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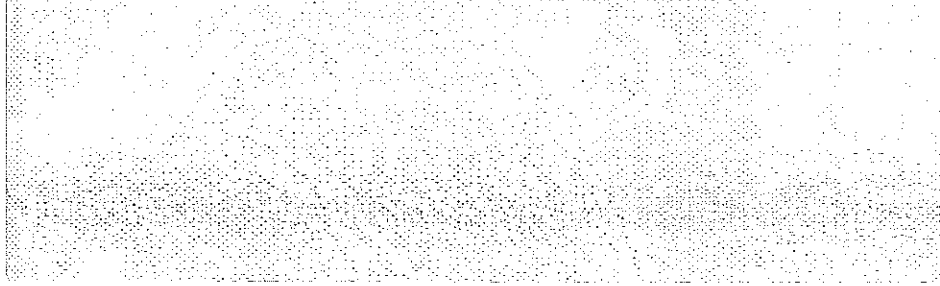
**CORROSION EVALUATION OF CALCIUM MAGNESIUM
ACETATE (CMA), SALT (NaCl), AND CMA/SALT SOLUTIONS**



MATERIALS and TECHNOLOGY DIVISION



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TD870 .M32 1988 c.1 c. 3
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**CORROSION EVALUATION OF CALCIUM MAGNESIUM
ACETATE (CMA), SALT (NaCl), AND CMA/SALT SOLUTIONS**

R. L. McCrum

**Research Laboratory Section
Materials and Technology Division
Research Project 82 G-259
Research Report No. R-1295**

**Michigan Transportation Commission
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Lansing, December 1988**

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ABSTRACT

Calcium magnesium acetate (CMA) has been selected in Federal Highway Administration sponsored research as being among the most viable salt (NaCl) substitutes for highway deicing.

This study documents the corrosiveness of a water solution of CMA compared with that of an equivalent (for deicing purposes) concentration of NaCl in water, in identical exposure environments for the major structural metals currently used in Michigan's highway system. Additional work with most of the same structural metals has been performed in distilled water alone, simulated acid rain, a commercially available rust inhibitor with $MgCl_2$, the same rust inhibitor with NaCl, and CMA and NaCl mixtures (CMA/NaCl weight ratios of 1.75, 0.46, 0.11, and 0.03 with NaCl concentration held at 3.5 percent). Electroslag and submerged arc welds (representing the major weld chemistries used on Michigan's structures) in weathering steel (ASTM A588) were also exposed to CMA and NaCl solutions.

Results are reported in detail for structural (bridge) steels, steel bar reinforcement for concrete, steel prestressing strand for concrete, some aluminum alloys, galvanizing, and some galvanic couples. Performance is rated by average corrosion, maximum pit depth, crevice corrosion, maximum crevice pit depth, and loss of tensile strength (effective cross-sectional area reduction).

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 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 (roughly \$30/ton). The lower estimate comes from a report sponsored by the Salt Institute and the higher estimate from a report sponsored by the U. S. Environmental Protection Agency (1, 2). The lower estimate primarily considers corrosion damage while the higher one also takes into consideration environmental effects.

While the cost of salt has remained relatively constant since the estimates of the damage done by salt were first made, almost everything else has gone up in price. Allowing for an average 5 percent inflation per year, the damage, in today's money, probably is closer to 12 to 40 times the cost of salt (i.e., \$360 to 1200/ton of rock salt).

To aid in solving the problems created by rock salt, the Federal Highway Administration (FHWA) sponsored research to find an alternate deicer that could be produced at less cost than the monetary amount of the damage done by salt. As a result of this research, calcium magnesium acetate (CMA) has been selected as the most suitable candidate (3). Although more expensive initially, CMA, unlike NaCl, tends to inhibit corrosion.

While some qualitative studies of the corrosiveness of CMA had been made for a few metals (prior to the start of this evaluation in late 1983), more comprehensive quantitative studies have been needed to supply the information necessary to properly evaluate potential long-term cost effectiveness.

A fairly long list of questions needs to be answered. How much more corrosion occurs when NaCl is present than when CMA alone is present? How does this compare with the corrosion performance of water by itself? Do different materials (i.e., different compositions of steel, aluminum alloys, galvanized materials, etc) perform differently? Is crevice corrosion (accelerated corrosion associated with overlapping surfaces) as much, or more, or less of a problem in CMA? Does CMA affect the normal (i.e., salt environment) performance of galvanic (dissimilar metal corrosion)

couples such as weld metal/base metal combinations? How does NaCl (residual or otherwise) affect the performance of CMA? This report attempts to answer many of these questions as well as suggest directions for additional research.

LABORATORY PROCEDURE

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. The following groups of metals were represented, essentially identically, in all of the exposure environments except as noted (some additional specimens were included in the NaCl and CMA exposure environments that were not used in the other exposure environments):

1) Bridge Steels:

Bare - ASTM A572, A588, A588 previously exposed to NaCl environments, and A36 for both open and 'sheltered' (tensile specimens) exposures. ASTM A588 for both 'loose' and 'tight' welded lapped joints (CMA and NaCl exposure environments only).

Painted - (CMA and NaCl exposure environments only) - ASTM A572, A588, A588 previously exposed to NaCl environments, and A36 with epoxy top coat over zinc-rich primer. ASTM A572 and A36 bolted lapped joints with epoxy top coat over zinc-rich primer.

2) Bar Reinforcement for Concrete:

Uncoated - ASTM A706 or Grade 60 of either A615, A616, or A617.

Epoxy Coated - ASTM D3963

Stainless and Stainless Clad - AISI 300 Series.

3) Aluminum:

Sign Materials - Aluminum alloys 2024, 5052, and 6063T6.

Bridge Expansion Joint - Aluminum alloy 6061T6.

4) Prestressing Strand:

ASTM A416 Grade 270.

5) Galvanizing (CMA and NaCl exposure environments only):

Bridge Expansion Joint - ASTM A715 Grade 50 with ASTM A153 coating.

Steel Post (Brace) - ASTM A36 with ASTM A123 coating.

Bridge Guard Railing - ASTM A500 Grade B with ASTM A153 coating.

6) Galvanic Couples (CMA and NaCl exposure environments only):

Stainless Steel Fastener - AISI 300 Series/Aluminum alloy 6063T6.

Stainless Steel Nut - AISI 300 Series/Galvanized Bolt, ASTM A153.

7) Guardrail:

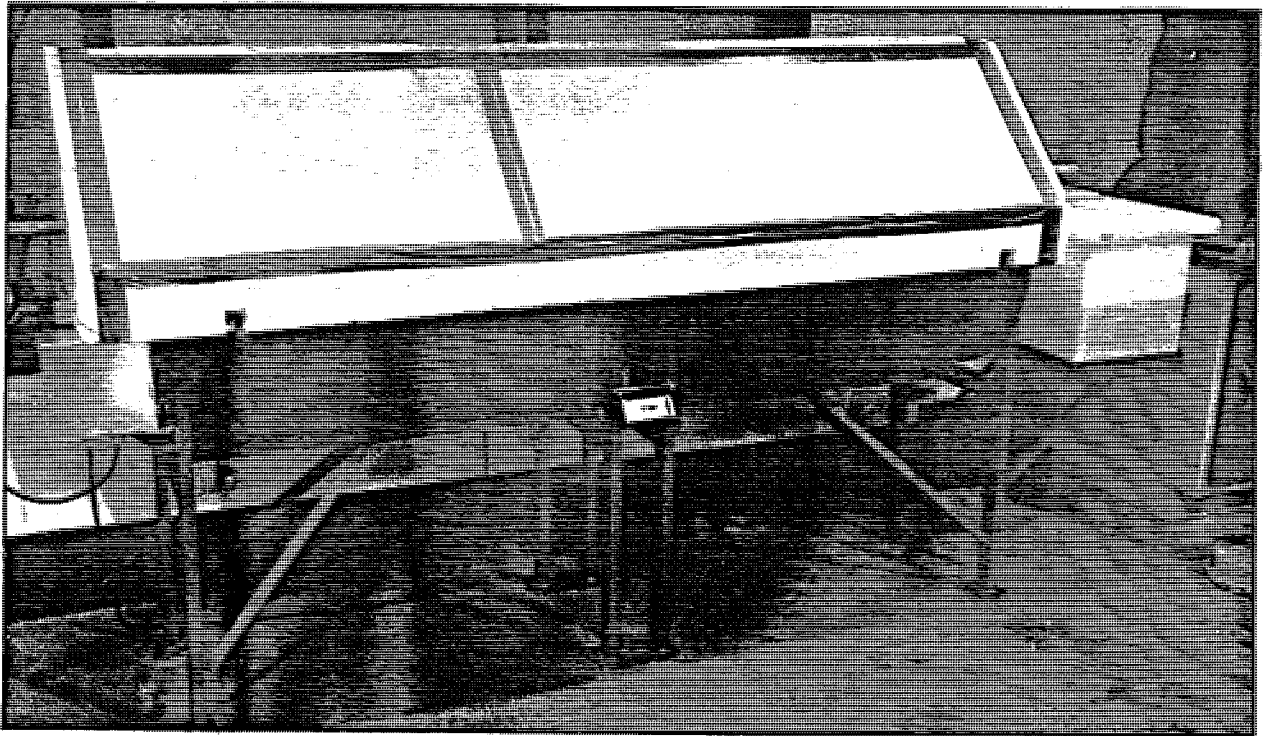
Weathering Steel - AASHTO M180 Class B Type 4.

Galvanized - AASHTO M180 Class B Type 2.

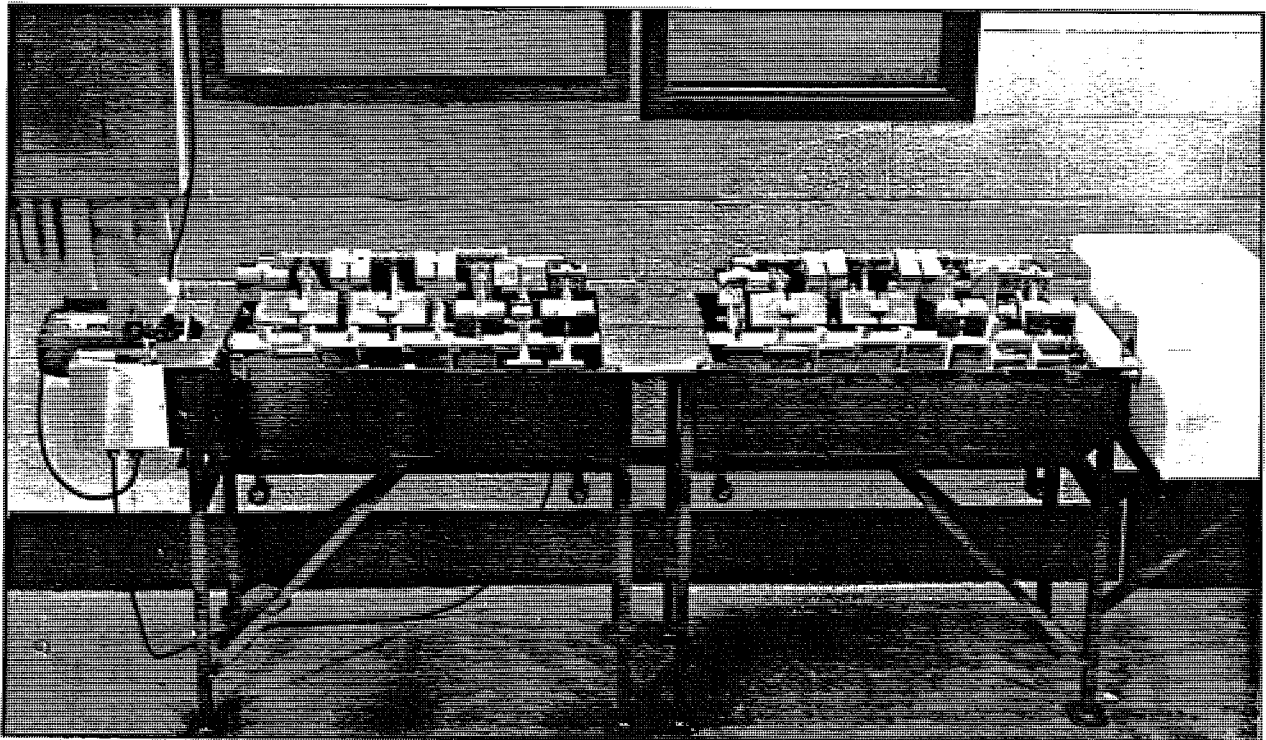
In almost all cases, four essentially identical specimens were prepared from each material for both the CMA and NaCl test environments. For the other test environments, typically only three specimens were used. For several of these other tests, however, a fourth specimen was added to the exposure environment 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 10 to 35 sq in. The bridge steels and the weathering steel guardrail were sand-blasted to remove all mill scale and surface oxide. All specimens were 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) and end-anchored, while the other strand was left unloaded. Specimens were removed for evaluation at three and six months. For the other test solutions, freely exposed 1-ft lengths of strand were used.

