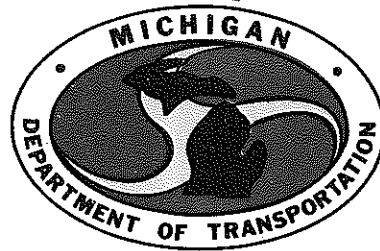


MICHIGAN DEPARTMENT OF TRANSPORTATION
M•DOT

CORROSION AND ALTERNATE DEICERS
Interim Report



MATERIALS and TECHNOLOGY DIVISION

MICHIGAN DEPARTMENT OF TRANSPORTATION
M•DOT

CORROSION AND ALTERNATE DEICERS
Interim Report

Ronnie L. McCrum

Research Laboratory Section
Materials and Technology Division
Research Projects 82 G-259 and 88 G-271
Research Report No. R-1315

Michigan Transportation Commission
Barton LaBelle, Chairman;
Charles Yob, Vice-Chairman;
William C. Marshall, Hannes Meyers, Jr.,
Irving Rubin, Richard White
Patrick Nowak, Director
Lansing, October 1991



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ACTION PLAN

1. Materials and Technology Division

- A. Distribute copies of report to Maintenance and districts with cover letter indicating how this shows that field corrosion performance of alternate deicers may not be as good as the laboratory results that most manufacturers use to declare their product a 'proven' success.**

2. Engineering Operations Committee.

- A. No action necessary upon approval of this report.**

ABSTRACT

Sodium chloride (NaCl) has long been used as a deicing agent for highways, due to its ready availability, low initial cost, and adequate performance as a deicer. NaCl, however, produces a highly corrosive environment for all metals used in the highway system, has a damaging effect on concrete that is exposed to repeated freezing and thawing, and in large enough quantities can pose environmental problems. Estimates of the damage done by NaCl have ranged from roughly 6 to 40 times the initial cost of the salt with most (usually 90 percent or more) of the economic damage being associated with corrosion. The high ultimate cost of salt has prompted a market of alternate deicers that are cost competitive with the 'true' cost of NaCl. While laboratory testing of these products can be indicative of what field performance may be, many variables that cannot be easily added in a laboratory setting can influence real world results. Current results of both laboratory and field testing performed by the Michigan Department of Transportation are summarized for a number of alternate deicers. Differences between the field results and reported laboratory results necessitate a discussion of some of the factors that can make the real world vastly different from a laboratory environment and stress the need for more widespread use of realistic field testing of the corrosion performance of alternate deicers.

INTRODUCTION

Starting in the 1950's Michigan, as most northern states, began implementing a 'bare pavement policy' for winter road maintenance that has continued to this time on certain high priority heavily traveled routes. While rock salt (NaCl) is relatively abundant and, at least initially, a very cheap deicer that effectively provides bare pavements for safe winter driving, it is by no means cheap in the long run. The salt-accelerated corrosion of vehicles, bridges, guardrail, sign structures, and reinforcing steel in concrete (with resulting concrete deterioration) has led to ever increasing maintenance costs. As salt is washed from the roadways it infiltrates the surface waters and underlying ground water. In sufficient quantities, salt can pose health problems for humans, animals, and plants. The possibility of gradually increasing chloride (and sodium) levels in the ground water has been the subject of continuing investigations.

In the mid-seventies estimates of the damage done by salt ranged from 6 to 20 times its cost. The lower estimate comes from a report sponsored by the Salt Institute (1) and the higher estimate from a report sponsored by the U. S. Environmental Protection Agency (2). Some more recent estimates put the figure as high as 40 times the cost of salt (3).

To aid in solving the problems created by rock salt, the Federal Highway Administration (FHWA) sponsored research (4) to find an alternate deicer that could be produced at less cost than the monetary amount of the damage done by salt. Calcium magnesium acetate (CMA) was identified

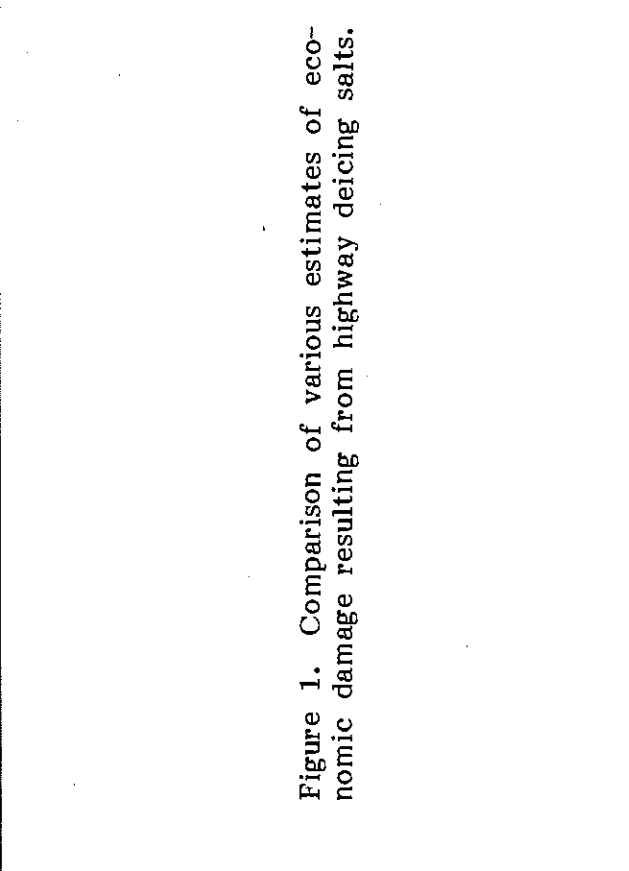
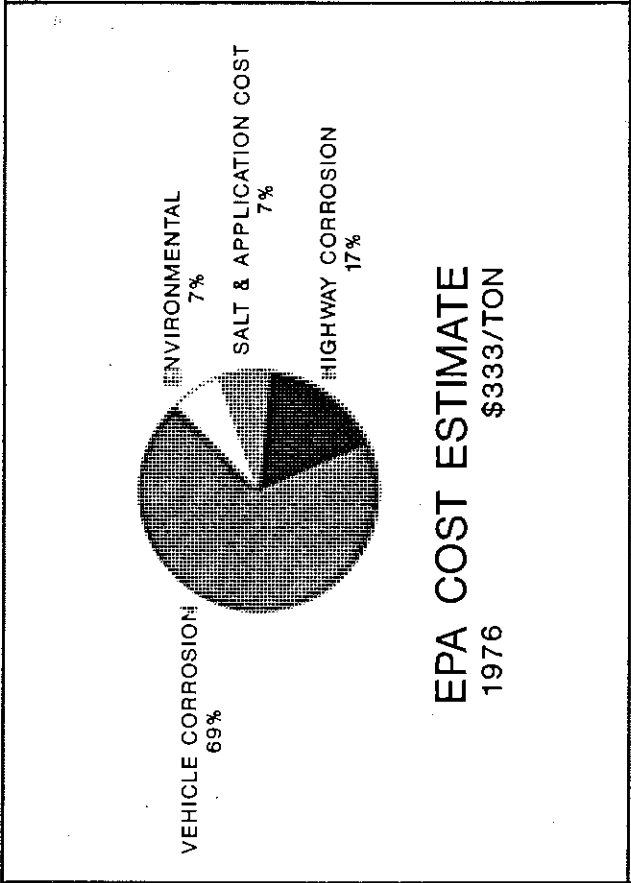
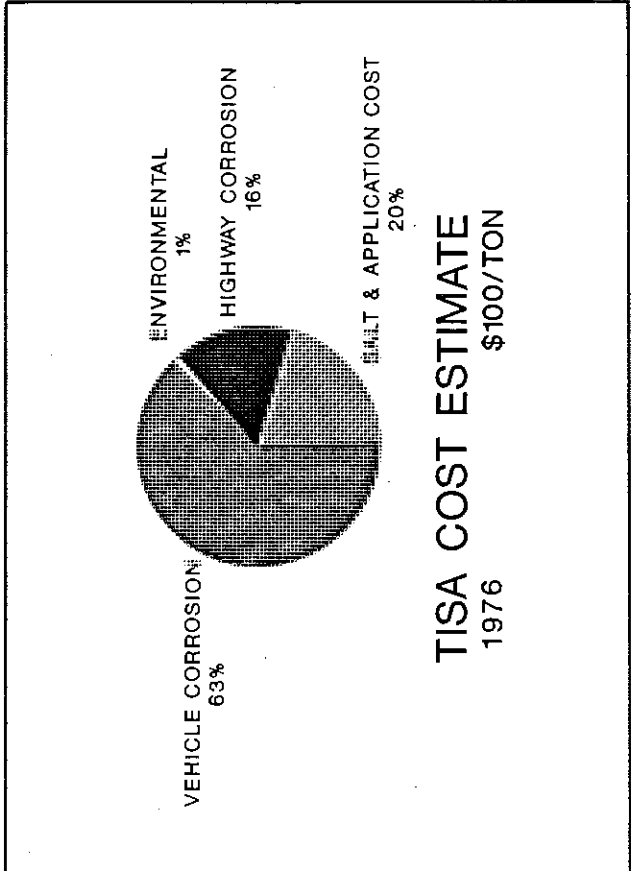


Figure 1. Comparison of various estimates of economic damage resulting from highway deicing salts.

from this research as one of the most viable candidates. Although much more expensive initially CMA, unlike NaCl, tends to inhibit corrosion and appears to be relatively harmless to the environment.

Given the high price of CMA and the relatively small percentage of the cost of salt-induced damage usually associated with environmental damage (Fig. 1), a number of corrosion inhibited salts have been proposed, principally by salt companies, as possible alternate deicers. Most of these inhibited salts do not cost much more than six times the cost of salt and, hence, may be more likely to result in actual savings (providing, of course, that these products actually reduce real world corrosion by a significant amount and are not damaging to the environment). Whether or not CMA can be cost effective depends on what the actual cost of the damage is and the relative importance of environmental concerns. Up-to-date estimates of salt-induced damage are presently being pursued in FHWA sponsored (as well as other) research efforts.

To be a viable candidate as an alternate deicer, a product must satisfy a number of requirements. Since a significant economic and safety advantage (1) is gained by road salting, no sacrifice in deicing ability can be tolerated. Since the major cost of salt, at least in currently available estimates, is the corrosion damage (Fig. 1), any alternate deicer must result in significant reductions in corrosion (preferably in the presence of salt since some residual salt would still be present for some years even with a complete replacement of deicing salt). Since most state (county, city, etc.) highway departments have limited budgets and vast responsibilities other than road salting, and alternate deicers are expensive, the cost of an alternate deicer must be 'reasonable.' It must be either within the limits of savings that can be achieved by the highway department through the use of the alternate deicer or within the limits of this savings combined with whatever additional funding the existing political climate can justify and provide. Additionally, an alternate deicer should not induce other problems with either economic, safety, or environmental consequences that could significantly reduce its potential savings.

While corrosion performance is a major concern of an alternate deicer and the principal intended topic of this writing, the other requirements are also important and worth some discussion in the text that follows.

Michigan's corrosion evaluation of alternate deicers started in the early eighties with accelerated laboratory testing and, given some of the concerns about how well the laboratory environment can simulate the real world, has gradually advanced to more realistic field testing. While accelerated laboratory testing can give quicker answers, correct answers are of primary importance given the high cost of alternate deicers. Before one invests the possibly millions of additional dollars for an alternate deicer there should be no question about how well it works and whether or not it may have adverse consequences that complicate its use.

PROCEDURE

Laboratory Evaluation

Laboratory testing has been done using solutions of highway deicing salt (NaCl), calcium magnesium acetate (CMA), four different mixes of salt and CMA, distilled water, simulated acid rain, Freezegard + PCI (Polymeric Corrosion Inhibitor), and Quicksalt + PCL.

Specimens were selected to represent most of Michigan's currently used highway structural metal applications with special attention being given to those most directly exposed to highway deicing salts. While painted bridge steels, bar reinforcement for concrete, aluminum alloys, galvanizing, guardrail materials, and a few galvanic couples were also tested, the results for only the following groups of metals will be discussed in detail here.

1) Bridge Steels:

ASTM A572, A588 (weathering steel), A588 previously exposed to NaCl environment, and A36 for both open and 'sheltered' (tensile specimens only) exposures.

2) Prestressing Strand (more elaborate testing was performed in the NaCl and CMA exposure environments):

ASTM A416 Grade 270.

In almost all cases, four essentially identical specimens were prepared from each material for both the CMA and NaCl test environments. For the other test environments, typically only three specimens were used. For several of these other tests, however, a fourth specimen was added to the exposure environment near the end of a test to help assess what effect, if any, the buildup of corrosion products and intermediaries (in the test solution) might have on the observed differences in corrosion rate with time (i.e., corrosion passivation). Sizes of the specimens are such that the total surface area of a specimen may vary from 20 to 35 sq in. The bridge steels were sand-blasted to remove all mill scale and surface oxide. All specimens were cleaned, weighed and measured.

For the CMA and NaCl test environments, the prestressing strand specimens were placed inside lengths of heavy electrical conduit, two strands to a conduit. The conduit provided both a dark, continuously moist environment that would more closely match the worst environments to which such strands might actually be exposed, as well as a support frame which would allow the strands to be tensioned to typical service loads. For each conduit, one strand was loaded in tension to approximately 70 percent of ultimate strength (28,900 lb or 13,110 kg) and end-anchored, while the other strand was left unloaded. Specimens were removed for evaluation at three and six months. For the other solutions, freely exposed 1-ft lengths of strand were used.

A weathering chamber was constructed to house the specimens for exposure to the various test environments (Fig. 2). Separate tanks held the CMA and NaCl solutions. For the other test solutions the tanks were subdivided with plexiglas partitions so that four different solutions could be tested at the same time. A common shaft rotating at intervals (1/6 turn every hour) periodically submerged the specimens. Rotation rate of the shaft was such that four complete revolutions were made each day. Dimensions of the chamber and the fluid level within the tanks were such that the specimens were submerged for approximately one-third of the time. For the CMA and NaCl exposures sufficient specimens of most materials were prepared to allow removal at intervals of three months for a year. For the other test environments, typically three specimens of each material were prepared for removal at approximately one-month intervals (the actual interval between specimen removals varied considerably as manpower was not always available at the preplanned removal dates).

