488	-394	94	0.072
Bottom epoxy	2	-107	-459	-352	-0.072
Top bare	CaCl ₂	-38	-36	2	0.0009
Bottom bare	2	-118	-85	33	0.008
Тор ероху	CaCl ₂	-89	-100	-11	-0.0025
Bottom bare	4	-294	-85	209	0.087

TABLE 11 FINAL POTENTIAL AND CORROSION-CURRENT DATA FROM THE CONCRETE BLOCKS

which metals would be exposed to the CMA as a deicer, however, are such that the metal would likely be in an active condition.

The active corrosion rates for the CMA solutions tested are about two to four times less corrosive than the corrosion rates of steel in sodium chloride. The corrosion rates of steel in calcium chloride and tap water were found to be both higher and lower than those in CMA solutions dependent upon the exposure conditions. Cast iron in the CMA solutions corroded at a rate about half that in the sodium chloride solutions. Aluminum in most of the CMA solutions did not have a measurable corrosion rate but was pitted by all concentrations of CMA. Aluminum was also pitted by the chloride-containing solutions.

Therefore, CMA used as a deicer should result in a lower corrosion of the exposed metals in bridge structures. Expansion joints, bridge railings, metal beams, and metal piers should last longer if CMA is substituted for sodium chloride. Automobile bodies may also be corroded less by CMA than by the sodium chloride deicer.

The effect of CMA on the corrosion of reinforcing steel would possibly not be substantially different from that of sodium chloride. The most damaging factor in the effect of sodium chloride is the corrosion currents forced as a result of potential differences between the steel in the decks. Large potential differences have been found across the surface of the top mat caused by uneven diffusion of the chloride ions to the top mat surface, and potential differences exist between top and bottom mats. The resulting macro cells are thought to be the reason the corrosion rates of the reinforcing steel in bridge decks have been high enough to cause costly damage in a short time.

The potential of steel in portland cement mortar and in simulated pore solutions shifts to active values greater than -600 mv by CMA. This is a result of changes in the pore solution composition. This shift in rebar potential caused by the presence of CMA can lead to the same sort of potential difference for reinforcing steel in bridge decks as that found with NaCl as a deicer. However, the diffusion rates of CMA compared to NaCl are not known. Other studies are therefore necessary to determine if the possibilities found in this study will be a serious problem.

In conclusion, CMA will corrode exposed metals less than will sodium chloride, but there may be little difference in the corrosion of reinforcing steel when CMA is used.

ACKNOWLEDGMENT

The authors would like to acknowledge the support the Federal Highway Administration for this project.

REFERENCES

- F. O. Wood. Survey of Salt Usage for Deicing Purposes (R. Baboian, ed.). Automotive Corrosion by Deicing Salts. National Association of Corrosion Engineers, Houston, Tex., 1979.
- J. Hale. Proceedings of the Northstar Workshop on Noncorrosive Winter Maintenance. Report No. FHWA/MN/RD-84/03, Minnesota Department of Transportation, St. Paul, 1983.
- 3. America's Highways: Accelerating the Search for Innovation. In Special Report 202: America's Highways: Accelerating the Search for Innovation. TRB, National Research Council, Washington, D.C., 1984.
- S. A. Dunn and R. U. Schenk. Alternative Highway Deicing Materials. Bjorksten Research Lab, Inc., National Information Service, Springfield, Va., 1980.
- K. J. Kennelley. Corrosion Electrochemistry of Bridge Structural Metals in Calcium Magnesium Acetate. Ph.D. dissertation. University of Oklahoma, Norman, Okla., 1986.
- 6. M. D. Boren III. The Effect of Calcium Magnesium Acetate on the Corrosion of Reinforcing Steel in Concrete. M.S. thesis. University of Oklahoma, Norman, Okla., 1986.
- 1979 Annual Book of ASTM Standards, Part 10, Metals—Physical, Mechanical, Corrosion Testing. (R. P. Lukens et al., eds.) American Society for Testing and Materials, Philadelphia, Pa., 1979.
- Test Method TM-01-69. National Association of Corrosion Engineers, Houston, Tex., 1969.
- V. G. Luster. Corrosion Electrochemistry of Steel and Aluminum in Various Deicing Salts. M. S. thesis. University of Oklahoma, Norman, Okla., 1985.
- H. Farzammehr. Pore Solution Analysis of Sodium Chloride and Calcium Chloride Containing Cement Pastes. M.S. thesis. University of Oklahoma, Norman, Okla., 1985.
- C. E. Locke and K. J. Kennelley. Corrosion of Bridge Structural Metals by CMA. Final Report, FHWA Contract DTFH 61-83-0045, Washington, D.C., June 1986.

Publication of this paper sponsored by Committee on Corrosion.