An environmental weathering chamber was constructed to house the specimens for exposure to the various exposure environments (Fig. 1). Separate tanks held the CMA and NaCl solutions. For the other test solutions the tanks were subdivided with plexiglass partitions so that four different solutions could be tested at the same time. A common shaft rotating at intervals periodically submerged the specimens. Rotation rate of the shaft is such that four complete revolutions were made each day. Dimensions of the chamber and the fluid level within the tanks are such that the specimens are submerged for approximately one-third of the time. For the CMA and NaCl exposures sufficient specimens of most



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 1. Environmental Weathering Chambers.

materials were prepared to allow removal at intervals of three months for a year. For the other tests, typically three specimens of each material were prepared for removal at approximately one-month intervals (the actual interval between specimen removals varies 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 (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. Six rows of eight rods were used in each tank for mounting the specimens (six rows of four rods for the subdivided tanks). Almost all specimens were mounted on the ends of the rods. Exceptions to this are the prestressing strands, both the conduit encased stressed and unstressed specimens and the 1-ft long specimens, and the bridge steel tensile specimens. These specimens were mounted to the sides of the rods either directly or indirectly to epoxy coated metal straps connected to rods on adjacent rows. These specimens being located under the other specimens and at a lower position on the rods are 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.

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. Specimens were mounted in identical patterns in both tanks so that any galvanic corrosion effects that might occur when the specimens were submerged would be approximately the same for all tanks.

Concentrations (by weight) for the CMA and NaCl solutions were initially set at 3.5 percent for the NaCl and 6.125 percent for the CMA. These represent concentrations that would have equivalent deicing (freezing point depression) abilities. Since a greater concentration of CMA must be used for deicing it has seemed appropriate to reflect this difference in our exposure environment.¹ Four different mixes of CMA and NaCl were also tested--concentrations (by weight) are 6.125 percent CMA with 3.5 percent NaCl, 1.6 percent CMA with 3.5 percent NaCl, 0.4 percent

¹This seems particularly appropriate since equiosmolar (equivalent deicing) concentrations have equivalent ionic concentrations, a factor which also helps to govern the likely rate of a chemical (i.e., corrosion, in this instance) reaction.

CMA with 3.5 percent NaCl, and 0.1 percent CMA with 3.5 percent NaCl. The salt was taken from one of our highway maintenance garages and is typical of that normally used in Michigan for highway deicing. The CMA was taken from the 98 tons furnished by the FHWA for field evaluations. (This is part of the 200-ton batch produced in 1982 by the FHWA-sponsored pilot plant in Bowling Green, Kentucky.) The Appendix contains an analysis of the compositions of both the CMA and NaCl used in this testing.

Simulated acid rain was prepared by making a solution with H_2SO_4 , $MgCl_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot H_2O$, 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 (4).

A commercially available rust inhibitor was evaluated with a 3.5 percent NaCl solution and separately with a 8.1 percent $MgCl_2$ solution. The $MgCl_2$ concentration is the deicing (osmolar) equivalent of the 3.5 percent NaCl solution.

Distilled water has been used to both prepare all initial solutions and maintain fluid level within the tanks. Fluid level was automatically controlled by means of floats in adjacent tank reservoirs so that any changes in solution concentration that might result from evaporation were minimized.

Groups of specimens were removed after approximately three-month or one-month intervals (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 may in turn be 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. All specimens were also examined for any peculiarities that might be of interest or importance.

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.

For the galvanized specimens, pre- and post-test thickness measurements were made of the galvanizing using a positector calibrated on National Bureau of Standards Coating Thickness specimens. The percentage of the surface still galvanized was evaluated where appropriate. Control specimens were included during the cleaning (oxide removal) process to estimate the loss of galvanizing resulting from the cleaning.

For the epoxy coated steel reinforcement specimens, sufficient epoxy was removed from the cut ends to evaluate the extent of rust undercutting.

Welded and bolted lapped joints were disassembled to examine the interior of the lap.

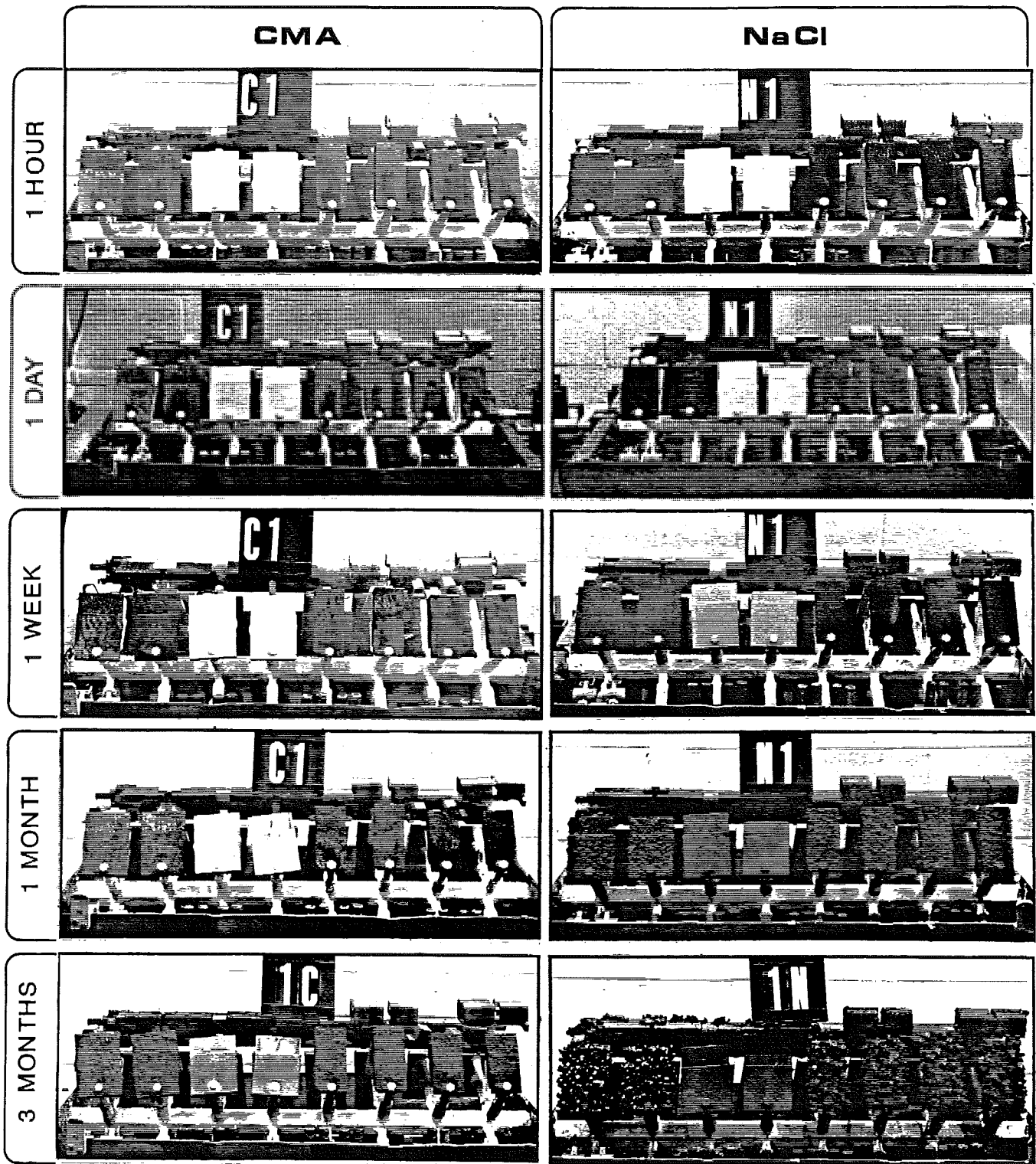
RESULTS

While the exposure environment used in this study is an accelerated weathering environment, 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 the same or roughly the same dimensions.

For the weathering environment used, the CMA weathered specimens, in general, experienced only about 1/4 to 1/15th the average corrosion of the NaCl weathered specimens with less severe pitting as well as less severe crevice-accelerated corrosion.

CMA and NaCl mixes 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



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

NaCl 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 one-tenth the current price of CMA alone.

Painted specimens (zinc-rich primer with epoxy topcoat) experienced no deterioration in either the CMA or NaCl solutions after one year's exposure.

Both distilled water and simulated acid rain were, in general, less corrosive than CMA by itself with distilled water being slightly less corrosive than the acid rain.