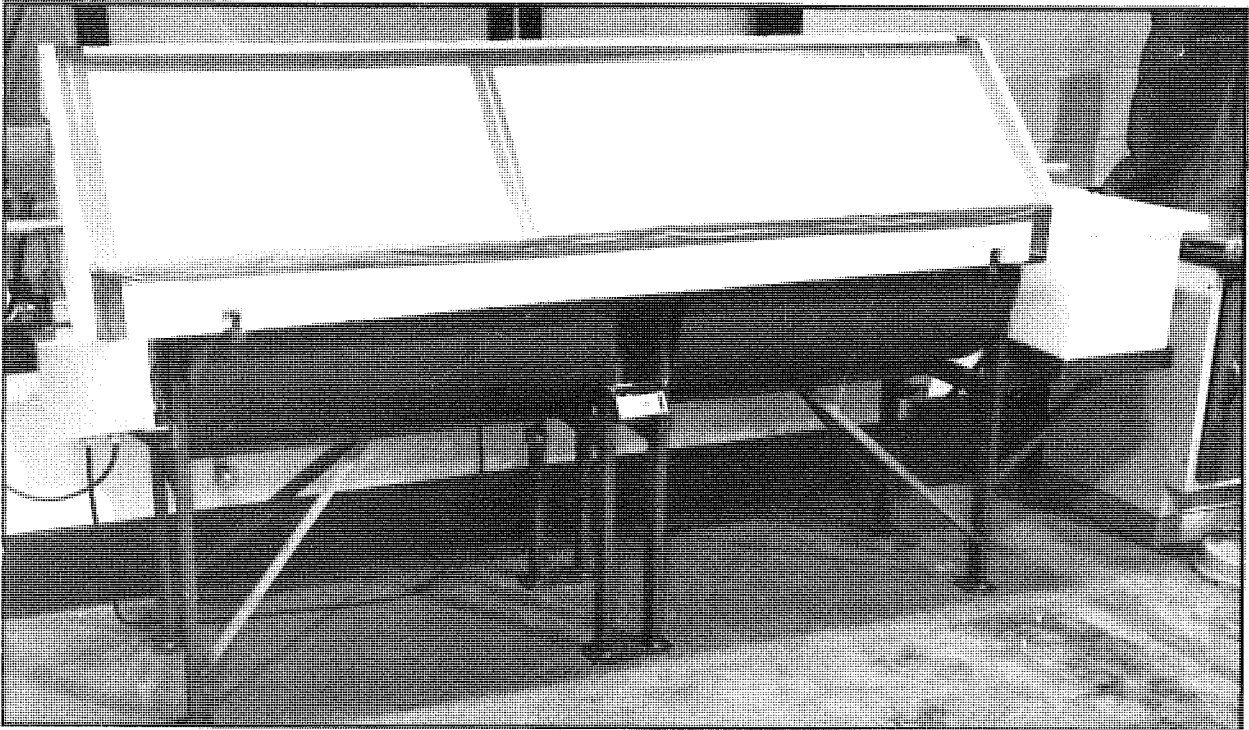
The common hood for both tanks houses ultraviolet lamps to simulate sunlight, and heating units to maintain an elevated temperature (approximately 115 to 120 F). The elevated temperature, and, to some extent, the simulated sunlight both aided in drying the specimens before the next wetting and helped accelerate corrosion so that differences between the test solutions would be more apparent. This type of environment constitutes what is typically referred to as a marine beach exposure.

Specimens were degreased with an organic solvent prior to being mounted on rods projecting from the common rotating shaft. Almost all specimens were mounted on the ends of the rods. Exceptions to this were the prestressing strands and the bridge steel tensile specimens. These specimens were attached to the sides of the rods either directly or indirectly to epoxy coated metal straps connected to the rods on adjacent rows. These specimens being located under the other specimens and at a lower position on the rods were subjected to a slightly different--more sheltered and damp--environment. Temperature and humidity stratification within the test chamber, as well as reduced direct light exposure, contribute to these particular specimens staying damp for a greater share of the time. These specimens were inadvertently subjected to what would roughly amount to a sheltered exposure environment.

Nylon fasteners with plexiglas clamps were used to mount the specimens in order to help electrically isolate the specimens from each other. This action helped to minimize the possibility of any galvanic (dissimilar metal) corrosion effects between different specimens.

Distilled water was used to both prepare all initial solutions and maintain fluid level within the tanks. Fluid level was maintained at a preset level to minimize changes in solution concentration that might result from evaporation.

Concentrations (by weight) for the CMA and NaCl solutions were initially set at 3.50 percent for NaCl and 6.125 percent for CMA. These represent



a) Enclosed—hood contains heating elements and ultraviolet lighting.



b) With hood removed and specimen exposed (in this instance with CMA on the left and NaCl on the right).

Figure 2. Weathering chambers used for laboratory evaluations.

concentrations that would have equivalent deicing (freezing point depression) abilities. Since a greater concentration of CMA must be used for equivalent deicing it seemed appropriate to reflect this difference in our exposure environments. Four different mixes of CMA and NaCl were also tested—concentrations by weight were 3.50 percent NaCl with 6.125 percent CMA, 1.6 percent CMA, 0.4 percent CMA, and 0.1 percent CMA.

Simulated 'acid rain' was prepared by making a solution of H_2SO_4 , $MgCl_2 \cdot H_2O$, $Ca(NO_3)_2 \cdot H_2O$, KOH, and MgO, that had a pH of 4.5 and the following ion concentrations (parts per million):

11 ppm SO_4^{--} ,	3 ppm Ca^{++} ,
9 ppm NO_3^- ,	1 ppm Mg^{++} ,
1 ppm K^+ , and	1 ppm Cl^- .

This solution represents the average composition of acid rain for a large number of different locations (5). This represents a one time exposure to acid rain since the concentrations were not maintained at, or returned to, this level but allowed to shift as corrosion occurred. In the real world, acid rain exposure can occur repeatedly (i.e., with each new rain).

Quicksalt + PCI was evaluated with the NaCl concentration at 3.50 percent. Freezegard was evaluated with the $MgCl_2$ concentration at 8.10 percent. The $MgCl_2$ concentration is the theoretical deicing (osmolar) equivalent of the 3.50 percent NaCl solution.

Groups of specimens were removed after approximately three or one-month intervals (initial testing was done for longer intervals than subsequent testing) depending on the solution involved for evaluation. The surface oxide was removed from all specimens in accordance with the appropriate procedure (for a given material) as specified in ASTM G1. All specimens were reweighed and weight losses determined. Knowing the original dimensions of the specimens, average corrosion rates and average corrosion losses were calculated.

For those specimens with relatively non-uniform pitting the worst pit depth was recorded for the freely exposed (open) surface. This value was in turn compared to the average corrosion rate to determine a pitting rate factor. For those specimens with noticeably different corrosion occurring around the area where the specimens had been gripped (crevice corrosion), the worst pit depth (crevice) was recorded.

Tensile specimens received the same evaluation treatment with the yield and tensile failure loads also being recorded. Comparisons of these values with those of control specimens and the initial size measurements allow one to make comparisons between the actual corroded strength (i.e., effective cross-section) and the expected corroded strength (i.e., projected or average cross-section) based on average corrosion losses.

This difference represents an indicator of the non-uniformity of pitting which, in turn, can significantly affect the corroded strength of small structural members.

The prestressing strand specimens (in the NaCl and CMA test environments only) were tested in tension to ultimate failure along with several control samples to determine losses in ultimate tensile strength.

Field Evaluation

Several different field evaluations relating to corrosion have either been performed or are in the process of being performed. The separate field projects have been arbitrarily designated as phases I, II, and III.

Phase I

United Salt's corrosion inhibitor was combined with regular deicing salt and used on one salt truck's regular route for one winter. Evaluation of this material included:

- 1) Subjective performance (as viewed by maintenance personnel using the material) as a deicing agent.
- 2) Effect on the rate of corrosion of reinforcing steel specimens placed in the concrete pavement.
- 3) Effect on the spalling/scaling rate of concrete specimens (both air-entrained and non-air-entrained) exposed to controlled freeze-thaw cycles in a laboratory environment. Several different ratios of inhibitor to NaCl were tested and compared to NaCl alone and CMA alone as well as several ratios of CMA to NaCl.

Phase II

This work is briefly summarized here since only partial results are currently available and it will be reported in full detail once all planned testing has been completed.

Metal specimens similar to those used in the Laboratory Evaluation have been placed on metal racks under selected highway bridges (i.e., a sheltered atmospheric environment with exposure to traffic spray).

Metal specimens selection, preparation, and placement follow roughly the same procedures as listed in the Laboratory Evaluation with the exception that flat rectangular racks were used to hold each group of specimens. The individual racks were placed between adjacent beams on the underside of similar bridges (i.e., similar traffic volumes) near traffic lanes. The racks were periodically (weekly) sprayed with solutions of the various alternate deicers being tested during the regular deicing season—late November to early March. While the racks would be exposed

to traffic-generated salt spray from below, the original intention was to have this amount of salt be only a small percentage of that added in the scheduled spraying. Salt wicks were placed on the racks to monitor the relative amount of salt received from the roadway and the planned spraying.

Individual racks were exposed to CMA, water alone, CMA/NaCl mixes, Freezegard + PCI, Quicksalt + PCI, NaCl alone, and several phosphate based inhibitor/salt mixes (i.e., United Salt's corrosion inhibitor, Domtar's TCI, and Cargill's CG-90 with and without surface saver). Only the first two groups (i.e., CMA and water alone) were placed on structures that did not have traffic below.

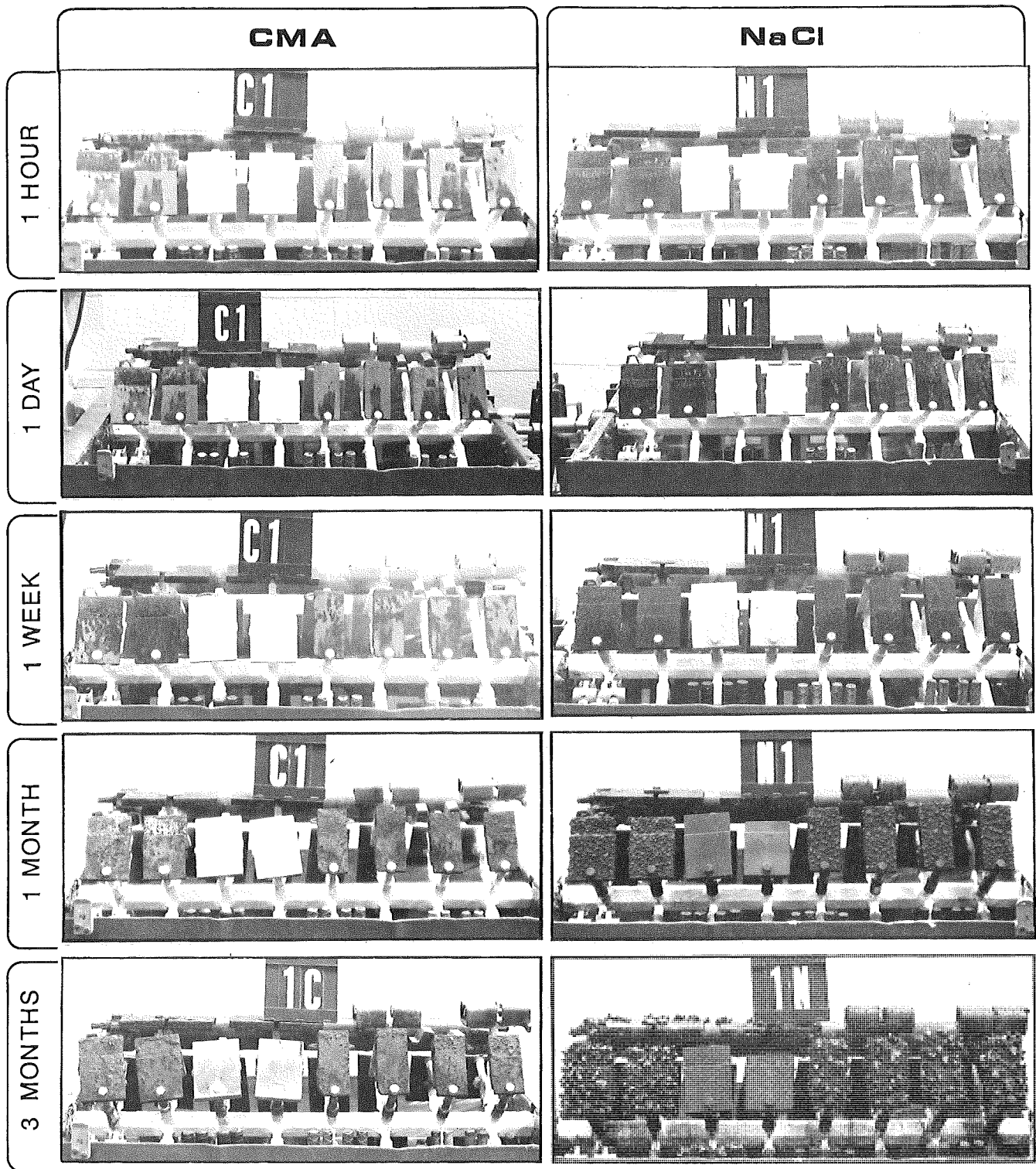
Salt wicks were removed periodically (monthly during salting season) and analyzed. Specimens were removed after one full year's exposure and cleaned and examined for average corrosion losses.

The salt contributed from the roadway was found to vary considerably with both position of specimens in rack and position of rack in structure as well as from one structure to another. Problems with the highly variable amounts of salt being received from the traffic spray will necessitate movement of the racks in future testing to ensure that the specimens are actually being exposed to the desired materials (i.e., proper inhibitor/salt ratio). While the salt wicks were intended to detect this problem so that corrections could be made relatively soon after first exposure of the specimens, a change in personnel doing the work resulted in the wick data not being correctly interpreted as early as would have been desirable.

Phase III

A number of simulated bridge deck slabs have been wired to a trailer-housed computer data acquisition system. The macrocell corrosion current between the top and bottom reinforcement mats is monitored by the computer system both before and after a given slab is exposed to a given alternate deicer. These slabs, left over from a previous project, have already been exposed to salt for some time (15-20 years) and have minor cracks extending from the 'deck' surface to some of the top mat reinforcement where active corrosion is taking place. This, along with a lack of an internal electrical connection between the top and bottom mats, makes these slabs ideal for providing an initial evaluation of many alternate deicers. While some of the alternate deicers will not penetrate intact concrete, such surface cracking often occurs early enough in the deterioration process that a substantial reduction in corrosion at this stage could result in a significant life extension of the affected deck.

Also of importance in deck performance is the relative ability of the alternate deicer (or corrosion inhibitor) to penetrate the concrete versus the penetration of the chloride ion; as well as the potential impact of the alternate deicer on future chloride ion penetration. While the project does not currently address this aspect of concrete reinforcement corrosion, some work of this nature may be added in the future.



Specimen identification: (left to right for both tanks)
 1) A588 welded lap-loose; 2) A588 welded lap-tight; 3) Painted A36 welded lap-tight; 4) Painted A36 welded lap-loose; 5) thru 8) A 588 previously weathered in a NaCl (highway) environment.

Figure 3. Visual time lapse comparison between the CMA and NaCl environments over the first three months.