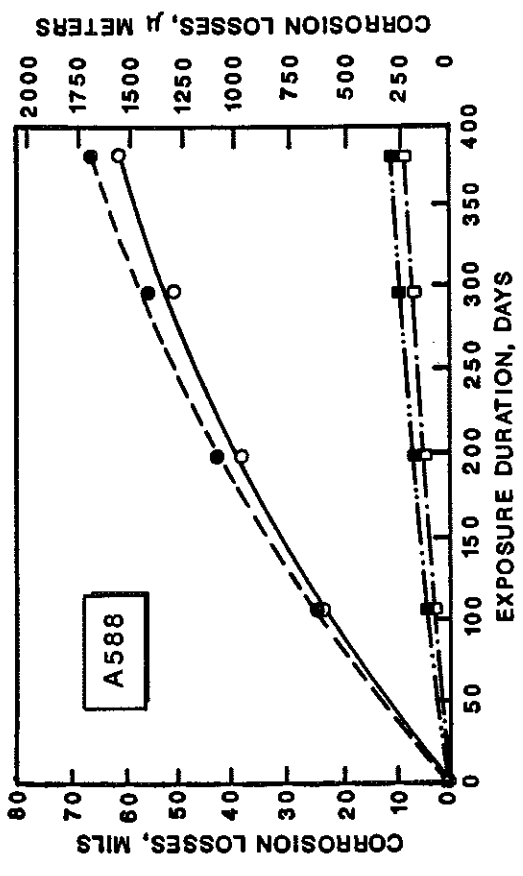
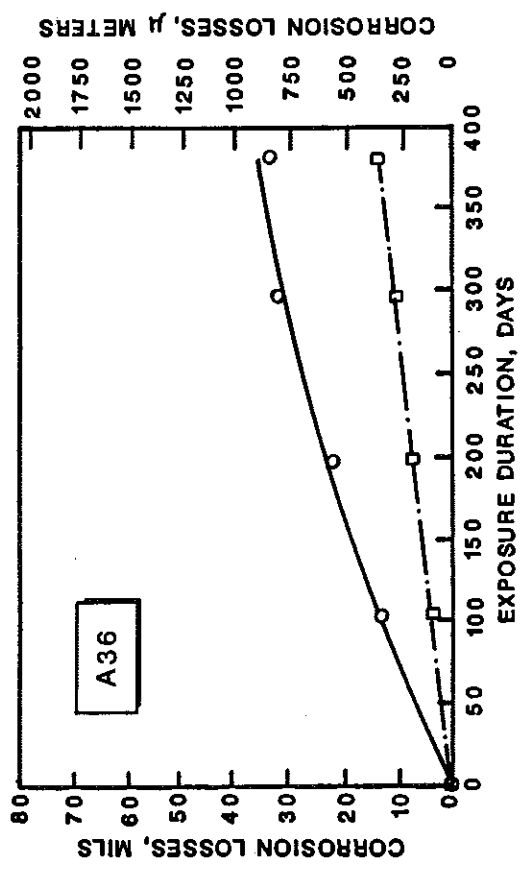
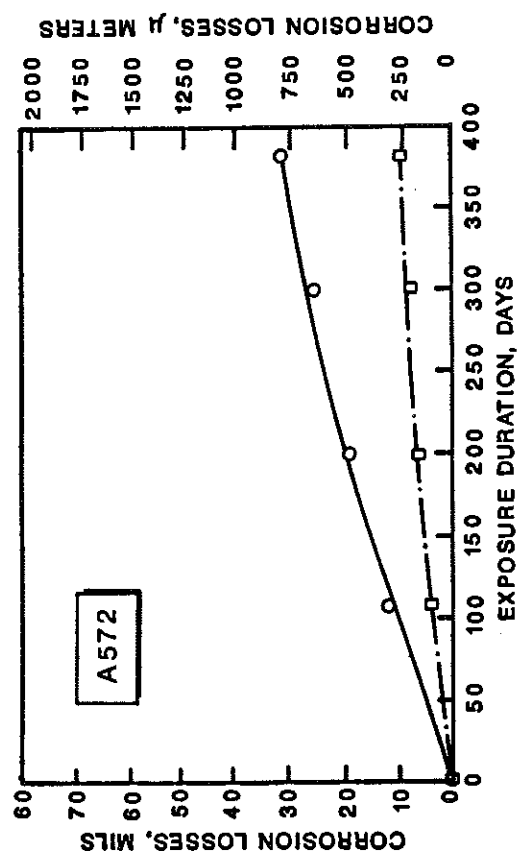
The rust inhibitor with $MgCl_2$ combination, in general, produced less average corrosion than the distilled water alone. The rust inhibitor with NaCl combination, in general, produced slightly greater average corrosion than CMA by itself, but considerably less than NaCl alone.

CMA and NaCl Exposures

Qualitative observation of the CMA and NaCl specimens from only several hours of exposure onward have consistently indicated considerably worse corrosion occurring in the NaCl environment. Figure 2 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. At no time during the twelve months of exposure was there any indication that the CMA environment was anywhere near as corrosive as the NaCl environment.

Major results of the evaluation are shown in Figures 3 through 10. The weathered condition of all the materials removed at three, six, nine, and twelve months is shown in Figures 11 through 17. All of the metals and metal coatings tested performed markedly better in the CMA environment. On the average, the CMA environment was only 1/4 to 1/15th as corrosive as the NaCl environment. Values varied with different materials as well as duration of exposure. Some of the more significant results are discussed in more detail for the individual metal groups.

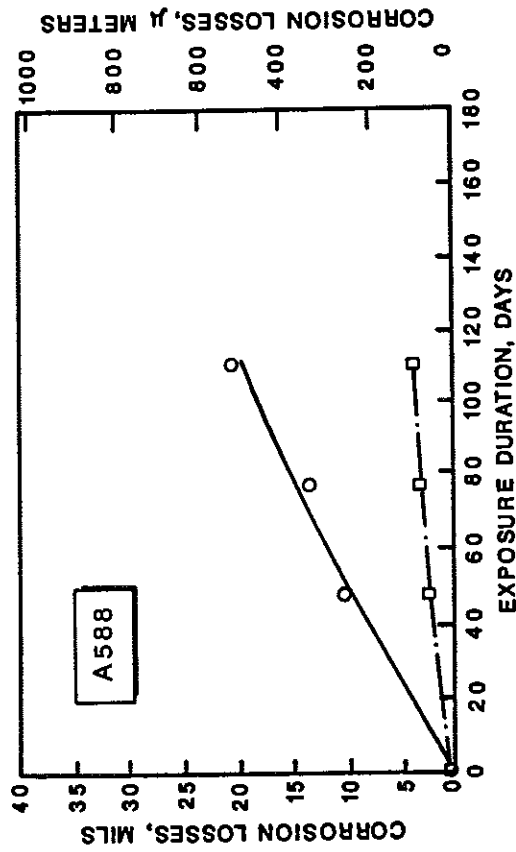
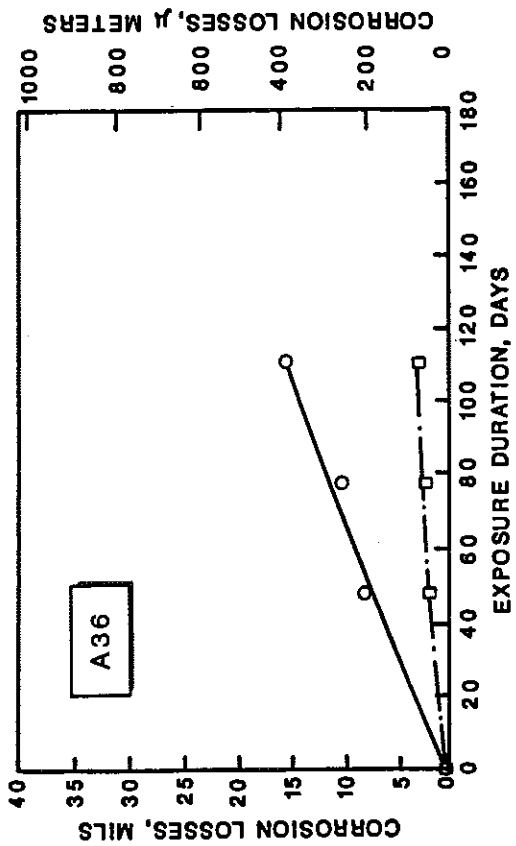
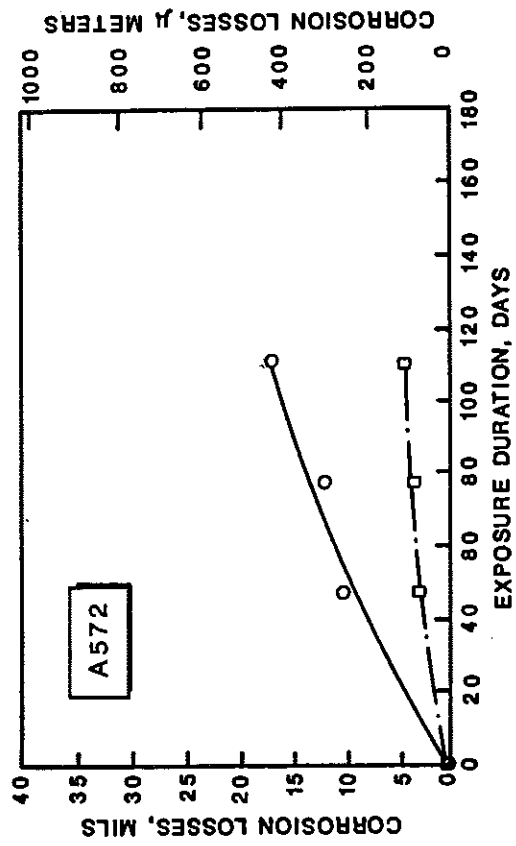
Bridge Steels (Figs. 3 through 8 and 11) - ASTM A36 and A572 steels (used in Michigan bridges in the painted state only) performed similarly for both environments with average corrosion in NaCl varying from approximately 3-1/2 (three months) to 2-1/2 to 3 (twelve months) times as bad as that in CMA. ASTM A588 steel performed slightly better than the other bridge steels in CMA although the differences were not great and performed markedly worse in NaCl. All of the so-called weathering steel applications (ASTM A588, weathering steel guardrail, and ASTM A588



LEGEND

- — NaCl, PLAIN
- — NaCl, PRE WEATHERED IN NaCl ENVIRONMENT
- — CMA, PLAIN
- — CMA, PRE WEATHERED IN NaCl ENVIRONMENT

Figure 3. Average corrosion losses of bridge steels in CMA and NaCl (open exposure).

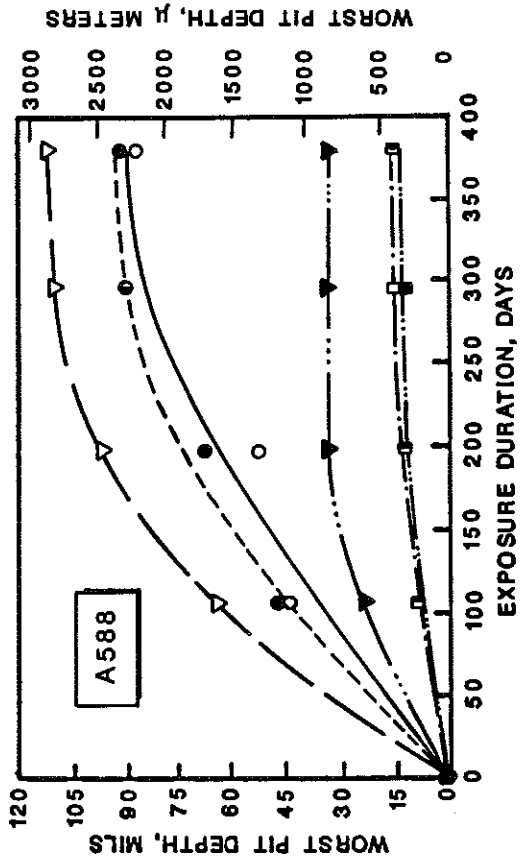
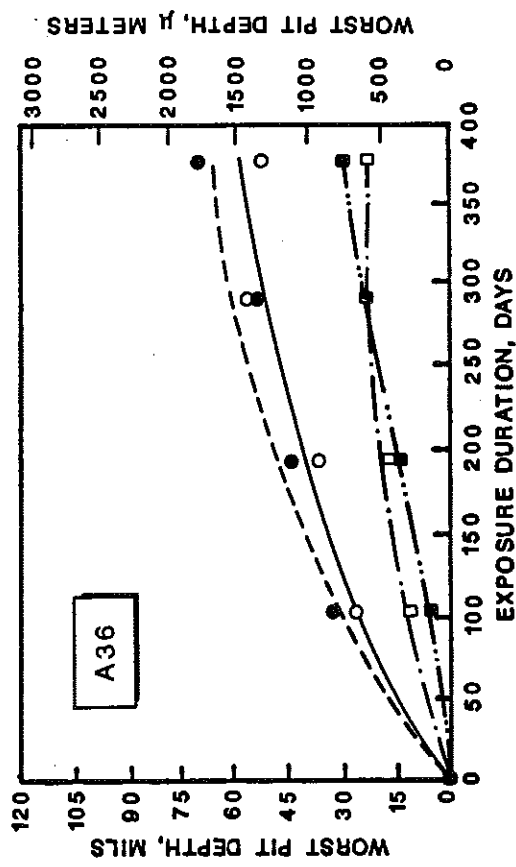
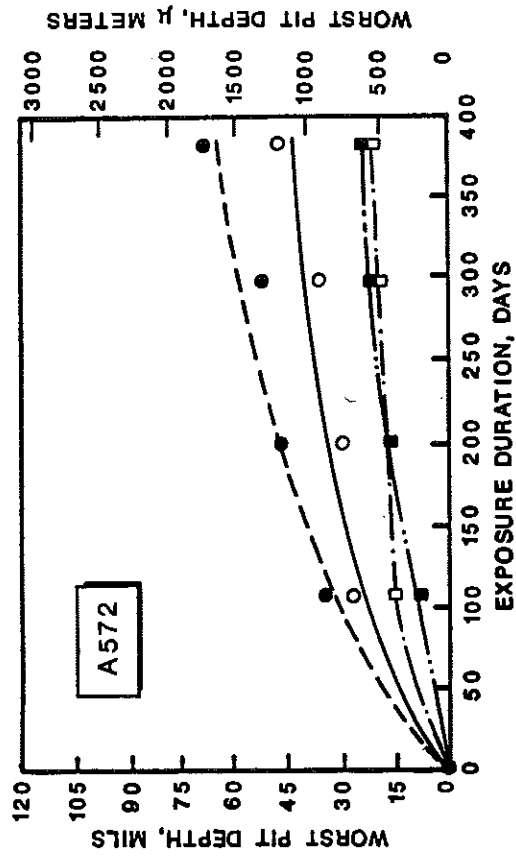


LEGEND

○ — NaCl

□ — CMA

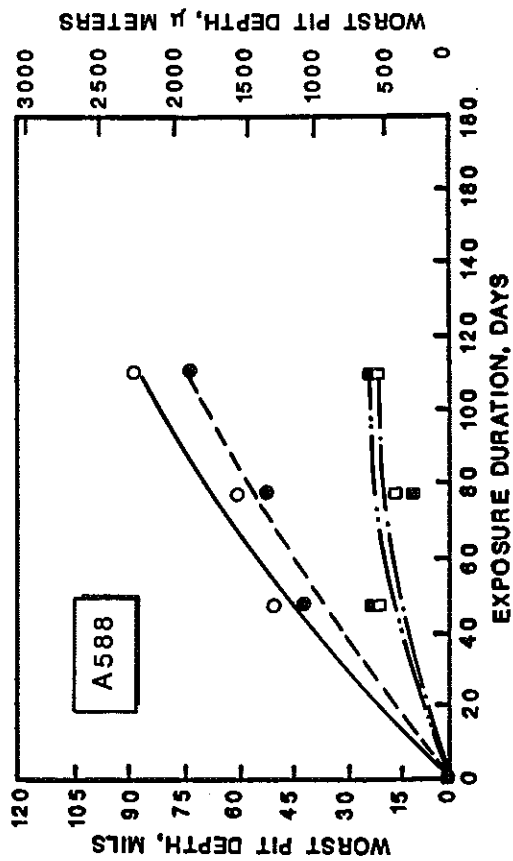
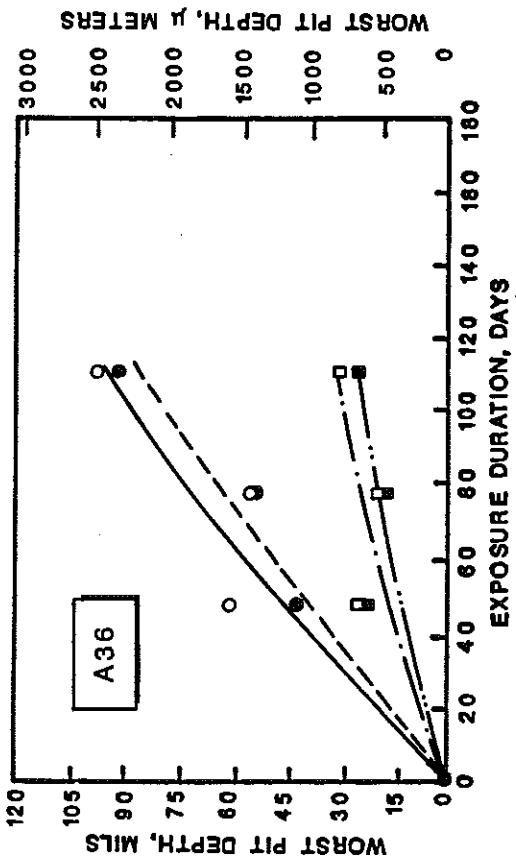
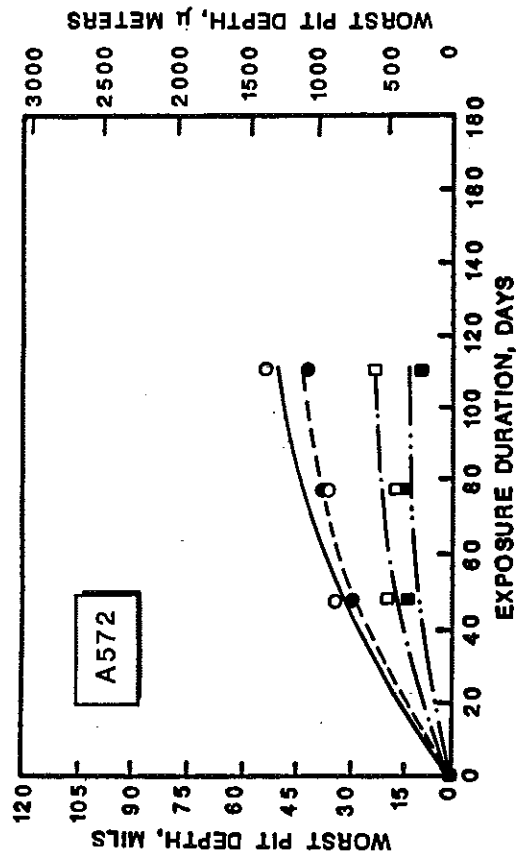
Figure 4. Average corrosion losses of bridge steel tensiles in CMA and NaCl (sheltered exposure).



LEGEND

- - NaCl, FREELY EXPOSED SURFACE
- - NaCl, CREVICE
- - CMA, FREELY EXPOSED SURFACE
- - CMA, CREVICE
- ▽ - NaCl, FREELY EXPOSED SURFACE, PREV. WEATHERED IN NaCl ENVIRONMENT
- ▼ - CMA, FREELY EXPOSED SURFACE, PREV. WEATHERED IN NaCl ENVIRONMENT

Figure 5. Worst pit depth of bridge steels CMA and NaCl (open exposure).



LEGEND

- - NaCl, FREELY EXPOSED SURFACE
- - NaCl, CREVICE
- - CMA, FREELY EXPOSED SURFACE
- - CMA, CREVICE

Figure 6. Worst pit depth of bridge steel tensiles in CMA and NaCl (sheltered exposure).