RESULTS

Laboratory Evaluation

This work has been previously reported (6), hence, only some of the more interesting results will be discussed here. Those interested in the original work may obtain a copy of the research report (R-1295) from the Michigan Department of Transportation.

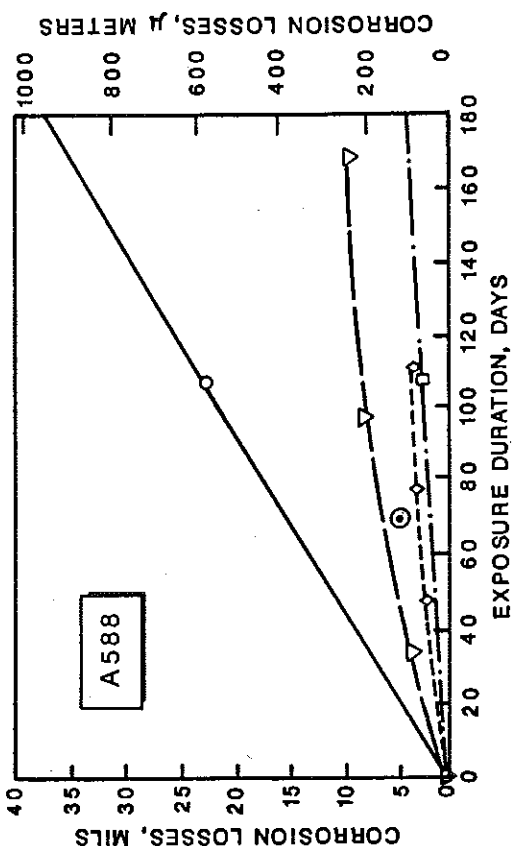
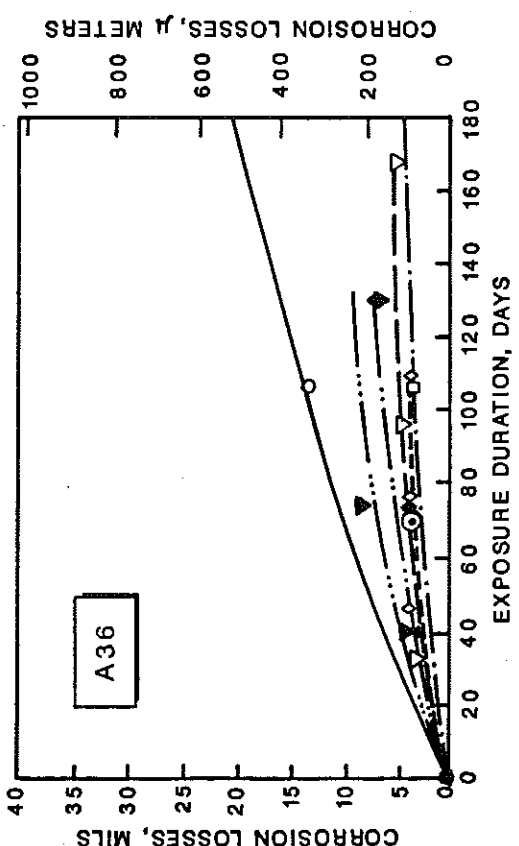
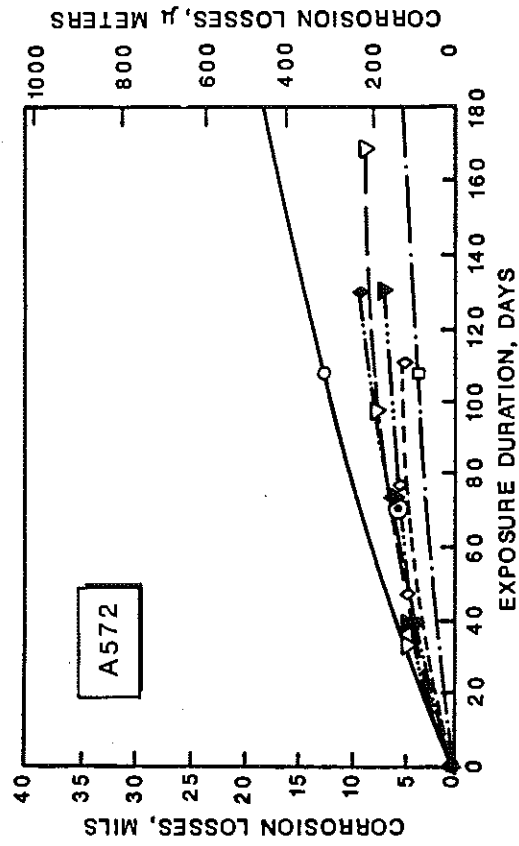
While the exposure environment used in this study is an accelerated weathering environment (i.e., marine beach), all specimens have been treated identically. Thus, relative differences observed between specimens are significant even though the absolute values may seem somewhat exaggerated.

Results for the CMA and NaCl exposures are discussed most intensively, with the results of all other exposures being compared against these references. Graphs, primarily, have been used to display the data since the corrosion rates for the various substances tested varied differently with time. This fact makes a single number comparison such as 'corroded twice as fast in NaCl' true for only one point in time and, hence, not as meaningful as would be desirable. For easier comparison between the various exposure environments, almost all graphs of a similar nature have identical or almost identical scaling of the coordinate axes.

Qualitative observation of the CMA and NaCl specimens from only several hours of exposure onward consistently indicated considerably worse corrosion occurring in the NaCl environment. Figure 3 illustrates the visual differences for initially identical sets of specimens in these two environments after one hour, one day, one week, one month, and three months.

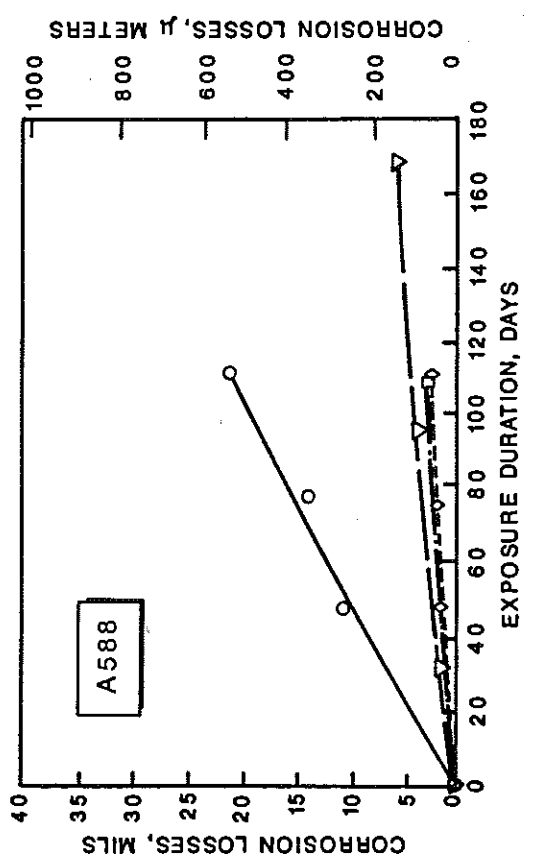
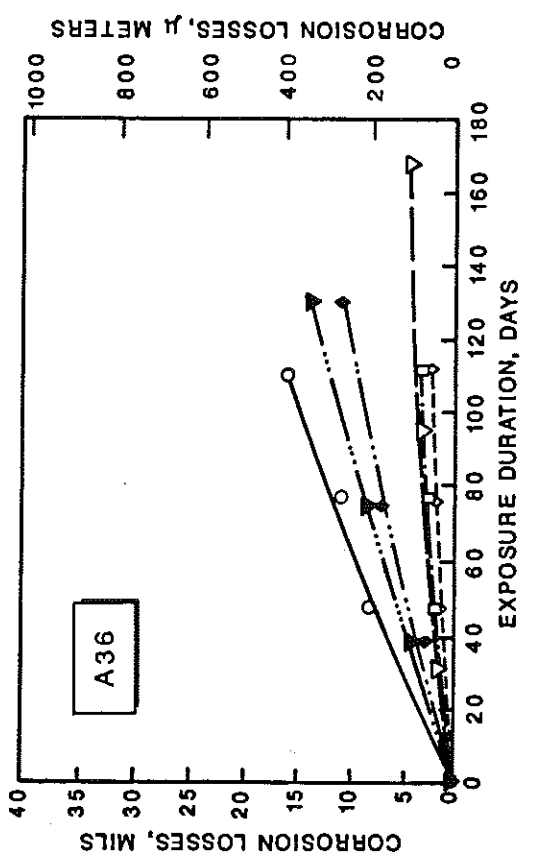
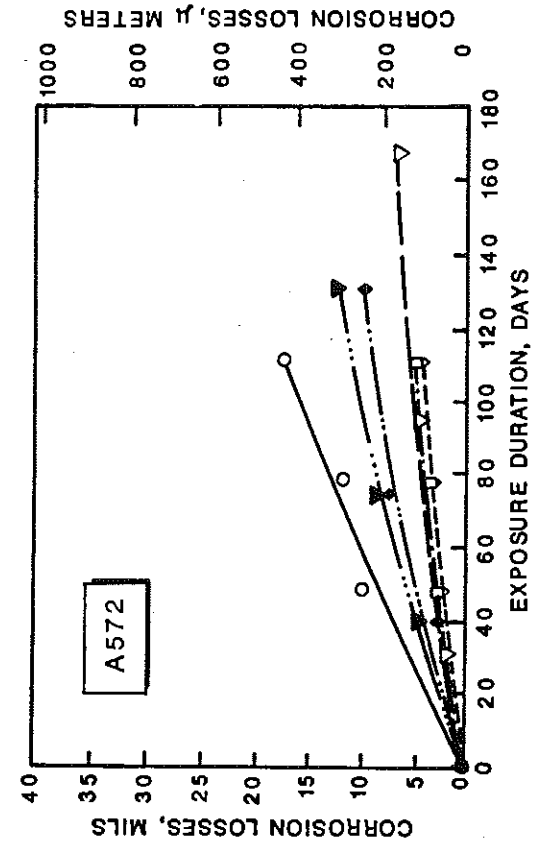
For the weathering environment used, the CMA weathered specimens, in general, experienced only about 1/3 to 1/6 the average corrosion of the similar specimens exposed to NaCl (Figs. 4 through 6).

Pitting, in general, was visibly and measurably worse for the weathering steels than for the other bridge steels in the NaCl environment and measurably better in the CMA environment. Worst pitting rates in CMA are in the 50 mils/year (127 micrometer/year) range after three months and in the 15 to 20 mils/year (38 to 51 micrometer/year) range after twelve months. Worst pitting rates in NaCl are in the 90 mils/year (230 micrometer/year) range after three months and in the 45 mils/year (115 micrometer/year) range after twelve months for ASTM A572 and A36 and in the 150 mils/year range after three months and in the 80 mils/year (203 micrometer/year) range after twelve months for ASTM A588. While the previously weathered A588 had worse pitting rates than the previously unexposed A588, this appears to be only a reflection of the previous pitting that had already taken place on these specimens. For both environments, A588 experienced noticeably more pitting and corrosion on the sheltered side (surface not directly exposed to light during rotation).



- LEGEND**
- — NaCl, 3 1/2%
 - — CMA, 6 1/8%
 - ◇ — 6 1/8% CMA, 3 1/2% NaCl
 - ▽ — 1.6% CMA, 3 1/2% NaCl
 - ◆ — 0.4% CMA, 3 1/2% NaCl
 - ▲ — 0.1% CMA, 3 1/2% NaCl
 - ⊙ — 1.6% CMA, 3 1/2% NaCl, 71 DAYS OF EXPOSURE BUT FROM DAY 97 TO DAY 168

Figure 4. Average corrosion losses of bridge steels in CMA and NaCl and mixes (open exposure).

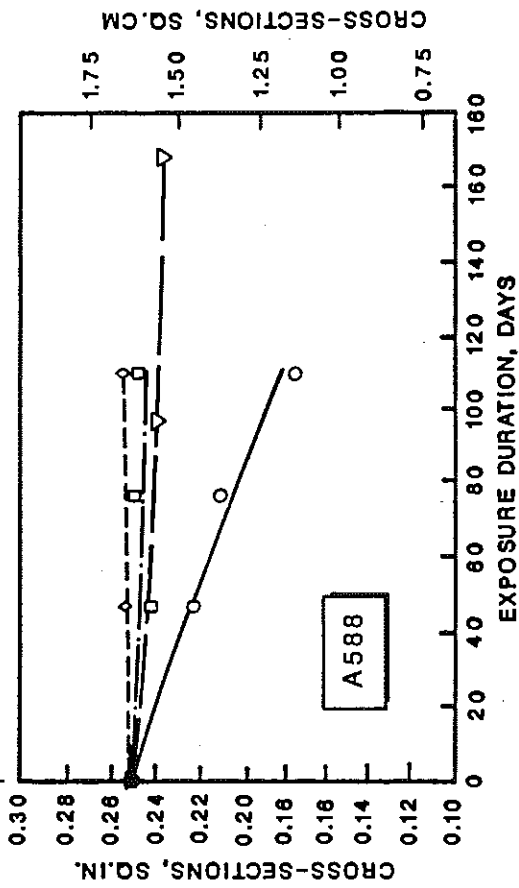
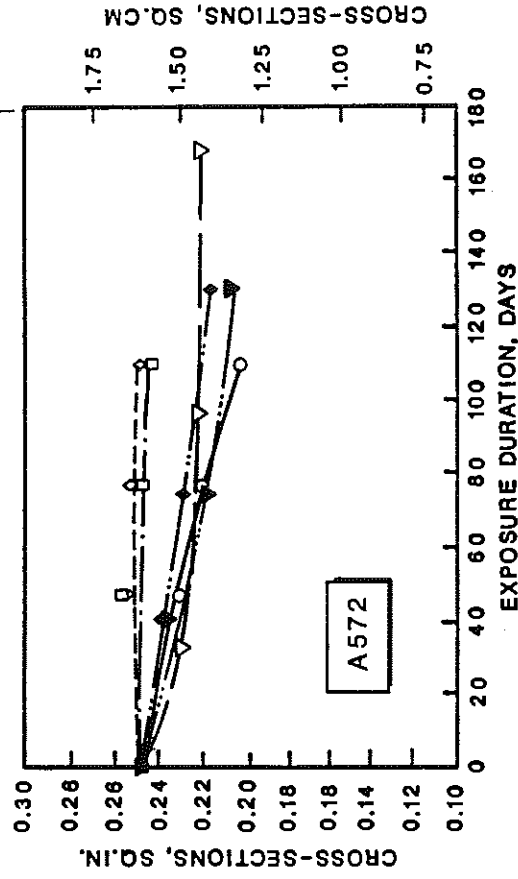
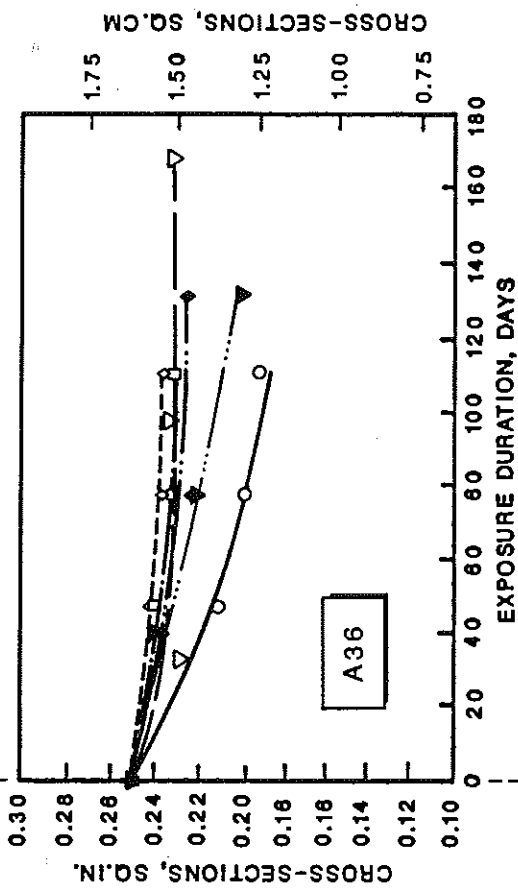


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — 6 1/8% CMA, 3 1/2% NaCl
- ▽ — 1.6% CMA, 3 1/2% NaCl
- ◆ — 0.4% CMA, 3 1/2% NaCl
- ▼ — 0.1% CMA, 3 1/2% NaCl

Figure 5. Average corrosion losses of bridge steel tensiles in CMA and NaCl and mixes (sheltered exposure).