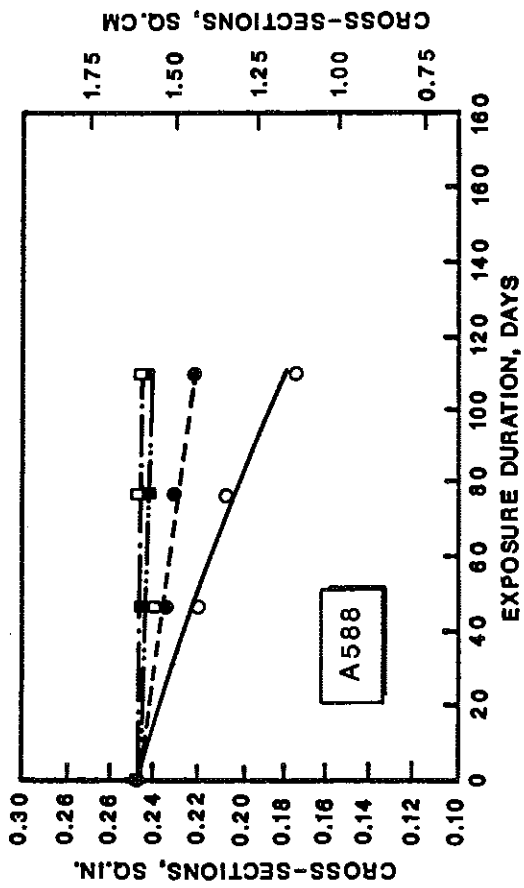
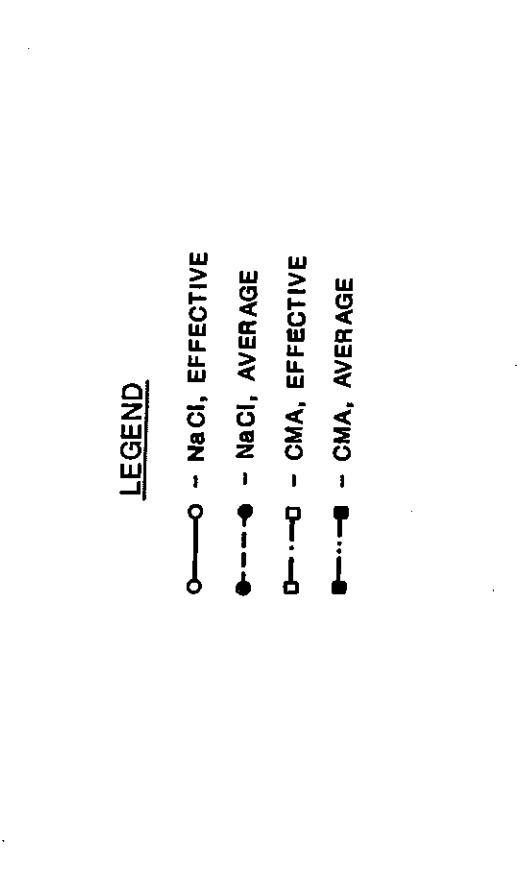
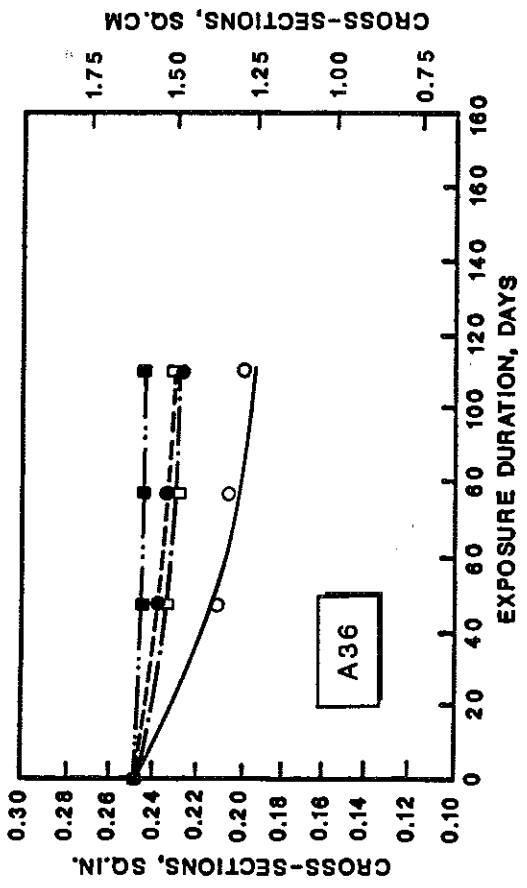
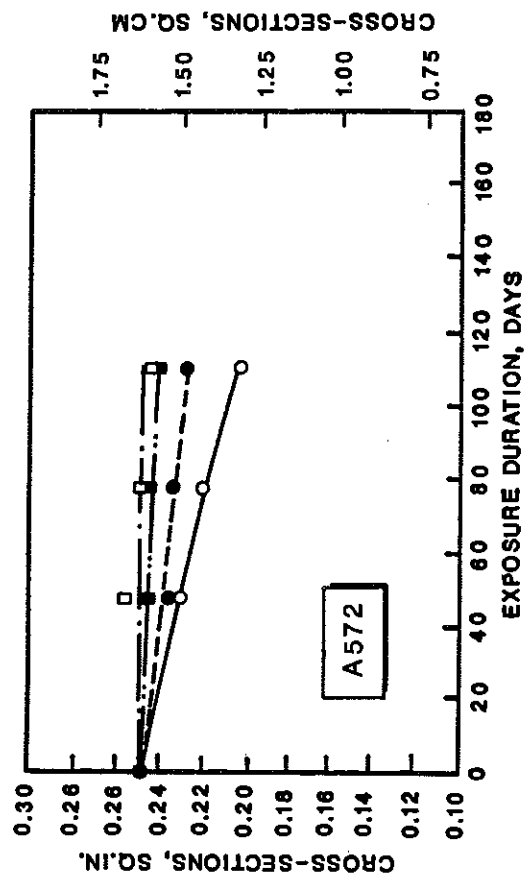
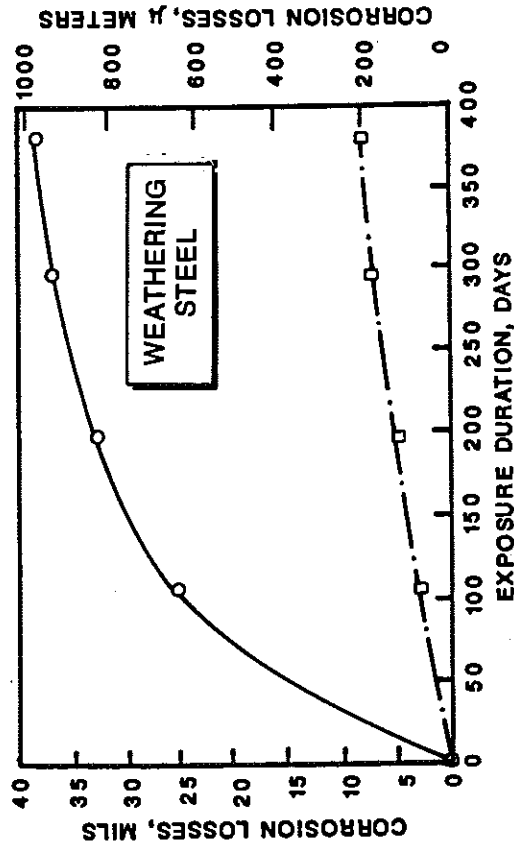
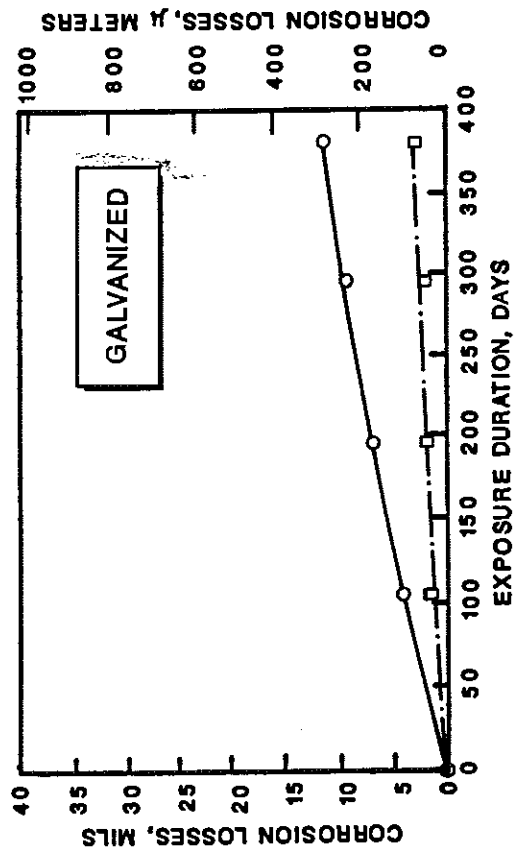
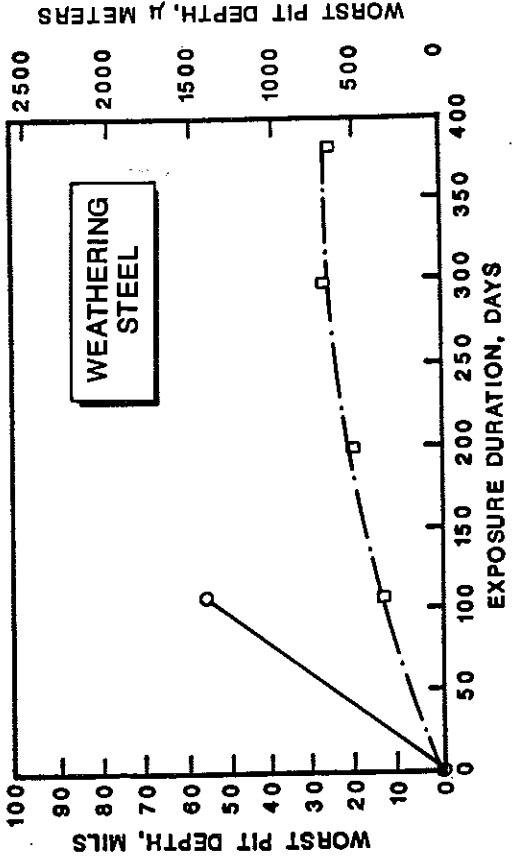
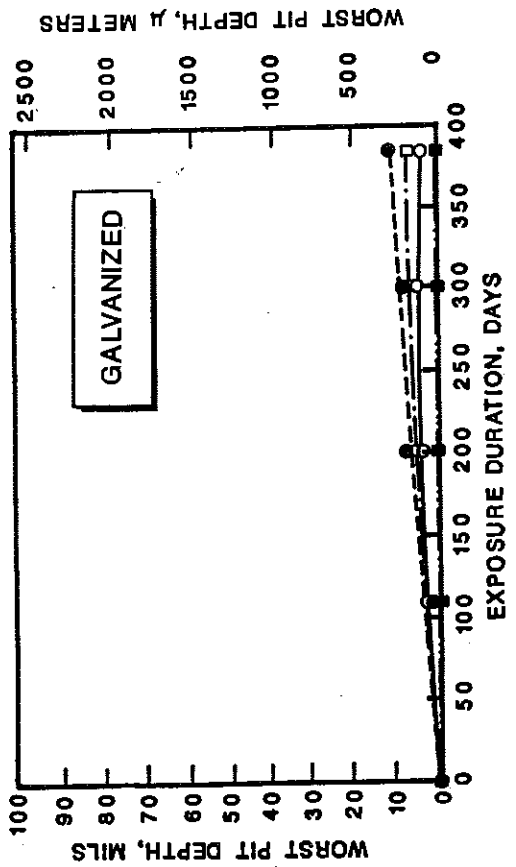


Figure 7. Effective and average cross-sections of bridge steel tensiles in CMA and NaCl (sheltered exposure).



LEGEND : ○ — NaCl
□ — CMA

Figure 8. Average corrosion losses of galvanized and weathering steel guardrail in CMA and NaCl (open exposure).



LEGEND : ○ — NaCl, FREELY EXPOSED SURFACE
● — NaCl, CREVICE
□ — CMA, FREELY EXPOSED SURFACE
■ — CMA, CREVICE

Figure 9. Worst pit depth of galvanized and weathering steel guardrail in CMA and NaCl (open exposure).

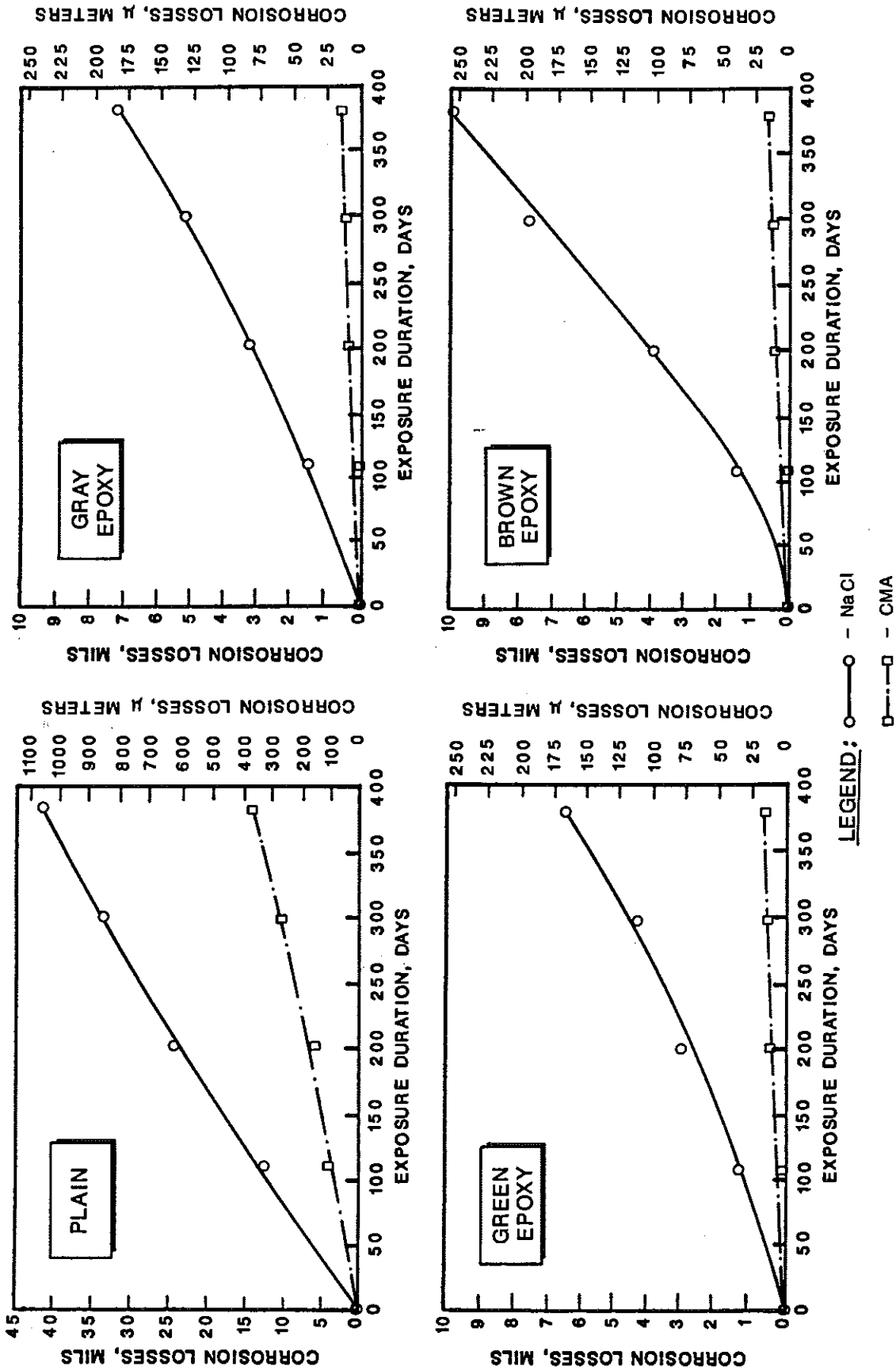


Figure 10. Average corrosion losses of steel reinforcement for concrete in CMA and NaCl (open exposure).

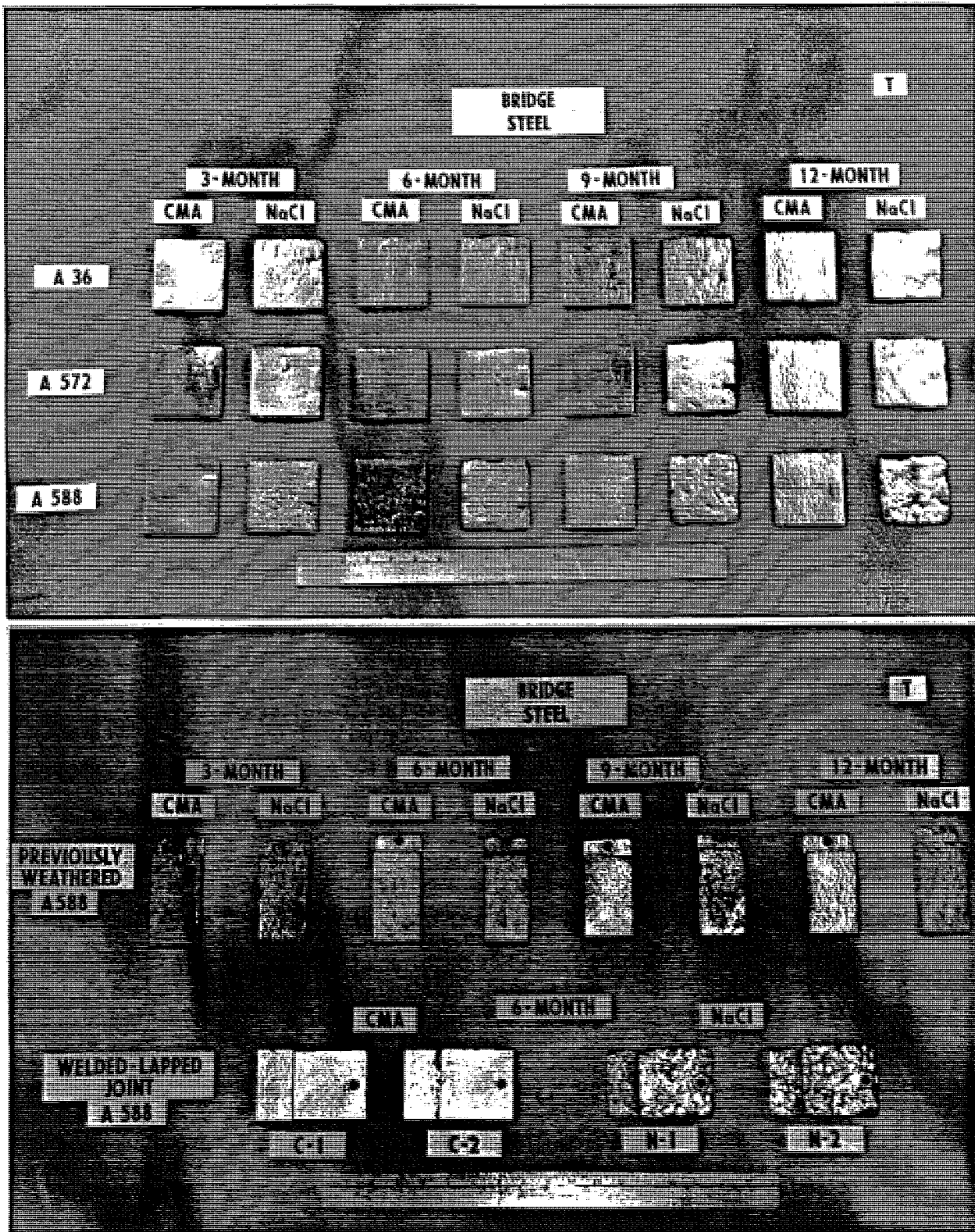


Figure 11. Structural bridge steels after 3, 6, 9, and 12 months exposure in CMA and NaCl.

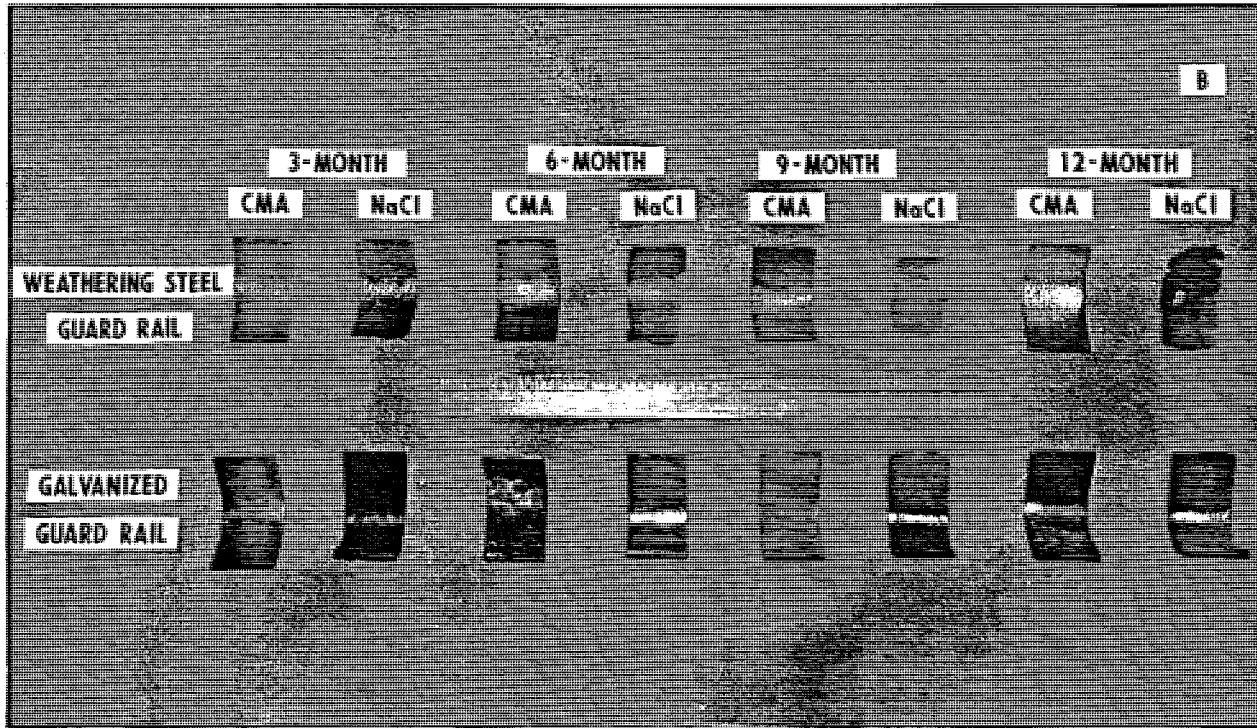


Figure 12. Galvanized and weathering steel guardrail after 3, 6, 9, and 12 months exposure in CMA and NaCl.

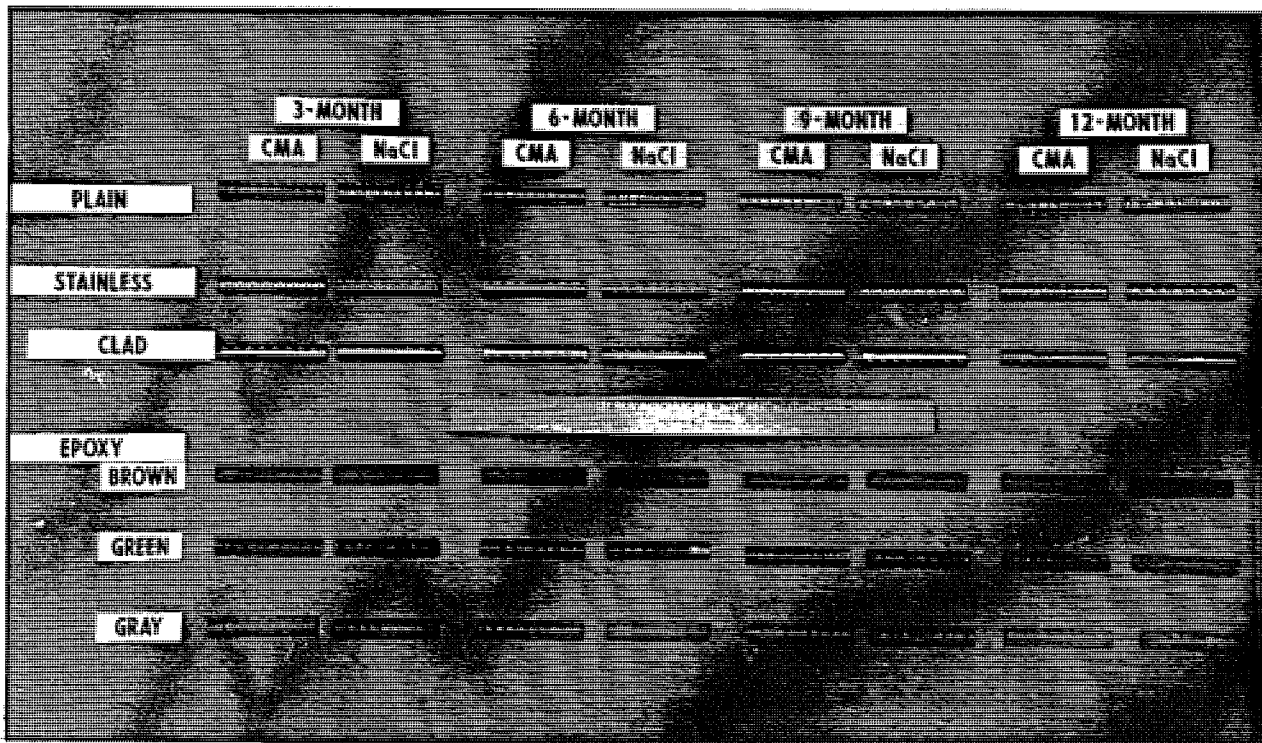


Figure 13. Steel reinforcement for concrete after 3, 6, 9, and 12 months exposure in CMA and NaCl.