EFFECTIVE

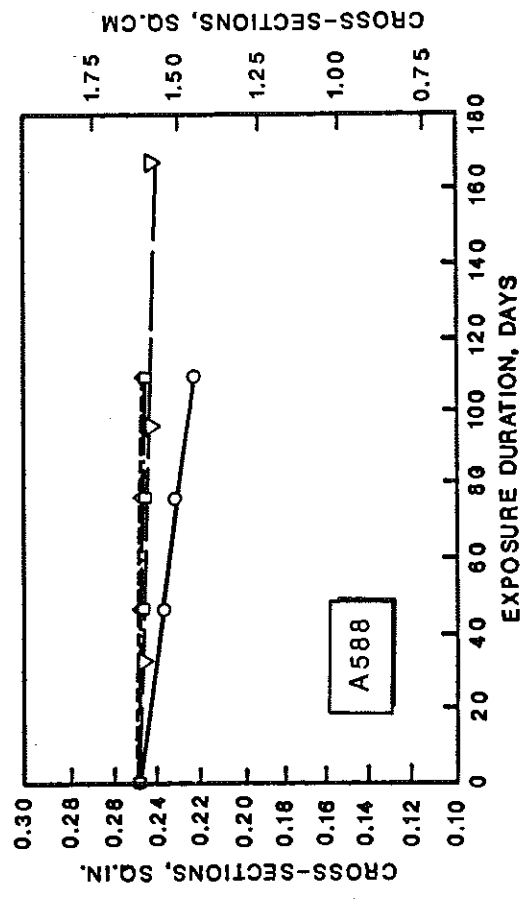
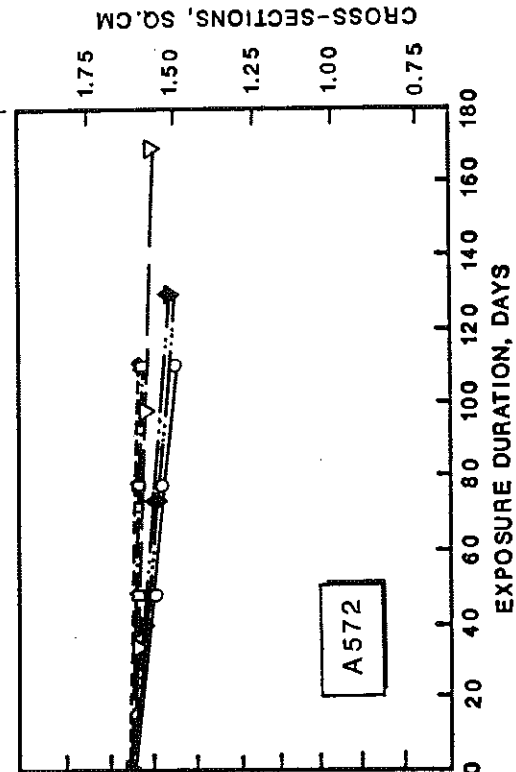
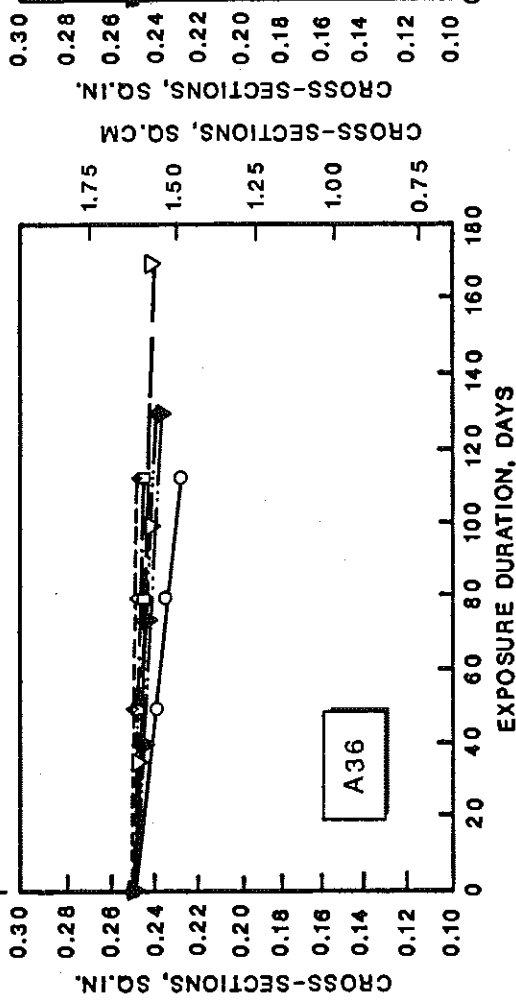


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — 6 1/8% CMA, 3 1/2% NaCl
- ▽ — 1.6% CMA, 3 1/2% NaCl
- ◆ — 0.4% CMA, 3 1/2% NaCl
- ▼ — 0.1% CMA, 3 1/2% NaCl

Figure 6. Effective and average cross-sections of bridge steel tensiles in CMA and NaCl and mixes (sheltered exposure).

AVERAGE



LEGEND

- - NaCl, 3 1/2 %
- - CMA, 6 1/8 %
- ◇ - 6 1/8 % CMA, 3 1/2 % NaCl
- ▽ - 1.6% CMA, 3 1/2 % NaCl
- ◆ - 0.4% CMA, 3 1/2 % NaCl
- ▼ - 0.1% CMA, 3 1/2 % NaCl

Figure 6 (cont). Effective and average cross-section of bridge steel tensiles in CMA and NaCl and mixes (sheltered exposure).

TABLE 1
STEEL STRAND FOR PRESTRESSED CONCRETE (ASTM A416) - CORROSION DATA

	Specimen	Strand ¹ Length, in.	Original		Weight Loss oz/%	Average Corrosion Rate (ACR), mils/yr surface	Ratio, $\frac{ACR, NaCl}{ACR, CMA}$	Worst Pit Depth, mils	Worst Pitting Rate (WPR), mils/yr/ surface	Ratio, $\frac{WPR}{ACR}$
			Surface Area, sq in.	Weight, oz.						
3 months	Tensioned									
	CMA	29.94	110.0	20.61	0.648/3.14	4.4	5.05	5	17.1	3.8
	NaCl	29.81	109.5	20.52	3.231/15.7	22.2		45	155	6.7
	Untensioned									
CMA	29.94	110.0	20.61	0.628/3.05	4.3	5.98	5	17.1	4.0	
NaCl	29.69	109.5	20.44	3.732/18.3	25.7		70	240	9.3	
6 months	Tensioned									
	CMA	29.88	110.0	20.56	1.111/5.4	4.1	3.44	10	18.3	4.5
	NaCl	29.50	109.0	30.31	3.825/18.8	14.1		60	110	7.8
	Untensioned									
CMA	30.13	110.5	20.74	1.171/5.6	4.3	4.30	10	18.3	4.2	
NaCl	29.63	109.5	20.40	5.021/24.6	18.5		100	185	10.0	

¹Center wire is 0.170 in. diameter and other wires are 0.164 in. diameter.

TABLE 2
STEEL STRAND FOR PRESTRESSED CONCRETE (ASTM A416) - PERFORMANCE DATA

	Specimen Environment	Ultimate Load, lb*	Reduction in Ultimate Load From Control Specimen lb/percent	Reduction From ASTM A 416 Re- quired Ultimate Load (41,300) lb/percent	Elongation, Percent
Control	No. 1	≥ 43,070			3-1/2
	No. 2	≥ 43,490			—
	No. 3	≥ 43,510			2
	Average	≥ 43,025			
3 Months	CMA Tensioned	≥ 40,675	~ 2,350/~ 5.45	≤ 625/≤ 1.5	3-1/2
	CMA Untensioned	≥ 41,700	~ 1,325/~ 3.10	Greater Than	4
	NaCl Tensioned	29,470	≥ 13,550/≥ 32.50	11,830/28.65	2-1/2
	NaCl Untensioned	27,160	≥ 15,865/≥ 36.85	14,140/34.25	4-1/2
6 Months	CMA Tensioned	40,720	≥ 2,305/≥ 5.4	580/1.4	4
	CMA Untensioned	≥ 40,420	~ 2,605/~ 6.1	≤ 880/≤ 2.1	4
	NaCl Tensioned	26,700	≥ 16,325/≥ 37.9	14,600/35.4	1
	NaCl Untensioned	22,140	≥ 20,885/≥ 48.5	19,160/46.4	0

*Some specimens failed in the grips and, hence, their true ultimate strength would undoubtedly have been higher. The uncertainty in these values is expressed in the table by the use of inequality signs where appropriate.

For the sheltered tensile specimens, worst pitting rates (worst pit depth/average corrosion rate) in NaCl are almost twice as large for ASTM A588 and A572 and almost four times as large for ASTM A36 than for the same materials when openly exposed. Worst pitting rates for these same materials in CMA are all roughly twice as large when sheltered.

Increases in the worst pit depth for the CMA exposed specimens, and to a lesser extent the NaCl exposed specimens, tended to decrease significantly for the later test intervals. This suggests the degree to which corrosion has a tendency to slow down or stop (passivate) at the original pit initiation sites and start up at new sites.

The large differences between the effective and average cross-section values for the tensile specimens demonstrate the inadequacy of using only average corrosion measurements for evaluating corrosion performance. While there is only a slight difference between the average cross-sections of the various bridge steels in NaCl and in CMA, there is a very noticeable difference between the effective cross-sections. The effective cross-sections of all of the bridge steels in CMA remain almost unchanged with continuing exposure duration while significant reductions occur in NaCl. While the deterioration of effective cross-section appears to accelerate with exposure duration for both A572 and A588 in NaCl, it appears to decelerate for A36. Changes in effective cross-section are also a measure, and probably a more important yardstick, of the tendency of corrosion to slow down or stop (passivate) at the original pit initiation sites. (While worst pit depth measurements give an indication of the spread or distribution of the tendency of corrosion to passivate or continue unabated, the effective cross-section gives an indication of the mean or general trend of behavior.)

The effective cross-sectional area differences between CMA and NaCl are especially noticeable in the prestressing strand (Tables 1 and 2 and Fig. 7).

The most significant result for the strand is the low ultimate strength of the NaCl weathered specimens. After three months, the value of one of the specimens is below 70 percent of the ultimate tensile strength, a normal working load, and the other is only marginally above it. After six months, both specimens were below 70 percent of ultimate strength with one of the specimens being just barely above 50 percent. While some losses in strength appear to have occurred for the CMA specimens, they are much smaller and are of approximately the same magnitude for both the three and six-month specimens.

While the strands exposed to CMA for six months showed essentially no change in ultimate strength from the three-month exposure batch, the corrosion loss measurements showed that they were continuing to corrode at close to the original three-month rate. Apparently corrosion had stopped (passivated) at the earlier sites and initiated at new ones. So even though metal loss continued, it occurred mostly at locations removed from the weakest area left by the initial three months of exposure.

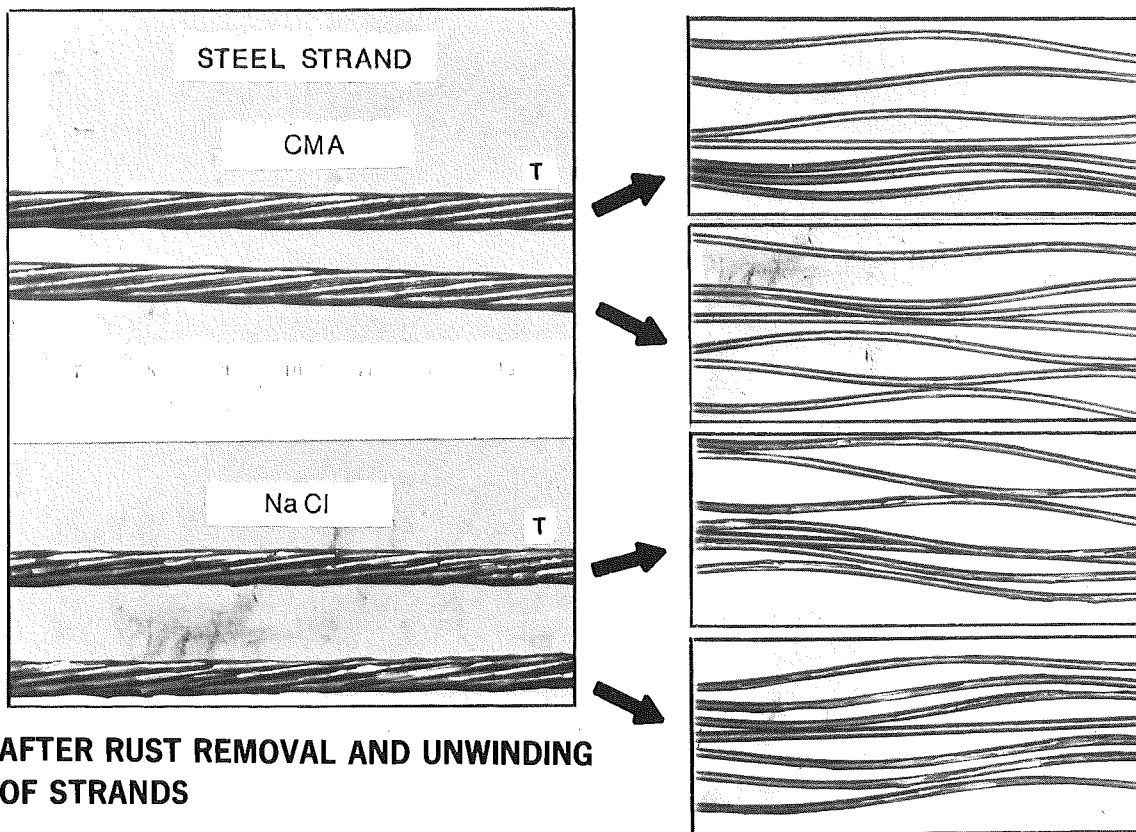
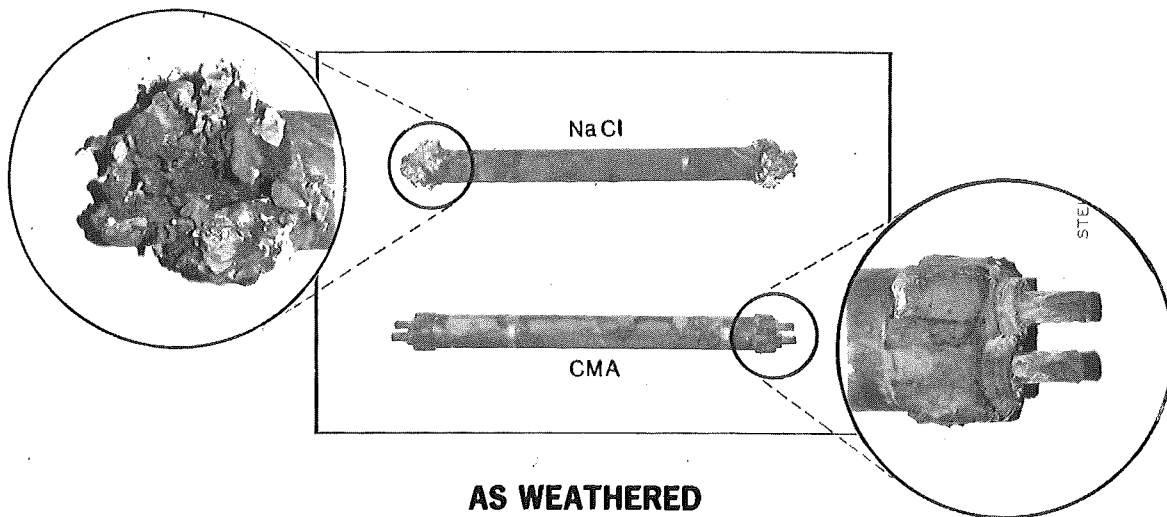


Figure 7. Steel prestressing strand for concrete after six months exposure in CMA and NaCl. (T indicates specimens that were under tensile load during exposure.)

For the NaCl exposure, the situation appears to be just the opposite. The additional losses in strength that occur during the second three months appear to be directly related to the additional corrosion losses. In other words, corrosion in the NaCl environment appears to continue essentially unabated in at least some of the original sites so that continued net section (strength) losses occur.

CMA and NaCl mixes (Figs. 4 through 6) performed much like pure CMA down to at least the 0.46 CMA/NaCl weight ratio (1.6 percent CMA and 3.5 percent NaCl solution). Lower weight ratio mixes still performed almost as well for the more openly exposed specimens, but performed almost as poorly as salt alone for more sheltered specimens (at least initially); longer exposure durations suggest that even at these low CMA/NaCl ratios there may be significant long-term benefits.

The results with CMA/NaCl mixes suggest that NaCl might be mixed with CMA to significantly reduce cost, yet retain almost all of the corrosion protection of CMA by itself. Projected price of such a mix may be as low as six times the price of the equivalent (for deicing purposes) amount of NaCl--almost 1/5 the current price of CMA alone.

Both distilled water and simulated acid rain (Figs. 8 through 10) were less corrosive than CMA by itself; with distilled water, naturally, being slightly less corrosive than the acid rain.

In general, average corrosion is less in both distilled water and simulated acid rain than in CMA alone for both open and sheltered exposures.

Worst pit depths are close to those of CMA alone for both distilled water and simulated acid rain with the acid rain being slightly worse than the distilled water. The average differences between distilled water and acid rain are smaller for the pit depth measurements than those for average corrosion.

The tensile specimens exposed to simulated acid rain appeared to experience a slightly greater loss in tensile strength than occurred in CMA alone. The values for distilled water alone were very close to those of CMA alone.

Freezegard + PCI (Figs. 11 through 13), in general, produced less average corrosion than the distilled water alone. Quicksalt + PCI (Figs. 11 through 13), in general, produced slightly greater average corrosion than CMA by itself, but considerably less than NaCl alone. Quicksalt + PCI performed similar to CMA/NaCl mixes.

CMA, Freezegard, and CMA/NaCl mixes provided more uniform pitting and consequently significantly smaller reductions in original strength (this is particularly relevant for objects with a small initial cross-section such as prestressing strand for concrete) and probably would result in better fatigue performance under cyclic loading as well.

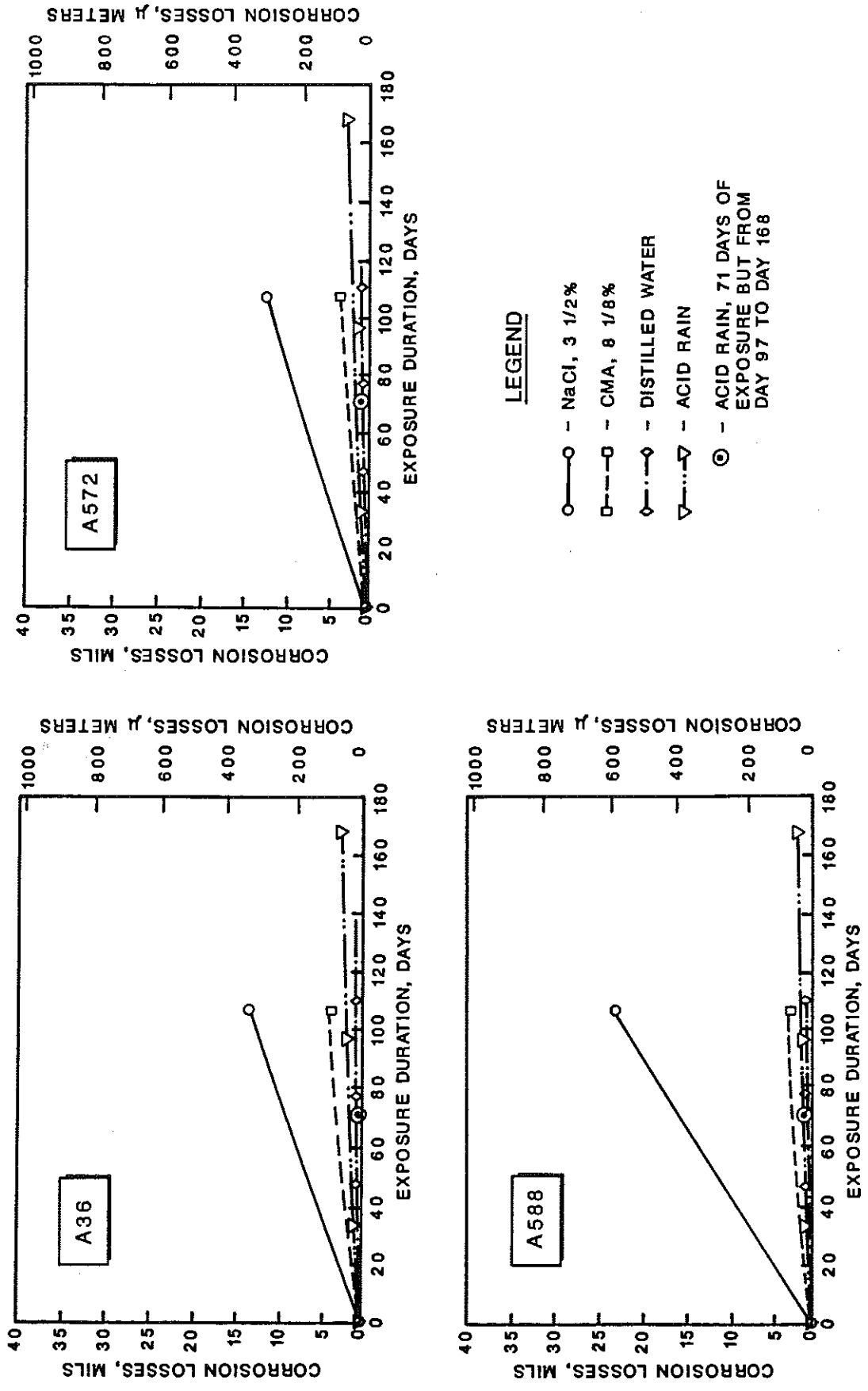
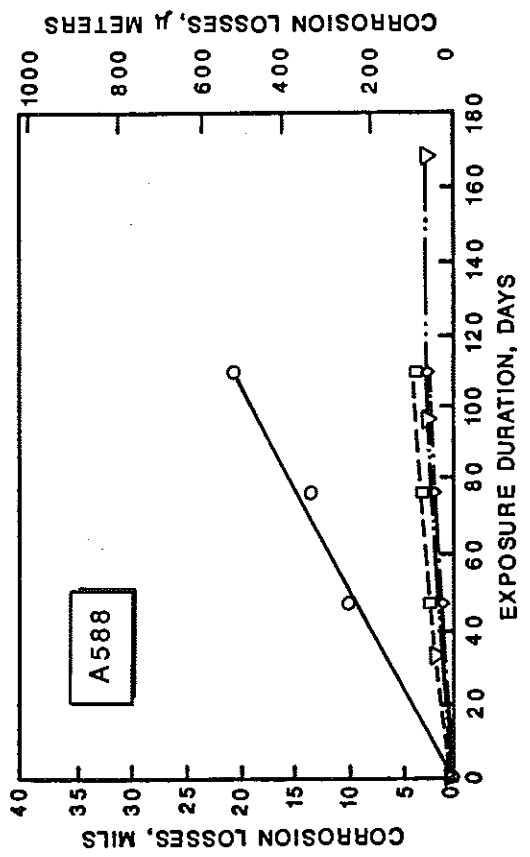
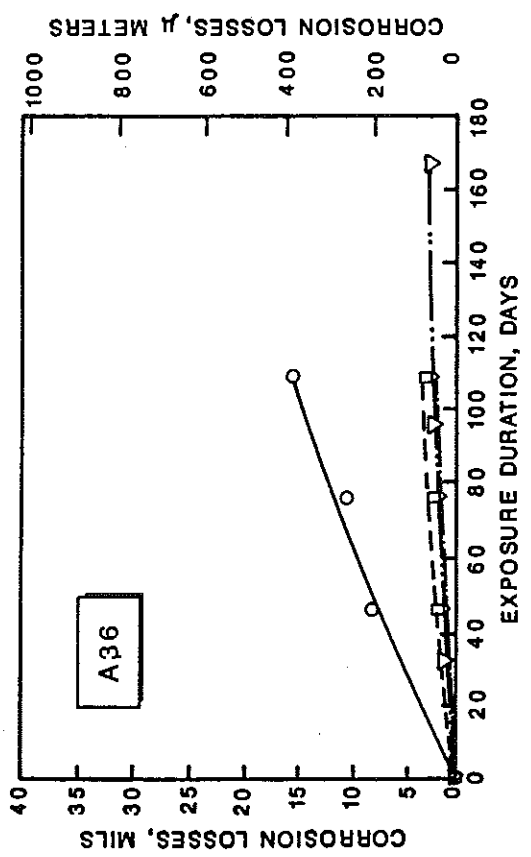
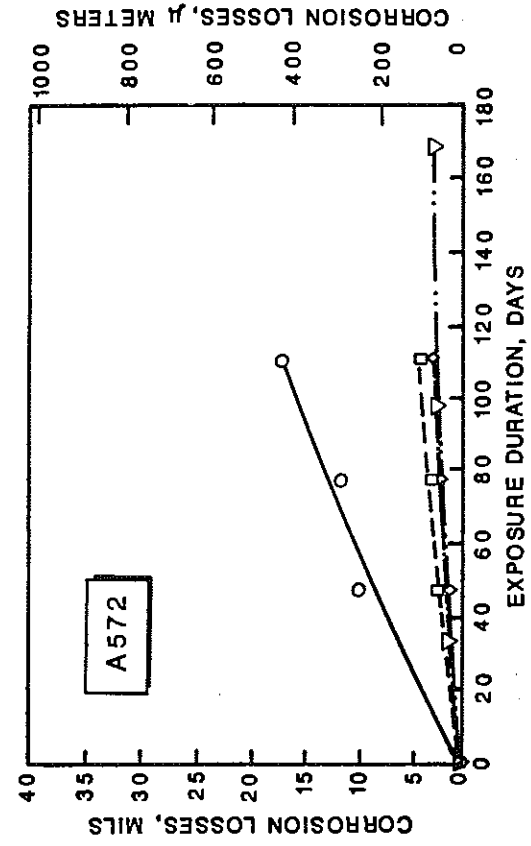


Figure 8. Average corrosion losses of bridge steels in distilled water and acid rain (open exposure).



LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — DISTILLED WATER
- ▽ — ACID RAIN

Figure 9. Average corrosion losses of bridge steel tensiles in distilled water and acid rain (sheltered exposure).