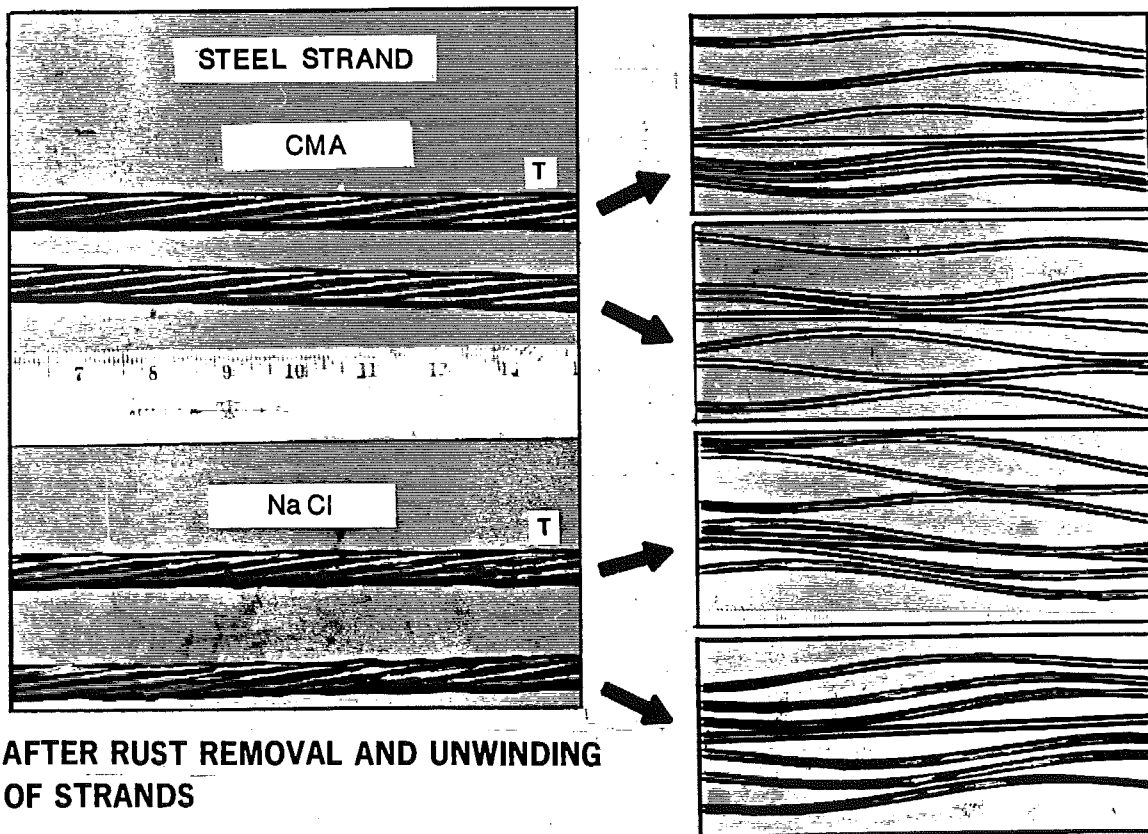
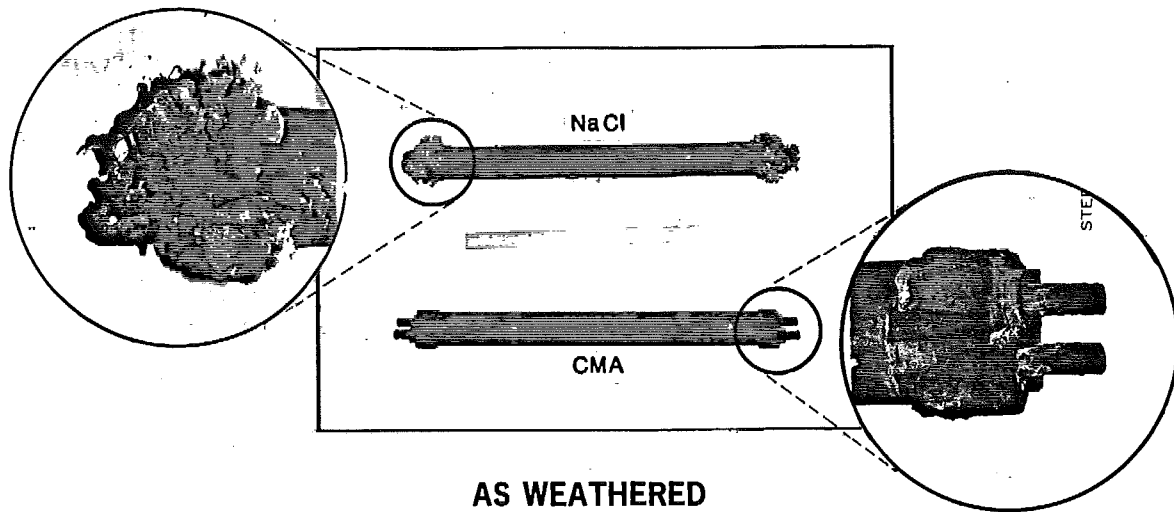


Figure 14. Steel prestressing strand for concrete after six months exposure in CMA and NaCl. (T indicates specimens that were under tensile load during exposure.)

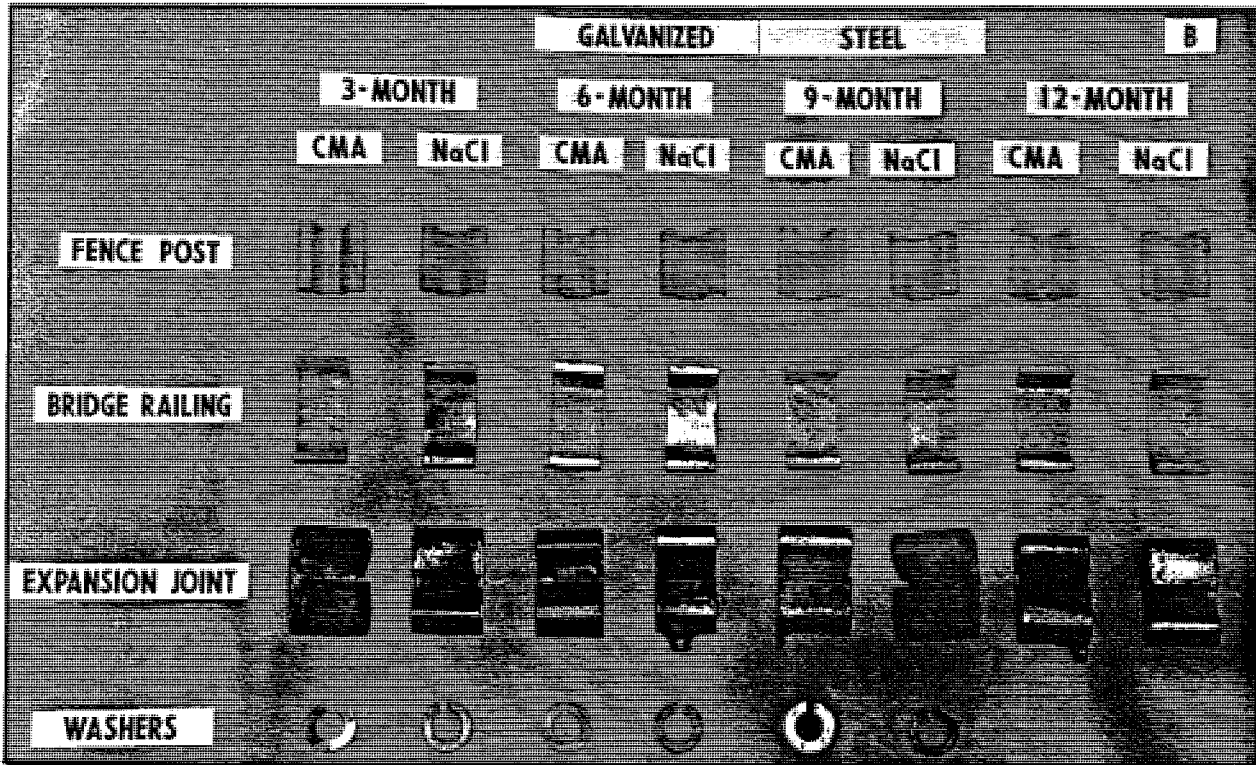


Figure 15. Galvanizing for various materials after 3, 6, 9, and 12 months exposure in CMA and NaCl.

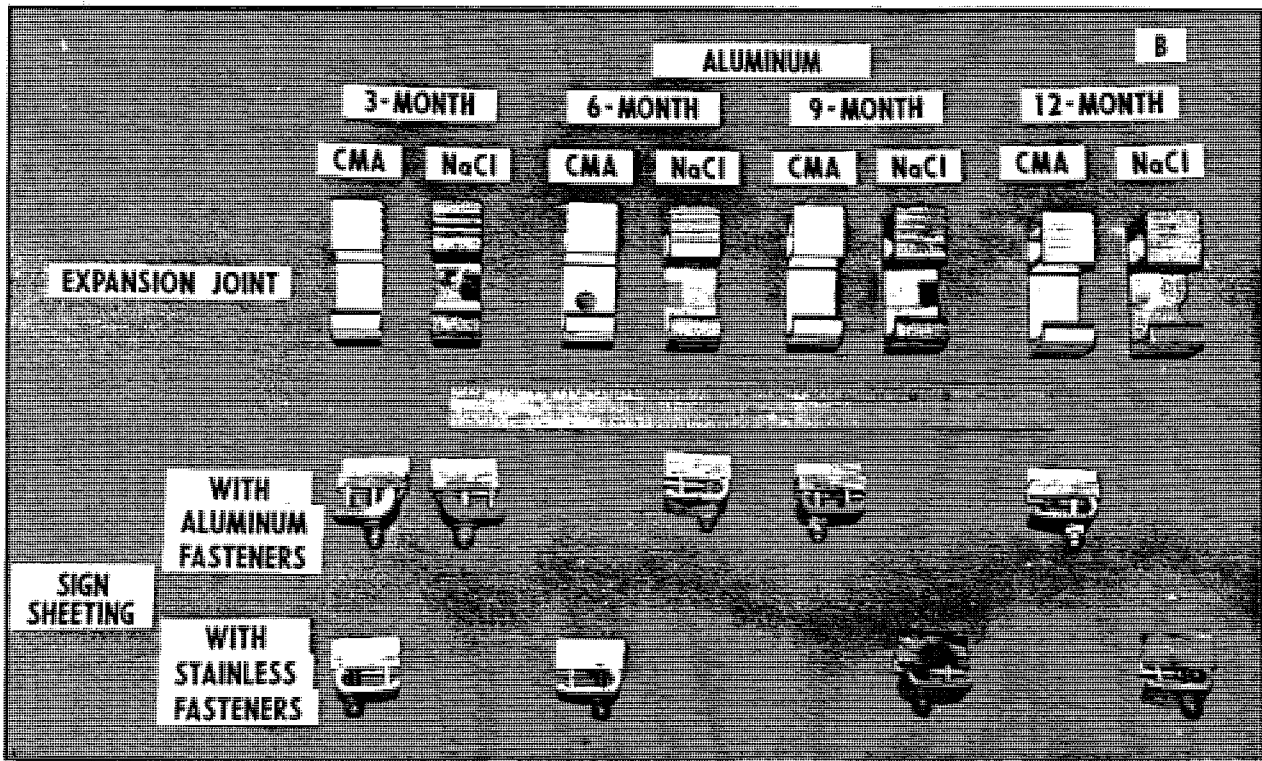


Figure 16. Aluminum after 3, 6, 9, and 12 months exposure in CMA and NaCl.