EFFECTIVE

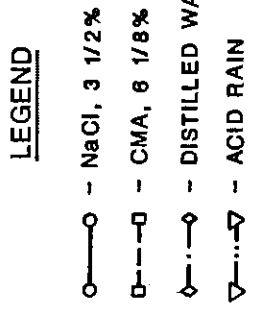
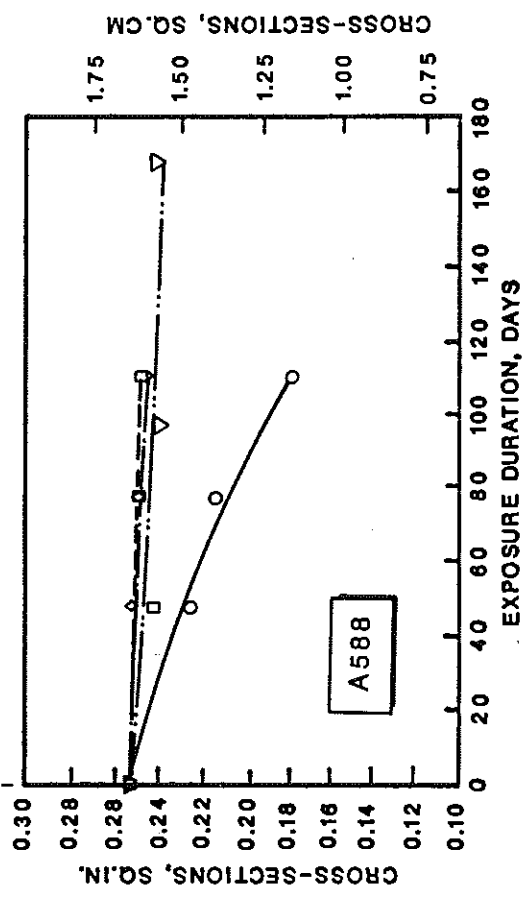
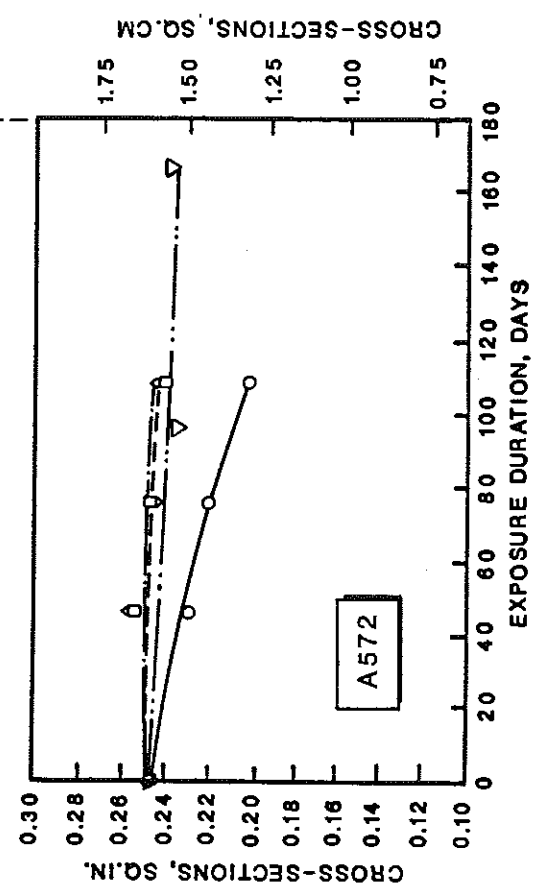
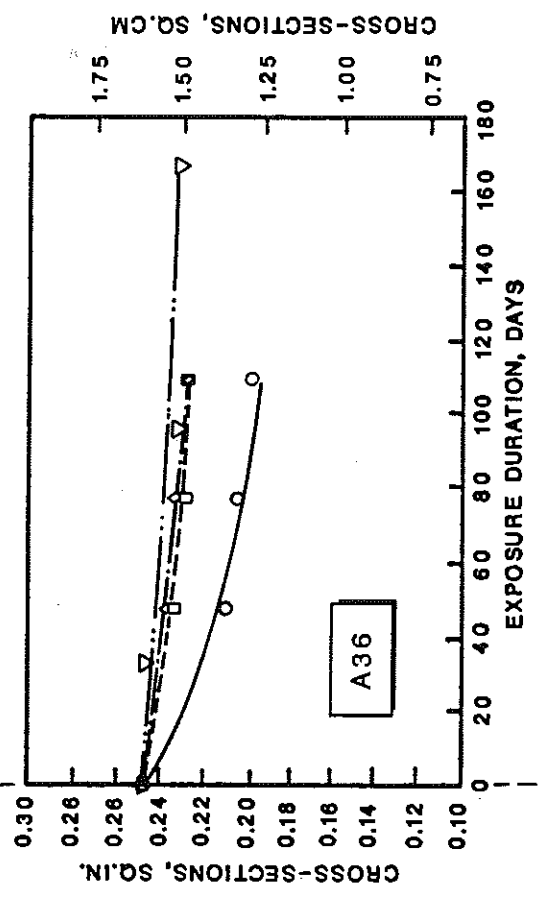


Figure 10. Effective and average cross-sections of bridge steel tensiles in distilled water and acid rain (sheltered exposure).

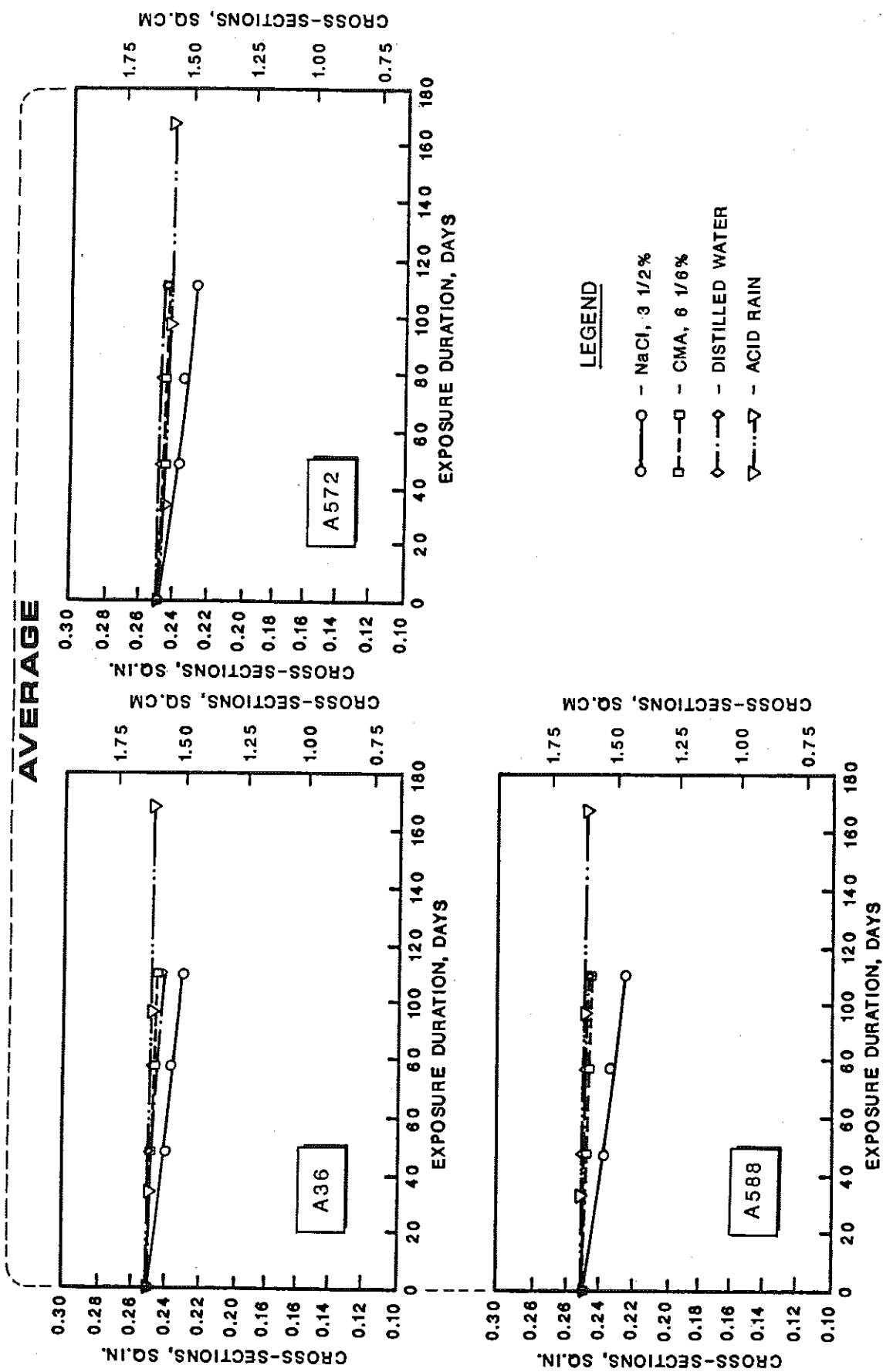
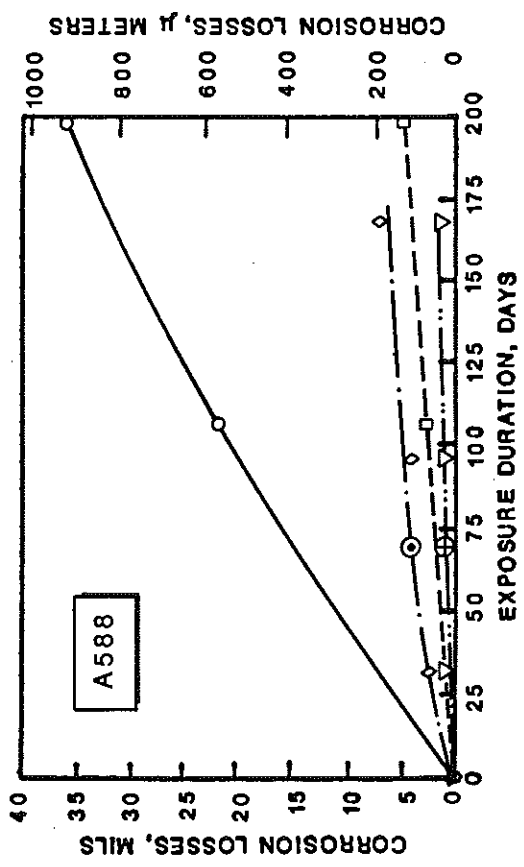
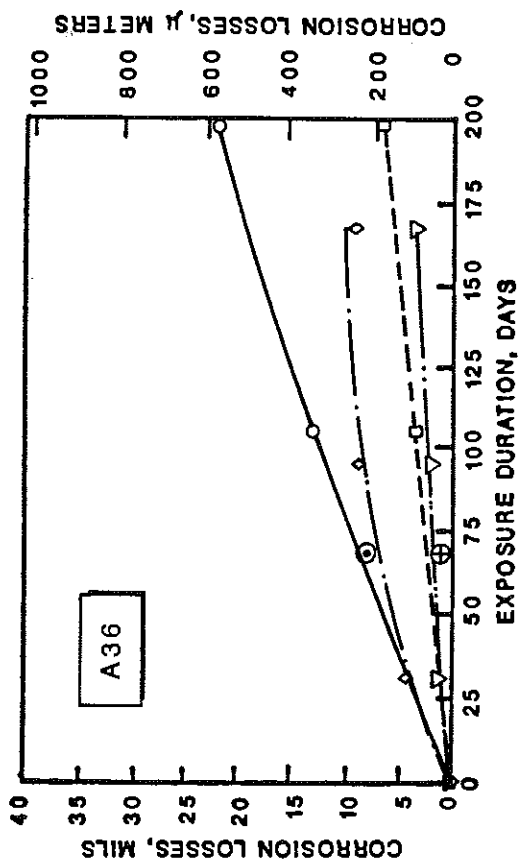
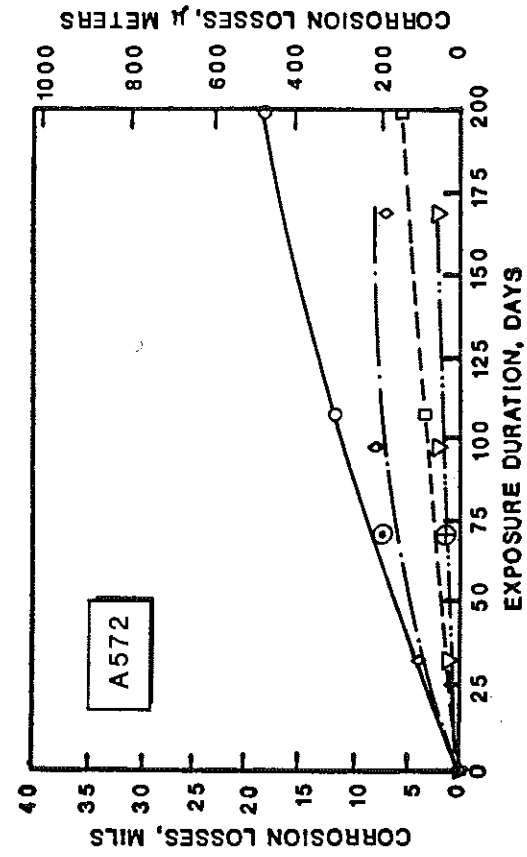


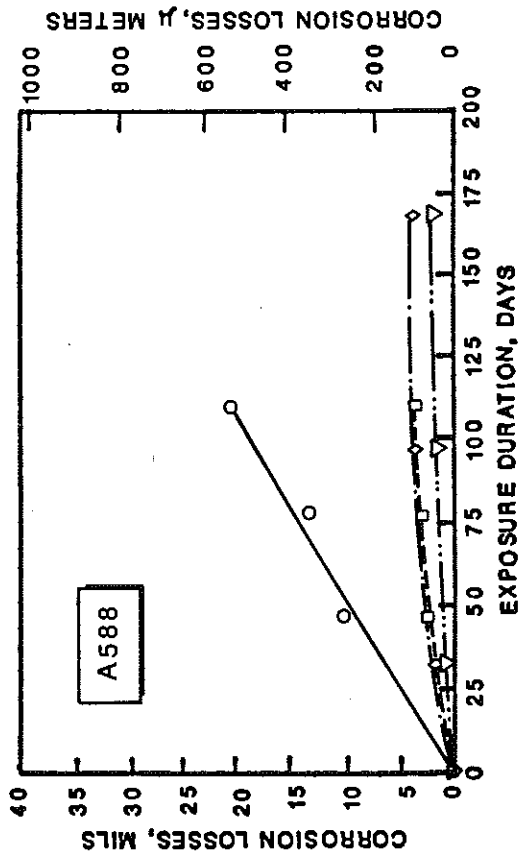
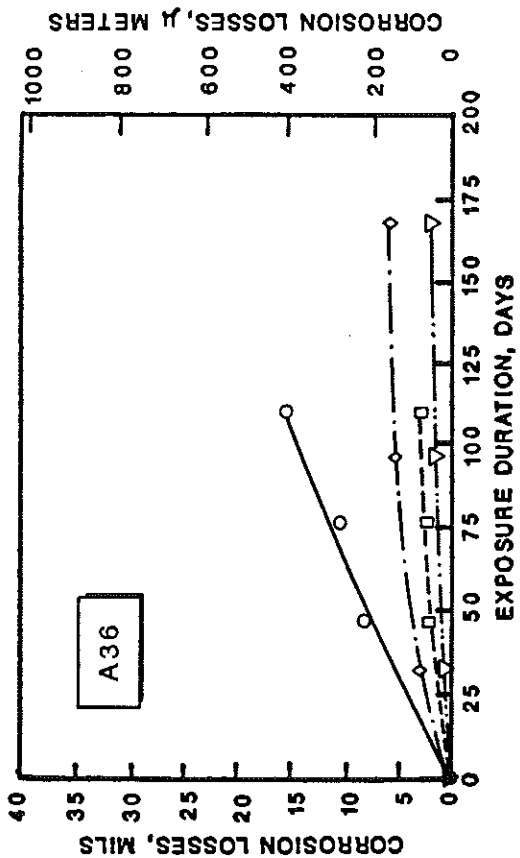
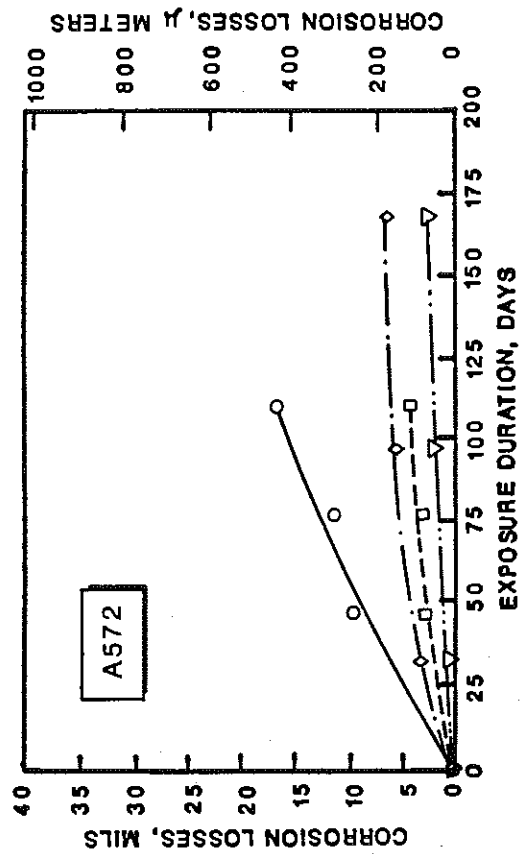
Figure 10 (con't). Effective and average cross-sections of bridge steel tensiles in distilled water and acid rain (sheltered exposure).



LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — Quicksalt + PCI
- ▽ — Freezegard + PCI
- ⊙ — Quicksalt + PCI, 71 Days
Exposure from Day 97 to Day 168
- ⊕ — Freezegard + PCI, 71 Days
Exposure from Day 97 to Day 168

Figure 11. Average corrosion losses of bridge steels in Quicksalt + PCI and Freezegard + PCI (open exposure).

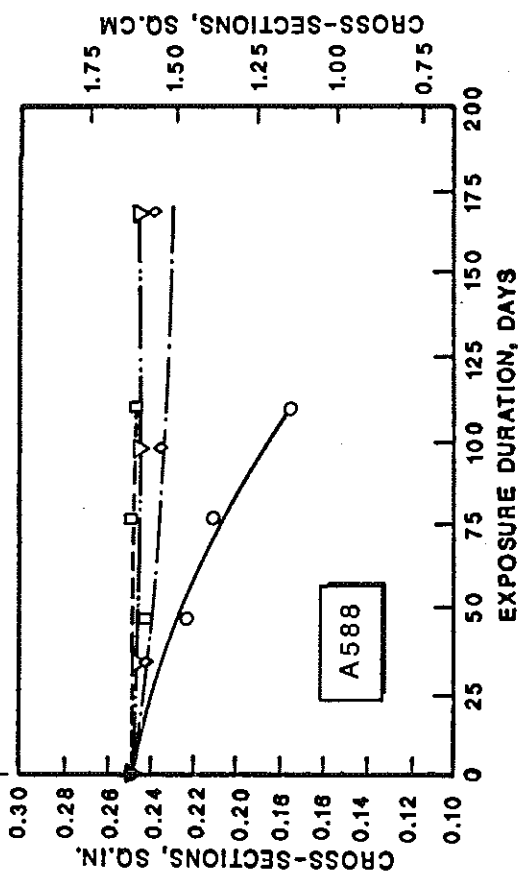
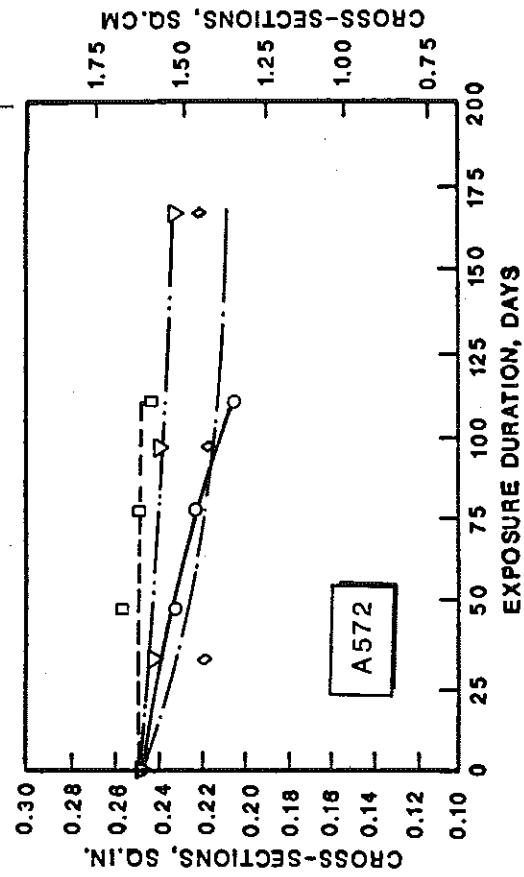
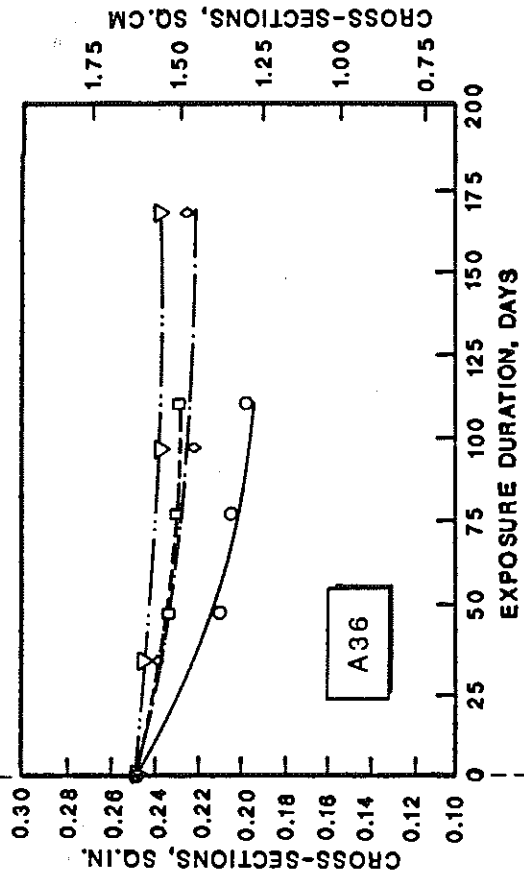


LEGEND

- - NaCl, 3 1/2%
- - CMA, 6 1/8%
- ◇ - QUICKSALT + PCI
- ▽ - FREEZEGARD + PCI

Figure 12. Average corrosion losses of bridge steel tensiles in Quicksalt + PCI and Freezegard + PCI (sheltered exposure).

EFFECTIVE

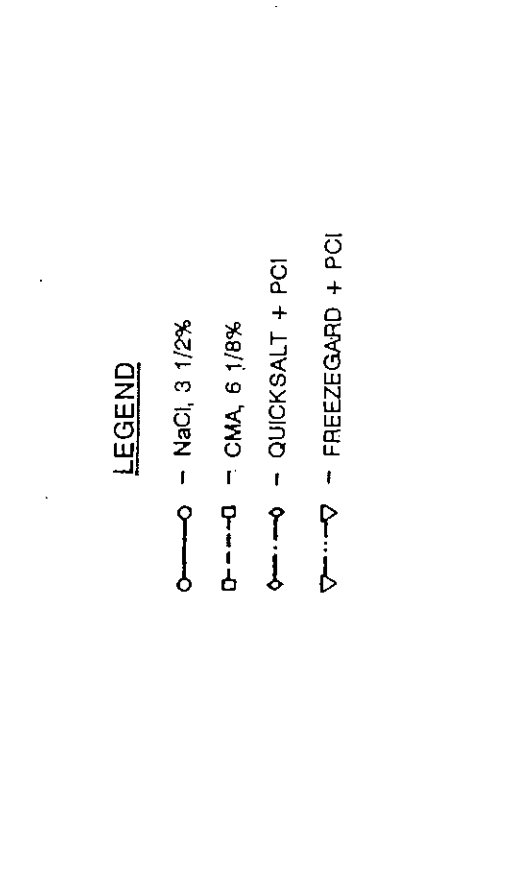
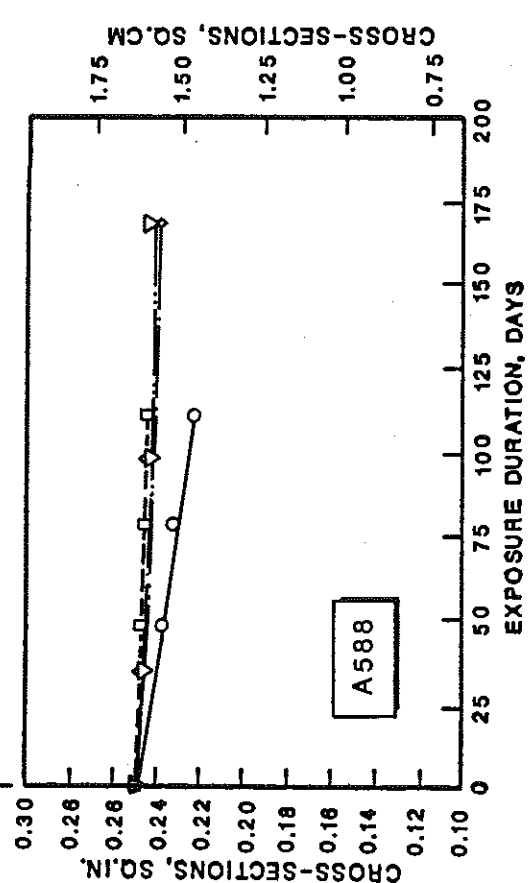
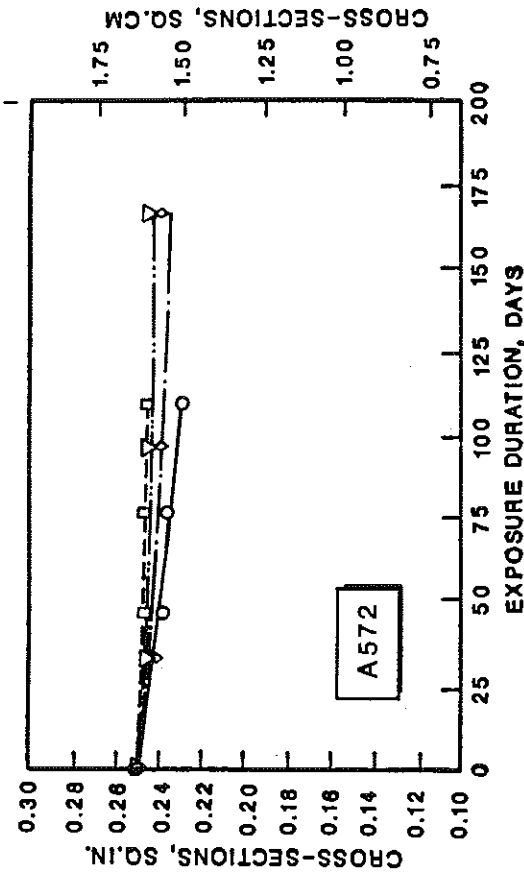
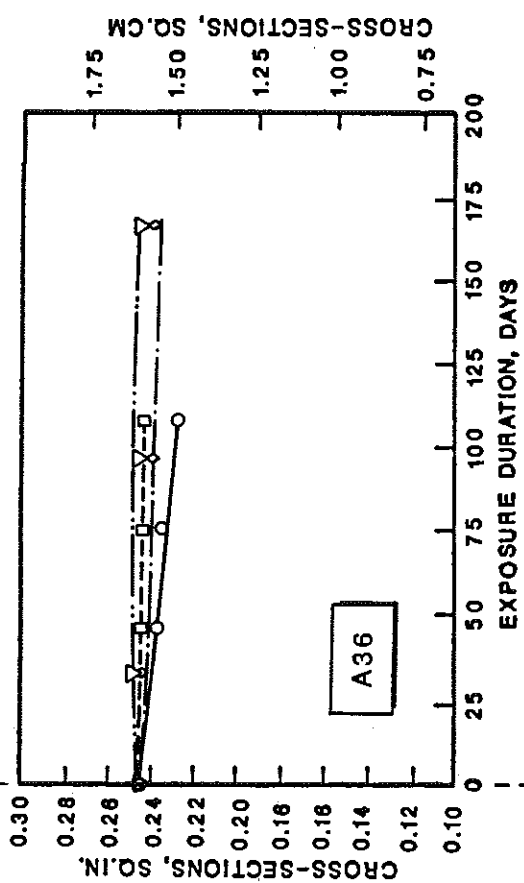


LEGEND

- - NaCl, 3 1/2%
- - CMA, 6 1/8%
- ◇ - QUICKSALT + PCI
- ▽ - FREEZEEGARD + PCI

Figure 13. Effective and average cross-sections of bridge steel tensiles in Quicksalt + PCI and Freezeegard + PCI (sheltered exposure).

AVERAGE



LEGEND

- - NaCl, 3 1/2%
- - CMA, 6 1/8%
- ◇ - QUICKSALT + PCI
- ▽ - FREEZEGARD + PCI

Figure 13 (cont). Effective and average cross-sections of bridge steel tensiles in Quicksalt + PCI and Freezegard + PCI (sheltered exposure).

The average corrosion performance of the alternate deicers tested in the laboratory is ranked in Figure 14 from best (top) to worst. Only Freezegard with PCI performed better than distilled water alone. Acid rain, at least as tested here, was only slightly worse than distilled water alone. CMA was worse than distilled water alone, and only slightly worse than the simulated acid rain. CMA/NaCl mixes were almost identical to CMA at the higher CMA/NaCl ratios (i.e., 1.75 and 0.46) and still showed some benefits at the lower CMA/NaCl ratios (i.e., 0.11 and 0.03). Performance of Quicksalt + PCI was roughly intermediate between the higher and lower ratio CMA/NaCl mixes. As expected salt alone performed the worst.

LABORATORY TESTING
• FREEZEGUARD WITH PCI
• ACID RAIN / DISTILLED WATER
• CALCIUM MAGNESIUM ACETATE
• CMA/NaCl MIXES & QUICKSALT WITH PCI
• NaCl ALONE

Figure 14. Relative ranking from best (top) to worst of the performance of all alternate deicers/environments evaluated in laboratory testing.

FIELD TESTING
• CALCIUM MAGNESIUM ACETATE
• WATER ALONE
• FREEZEGUARD WITH PCI
• CMA/NaCl MIXES
• QUICKSALT WITH PCI
• NaCl ALONE
• PHOSPHATE INHIBITORS

Figure 15. Relative ranking from best (top) to worst of the performance of all alternate deicers evaluated under field conditions.

Field Evaluation

Phase I

This work has been separately reported (7) and will only be summarized here. Those interested in the original work may obtain a copy of the research report (R-1313) from the Michigan Department of Transportation.

Inhibitor-treated salt appeared to function roughly as well as regular deicing salt as a deicer but resulted in much more frequent plugging of application equipment, at least for the first shipment of inhibitor which had a much smaller particle size than material supplied later. The larger material still tended to plug the equipment slightly more frequently than regular deicing salt.

Overall, the reinforcing steel specimens which were exposed to the corrosion-inhibitor-treated salt, experienced slightly more weight loss (on average) due to corrosion than the specimens that were not. Differences are not statistically significant, however, for the specimens subjected to just one winter (four months exposure). For specimens exposed to two winters (16 months exposure with just plain salt being used during the second winter on both the experimental and control sections of pavement) the differences are statistically significant at the $p = .05$ level (Tables 3 and 4).

TABLE 3
AVERAGE CORROSION RATE AFTER 4 MONTHS
(United Salt's Corrosion Inhibitor)

	Average Rate mils/year (micrometers/year)	Number of Samples	Standard Deviation
With Inhibitor	2.83 (7.19)	16	1.01
Without Inhibitor	2.75 (6.98)	39	1.07

TABLE 4
AVERAGE CORROSION RATE AFTER 16 MONTHS
(United Salt's Corrosion Inhibitor)

	Average Rate mils/year (micrometers/year)	Number of Samples	Standard Deviation
With Inhibitor	2.33 (5.92)	24	0.507
Without Inhibitor	2.05 (5.21)	23	0.325

The concrete freeze-thaw specimens exposed to the corrosion inhibitor had as much or more weight loss due to spalling than those exposed to pure NaCl, for both the air-entrained and non-air-entrained samples. Freeze-thaw specimens exposed to several CMA/NaCl ratios experienced less freeze-thaw damage than those exposed to the corrosion inhibitor as well as decreasing freeze-thaw damage as the concentration of CMA increased. Almost no freeze-thaw damage was experienced by the specimens exposed to CMA alone.

Phase II

While the currently available results are limited and have some problems (i.e., unplanned dilution of inhibitor/salt ratio), there is enough information of interest to warrant mention at this time.

Only the major results to date will be summarized here with more extensive results to be published after completion of the project. Figure 15 gives a relative ranking from best (top) to worst for the performance of all materials tested in this project on bridge steel alloys (this should be compared to Figure 14, laboratory results).

CMA had better average corrosion performance than water alone. This is just the reverse of our laboratory results. Freezegard + PCI was slightly worse than water alone--this is surprisingly good performance considering our unintended dilution of the inhibitor/salt ratio. CMA/NaCl mixes were roughly intermediate in performance to CMA and NaCl for the higher CMA/NaCl ratios tested and similar to salt alone for the lower CMA/NaCl ratios tested (here the results have probably been affected by the unintended 'inhibitor'/salt ratio dilution). Quicksalt + PCI was intermediate between the highest CMA/NaCl ratio and NaCl alone. All of the phosphate inhibitors (i.e., United Salt's corrosion inhibitor, Domtar's TCI, and Cargill's CG-90) performed worse than NaCl alone. The result for the phosphate inhibitors is to some extent surprising even though our intended inhibitor/salt ratios were significantly diluted. While this does not necessarily reflect the performance of these materials when used at the intended inhibitor/salt ratios, it does suggest that situations may arise where the phosphate inhibitors do not perform as desired. A vehicle that routinely drives through a limited area of exposure to these inhibitors may experience more, instead of less, corrosion as travel through other untreated areas decreases the inhibitor/salt ratio to which the vehicle is exposed.

Phase III

Problems with a data acquisition board giving results that fluctuated more with board temperature than the actual macrocell corrosion current have invalidated our first year's data. Data from this project will, however, be available in the future.

DISCUSSION

Laboratory vs. Field

While the laboratory provides a more controlled and often faster environment for testing the corrosion performance of alternate deicers, it may not always provide an adequate environment. The laboratory is not identical to the real world and, hence, may not provide a number of conditions that may be necessary for properly evaluating field/real life performance. The differences between our laboratory and field results help to demonstrate this (Figs. 14 and 15 and Tables 3 and 4).

For CMA and, especially, CMA/NaCl mixes the real world with its bacteria and other agents of biodegradation may deteriorate the CMA before it can perform the same corrosion protection observed in the laboratory (while the salt remains to do its damage).

For the alternate deicers that appear to act by establishing a barrier oxide layer that inhibits further corrosion, the relatively constant temperature of the laboratory may not adequately reflect what could happen under drastic temperature changes if the barrier and substrate have different coefficients of thermal expansion (as do most metals and their various oxides). The barrier cannot act if it is no longer tightly adhering to the metal. In fact, if the barrier is separated from the metal surface but still partially attached, it may act as a crevice which can greatly accelerate corrosion.

Laboratory testing of alternate deicers is seldom done at the low temperatures that are prevalent when deicers are actually used. Even if an alternate deicer provides corrosion protection at the higher temperatures of laboratory testing there is no guarantee that it will function exactly the same under lower temperatures. Temperature helps to determine the output products of any chemical reaction (i.e., oxidation in this case). An oxide that forms under the higher laboratory temperatures and functions satisfactorily as a barrier may not form or form less frequently under lower temperatures with another less desirable oxide taking its place.

Laboratory testing also occurs with a relatively fixed concentration of the alternate deicer or corrosion inhibitor/NaCl mix being present for the length of testing. Even in alternate wet/dry testing the concentration change is restricted to a level greater than or equal to the test solution. For some materials the greatest corrosion damage (or for that matter corrosion protection) occurs at certain concentrations that may or may not be represented by 'greater than or equal to the test solution.' In the real world, concentrations are not restricted to any particular value and may vary infinitely depending on the amount of moisture present and the relative solubility of the alternate deicer (and its individual components) with respect to NaCl. Differences in the solubility of the components of an alternate deicer may result in what can in the laboratory be a satisfactory mix not being so in the real world as the proper mix of materials shifts to an improper one.

Is there any component of the alternate deicer or corrosion inhibitor/NaCl mix that may attract moisture (i.e., more deliquescent than NaCl)? If so the additional time of wetness that can occur in the high humidity of some areas of the real world, such as Michigan, may result in an increase of overall corrosion even though the rate of corrosion when the material is wet is reduced.

Concerns over how well the laboratory simulates the real world have also been expressed by earlier researchers examining corrosion inhibited deicing salts (8, 9). Little difference was found between treated specimens and untreated specimens when exposed to the real world, although laboratory testing had been favorable.

ANNUAL BENEFITS OF ROAD SALTING (20 Storm Days)	ANNUAL COSTS OF ROAD SALTING (Millions of Dollars)																								
<p>1) LIVES SAVED IN REDUCED TRAFFIC ACCIDENTS</p> <p>2) LIVES SAVED IN REDUCED RESPONSE TIME TO MEDICAL EMERGENCIES</p> <p> a) Heart attacks</p> <p> b) Burns</p> <p> c) Home accidents</p> <p> d) Work accidents</p> <p>3) ENERGY SAVINGS</p> <p> a) .37 to 1.2 billion gallons of fuel saved</p> <p>4) ECONOMIC BENEFITS</p> <p> a) Reduced wage loss in lateness to work - \$7,600</p> <p> b) Reduced wage loss in work absenteeism - 3,000</p> <p> c) Reduced production losses - 7,000</p> <p> d) Reduced losses in goods shipment - 600</p> <p> e) Reduced fuel costs - 200</p> <p style="text-align: right;">TOTAL \$18,400 million</p>	<table border="1"> <thead> <tr> <th></th> <th style="text-align: center;"><u>EPA STUDY</u> *</th> <th style="text-align: center;"><u>TISA STUDY</u> **</th> </tr> </thead> <tbody> <tr> <td>UTILITIES</td> <td style="text-align: center;">10</td> <td style="text-align: center;">2</td> </tr> <tr> <td>VEHICLE CORROSION</td> <td style="text-align: center;">2,000</td> <td style="text-align: center;">643</td> </tr> <tr> <td>HIGHWAY BRIDGE DECKS</td> <td style="text-align: center;">500</td> <td style="text-align: center;">160</td> </tr> <tr> <td>TREES AND VEGETATION</td> <td style="text-align: center;">50</td> <td style="text-align: center;">0</td> </tr> <tr> <td>WATER SUPPLIES</td> <td style="text-align: center;">150</td> <td style="text-align: center;">10</td> </tr> <tr> <td>SALT COST, APPLICATION</td> <td style="text-align: center;">200</td> <td style="text-align: center;">200</td> </tr> <tr> <td style="text-align: right;">TOTAL</td> <td style="text-align: center;">\$2,910</td> <td style="text-align: center;">\$1,015</td> </tr> </tbody> </table>		<u>EPA STUDY</u> *	<u>TISA STUDY</u> **	UTILITIES	10	2	VEHICLE CORROSION	2,000	643	HIGHWAY BRIDGE DECKS	500	160	TREES AND VEGETATION	50	0	WATER SUPPLIES	150	10	SALT COST, APPLICATION	200	200	TOTAL	\$2,910	\$1,015
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<p>BENEFIT COST RATIO OF ROAD SALTING (20 storm days) - EPA Study * : 6.3 to 1</p> <p>- TISA Study **: 18.1 to 1</p>																									

* Murry, D.M. and Ernst, U.F.W. "An Economic Analysis of the Environmental Impact of Highway Deicing" Report No. EPA-600/2-76-105, US, Environmental Protection Agency, May 1976

** Brenner, R., and Moshman, J. "Benefits and Costs in the Use of Salt to Deice Highways", The Institute for Safety Analysis (TISA), Washington, D.C., November 1976

Figure 16. Benefits and cost of salt-enhanced deicing. (From Brenner, R., and Moshman, J. "Benefits and Costs in the Use of Salt to Deice Highways," The Institute for Safety Analysis (TISA), Washington, D.C., November 1976.

This section by no means intends to list all the important differences that can occur between the laboratory and the real world for the corrosion testing of alternate deicers. But this should at least help to demonstrate that laboratory results alone are not enough. While laboratory results are indicative that a product may work, there are still many questions left unanswered that demand more realistic evaluation to establish whether or not it will work in the real world. With the considerable expense that an alternate deicer can represent, it is imperative that the suitability of the product be clearly and unequivocally demonstrated before such a large monetary commitment is made.

Economics

While the economics of alternate deicers is not intended as the primary topic of this writing, economics is a major driving force for doing this corrosion research and is the final determinant in whether or not an alternate deicer can be used. With this in mind, it would seem worthwhile to discuss at least some of the relevant economics and how they relate to Michigan.

While a lot of current talk about deicing seems to focus more on the damage done by NaCl and gives various figures on the damage associated with its use, there's another side of this issue that deserves mention. Highway deicing results in significant benefits that cannot be ignored. Figure 16 indicates that the savings of highway deicing far outweigh the estimated damage.

Numerous older writings (10, 11, 12, and many others too numerous to mention), centering around that period of time (late 50's and early 60's) when bare pavement highway deicing as we know it today first came into being, corroborate the rationale for using deicing salts. Both economic advantage and improved safety are considered. Wirshing (10) estimated that the economic savings for Detroit alone could exceed \$100,000,000 (1956 dollars) per year based on several economic considerations like the average worker being 30 minutes late to work because of icy conditions during 35 storms. At that time only \$875,000 (\$300,000 of which was for salt) was spent annually for snow removal in Detroit.

Many have come to accept our bare pavements as the norm, having become accustomed to them over the last twenty-some years, and now tend to emphasize the negatives of salt use without thinking about the benefits. While it is appropriate to address the damage that salt does, one should keep the benefits in mind also. Or, in other words, no sacrifice in the ability of an alternate deicer to maintain bare pavements, compared to NaCl, can be tolerated.

Currently the price of alternate deicers varies from almost \$700 per ton for CMA to roughly \$150 per ton for most of the corrosion-inhibitor-treated NaCl. These prices range from roughly 30 to 6 times Michigan's current cost of salt (roughly \$25 per ton) and are within the range of estimates for the damage done by salt (Fig. 1). While it would appear, based

on the magnitude of some of these damage estimates, that the cost of an alternate deicer could be readily made up from the projected savings; the real world is, unfortunately, seldom so simple.

Many of the damage estimates were made in the mid 70's and some later ones are simply updated extrapolations (allowing for inflation of the damage estimates). Since the early estimates much has been done to improve both the highway environment and auto bodies to make them more resistant to the damage by salt. Our highway metal structures use corrosion resistant alloys, zinc coatings, and special coating (i.e., paint) systems designed to resist the corrosive effects of salt. Our highway concrete structures use epoxy coated steel reinforcement, air entrained concrete, latex overlays, and epoxy sealers on the deck; the combined effect of these added treatments makes it more difficult for salt to enter the concrete and to have a less serious consequence once it does. Car manufacturers have improved the corrosion resistance of their cars; many metal parts have been replaced with plastics and others coated with zinc or a corrosion resistant paint system. Almost all of this corrosion protection of the highway environment has taken place since the original damage estimates were made and hence a lot of the damage that once occurred either has been eliminated or significantly reduced. An FHWA sponsored research project is currently estimating the amount of salt damage that occurs today. Once established, this updated figure should help to clarify the realistic potential savings that exist currently.

The cost of an alternate deicer, even a 'cheap' one, is considerable. For an average winter, Michigan's Department of Transportation uses roughly 350,000 tons of salt on Michigan's major trunklines. This amounts to almost \$9,000,000 for the salt alone. A corrosion inhibitor treated salt would cost almost \$54,000,000 and CMA would run around \$245,000,000. This compares to our Maintenance Division's total winter maintenance budget of approximately \$29,000,000. Significant additional funding would be necessary to convert all of Michigan's roadways to an alternate deicer.

Counties, cities, townships, etc., have their own highway or road agencies which take care of their own highway deicing. Since these agencies combined use roughly the same amount of salt as the Michigan Department of Transportation, funding would have to be roughly double (i.e., \$108,000,000 and \$490,000,000, respectively) for replacement of salt throughout the entire state.

Future Work

The Michigan Department of Transportation will continue to evaluate alternate deicers in a search for the most cost effective one that is suitable for our deicing and corrosion environment. Deicing and corrosion performance of alternate deicers will continue to be evaluated by the Research Laboratory of the Materials and Technology Division as circumstances warrant. The Transportation Planning Services Division has contracted with an environmental consulting firm (Public Sector Consultants, Inc. of Lansing, Michigan) to prepare a comprehensive Environmental Impact Statement on the possible use of alternate deicers that will focus on economics and safety as well as environmental impact.

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