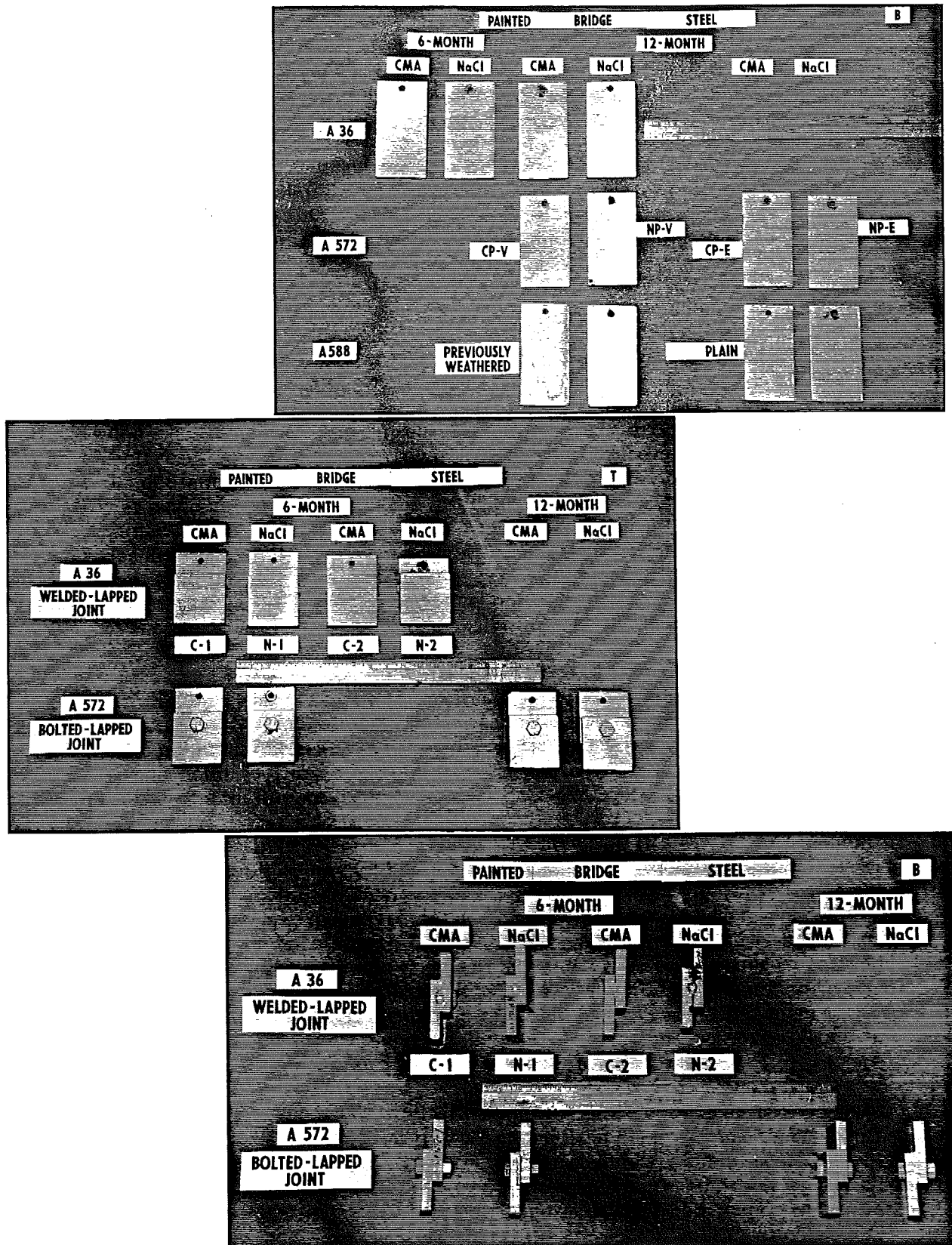


Figure 17. Painted specimens of bridge steels after 6 and 12 months of exposure in CMA and NaCl.

with previous NaCl exposure) experienced from roughly 8 (three months) to 6 (twelve months) times as much average corrosion in NaCl as in CMA. The weathering steels, at least for this particular test environment (i.e., marine beach) and an open exposure, experienced roughly twice the average corrosion in NaCl that the other bridge steels did.

For the more sheltered tensile specimens, ASTM A588 performance (average corrosion) was slightly better in NaCl (compared to its performance when openly exposed) while the other bridge steels performed slightly worse. All of the bridge steels performed essentially the same in CMA whether sheltered or openly exposed.

The average corrosion rates of the previously exposed (to NaCl) weathering steel were slightly higher than their non-weathered counterparts. This small magnitude of difference is probably due to the previously pitted surfaces of these specimens (i.e., pits increase surface area of steel subjected to corrosion and the amount of corrosion that may occur is directly proportional to the available surface).

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 range after three months and in the 15 to 20 mils/year range after twelve months. Worst pitting rates in NaCl are in the 90 mils/year range after three months and in the 45 mils/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 range after twelve months for ASTM A588. While the previously weathered A588 has 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 in general on the sheltered side (surface not directly exposed to light during rotation).

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.

For the NaCl environment, A588 experienced noticeably more severe crevice corrosion (i.e., metal ion concentration cell corrosion) around the plexiglass clamps that secured the specimens in place. All of the bridge steels experienced noticeably worse crevice corrosion in the NaCl environment.

In general, significantly worse pitting occurred for crevices than for openly exposed surfaces in the NaCl environment. This was most evident for ASTM A572. For the CMA environment worst pitting rate differences between crevices and openly exposed surfaces were essentially negligible.

Increases in worst pit depth (open) 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 (sheltered) 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. This is 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 the behavior.)

Originally the rotation of the specimens in the weathering chambers was intended to allow sufficient drying time between dunkings that all specimens would be undergoing wet-dry cycling. After somewhere between one and one-half and two and one-half months of exposure, however, the oxide build-up on many of the steel specimens in the NaCl environment became great enough that they remained wet for the complete cycle. While this constitutes a more severe environment than was originally planned for this testing, it is not an unrealistic environment. Investigation of Michigan's weathering steel bridges has indicated that such pockets of moisture can exist for long periods of time on some portions of a structure (e.g., lower web and flange of beams over traffic lanes and behind the link plates of cantilevered expansion joints) (5). Additionally, the pitting ratio (i.e., worst pit depth/average corrosion losses) of our worst actual environments has been found to be on the order of 3.5. This compares favorably with the three-month and later values found in this study.

For the welded lapped joints, which were only tested for the weathering steels (A588), crevice corrosion interior to the lapped surfaces was not nearly as severe as the corrosion on the freely exposed surfaces for both exposures. While there was slightly more corrosion (interior) for the loose (as opposed to tight) joints, this difference is very minor and apparently only a reflection of the amount of clearance between lapping surfaces that could fill with oxide before compressive forces slowed or stopped further corrosion. Crevice corrosion exterior to the lapped joint was overshadowed by the extreme corrosion rate of the freely exposed surface in NaCl and amounted to only 5 to 10 mils in CMA after twelve months exposure.

The electroslag and submerged arc welds in weathering steel (A588) all performed dramatically better in CMA. While there were no instances in which the weld metal was sacrificial to the base metal for either exposure, there were instances where the heat affected zone (HAZ) of the base metal (both electroslag and submerged arc) and the HAZ of previous weld passes (submerged arc welds) corroded faster than surrounding base metal or weld metal.

Guardrail (Figs. 8, 9, and 12) - The weathering steel guardrail performed essentially identically to the A588 bridge steel. While the average corrosion rate of the guardrail appears to be decreasing with time at a greater rate than for the bridge steels, this is most likely only a reflection of the decreased surface area of the severely corroded specimens.

Pitting in the NaCl environment perforated the weathering steel guardrail material before even three months had passed. This made it impossible to calculate worst pitting rates and ratios of worst pitting rate to average corrosion rate for this material.

The galvanized guardrail performed, as expected, much better than the weathering steel in both exposure environments.

Crevice corrosion was not evident for either of the guardrail materials in the CMA environment.

Steel Reinforcement for Concrete (Figs. 10 and 12) - The uncoated steel reinforcement performed similarly to the bridge steels ASTM A36 and A572. The irregular shape of this material made pit depth measurements difficult and hence these measurements and related calculations were not performed.

The stainless steel reinforcement had negligible corrosion in both exposure environments.

The stainless clad reinforcement experienced negligible corrosion of the stainless coating, but some corrosion of the plain steel interior did occur at the exposed ends. This varies from 5 to 15 mils after three months to 15 to 45 mils after twelve months for the CMA specimens and from 30 to 60 mils after three months to 180 to 240 mils after twelve months for the NaCl specimens.

For the CMA exposure, the epoxy coated specimens experienced only minor corrosion on the unprotected cut ends. Rust undercutting from the cut end had not progressed more than roughly 1/8 in. even after twelve months. The remainder of the epoxy coating remained intact. All three epoxy coatings performed similarly.

For the NaCl exposure, the epoxy coated specimens experienced, at least initially, the most corrosion damage at the unprotected cut ends. At three months the epoxy coating had been rust undercut up to 1/4 in.

from the cut end, while the remainder of the epoxy coating was still well intact. At nine and twelve months some specimens had rust undercutting up to 1 in. from the cut ends and rust breaks elsewhere in the epoxy coating. The rust breaks removed from the ends were typically located at the normal deformations in the steel that are intended to give the reinforcement gripping strength. The breaks in these areas suggest problems with non-uniform coating thickness around the deformations and/or possible problems with adequate cleaning or surface preparation of these areas prior to epoxy coating.

Prestressing Strand (Tables 1, 2 and Fig. 14) - The major strand data are included in Table 1. The control specimens, being from the same original roll as all of the test specimens, should be representative of the original state of the strand specimens. All of the control and almost all of the CMA specimens that were loaded to ultimate failure broke in the grips. Hence, the true ultimate tensile strengths would, undoubtedly, have been greater. The uncertainty in these values is expressed in the tables by the use of inequality symbols where appropriate.

The most significant result is the low ultimate strength of the NaCl weathered specimens. After three months, the value for one of the specimens is below 70 percent of the ultimate tensile strength (28,900 lb), 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.

Surface appearance of the NaCl weathered specimens is also much worse. After three months, pitting approached up to 40 percent (approximately 70 mils) of the initial individual wire diameter of 165 mils and up to 65 percent (approximately 100 mils) after six months.

Pitting for these specimens is, in general, present almost exclusively on the outer surfaces of the outer wires of the strands with the central wire experiencing only minor corrosion. The major corrosion occurring in this instance appears to be a form of crevice corrosion known as a metal ion concentration cell. For this type of cell, corrosion occurs primarily exterior to the crevices formed between adjacent surfaces. The primary driving force for this corrosion reaction is the difference in the metal ion concentration that occurs between the crevice interior and its surroundings. This type of corrosion reaction normally progresses until the corrosion products exterior to the crevice have equalized the metal ion concentrations. A washing/wetting cycle that removes the soluble metal ions from the crevice surroundings starts the accelerated corrosion process all over again. Localized corrosion rates for such crevice-accelerated reactions can be 10 to 100 times greater than would otherwise occur for comparable environments.

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	17.1	3.8
	NaCl	29.81	109.5	20.52	3.231/15.7	22.2	5.05	45	155	6.7
	Untensioned									
6 months	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
	Tensioned									
	CMA	29.88	110.0	20.56	1.111/5.4	4.1	3.44	10	18.3	4.5
6 months	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.

Such a situation may arise in actual service under any set of circumstances that allows deicing salt and water to gain access to the steel strand. Contributors include cracks in the concrete, breaks in the plastic sheathing covering the strand, leaking anchorage plugs and bleed voids (6).

For the CMA exposure the tensioned strand performed essentially the same as the untensioned strand. While some small differences are shown in Table 2, these differences are on the same order of magnitude as the differences that occurred between the original control specimens.

For the NaCl exposure the tensioned strand performed markedly better with respect to both corrosion losses and ultimate strength losses than the untensioned strand. This is just the reverse of what would normally be expected. Apparently the built-in crevices within the strands are becoming effectively filled with corrosion products to the extent that they cannot accelerate corrosion as rapidly as initially. The difference between the tensioned and untensioned specimens are undoubtedly the indirect result of both the narrowing of the interwire spacing as the strand is loaded and the final tensile load state of the individual wires. The narrower spacing would allow the crevices to become filled sooner and the retained tensile load in the wires would make initial deformation of the wires by rust expansion forces more difficult. Other investigations have found that such crevice corrosion can continue operating although at a reduced rate as long as the crevice boundaries are not strong enough to prevent deformation by rust expansion forces (typically greater than or equal to 1200 lb/sq in.) (7).

While such crevice filling can slow this particular crevice corrosion reaction, it can only delay (and not stop) eventual strand failure. Even if the individual wires were initially stiff enough to prevent deformation, at some point in the corrosion process they will eventually be thin enough that they can no longer do so.

Differences in the corrosion rates (Table 1) of the three and six-month specimens combined with the ultimate strength results (Table 2), suggest some other important differences between the CMA and NaCl exposures. 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.

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.

Galvanizing (Table 3 and Fig. 15) - Significant performance differences were evident for the galvanized specimens. While performance was approximately uniform for all of the specimens exposed to NaCl, very noticeable differences were present among the CMA exposed specimens. As a result, the loss of galvanizing in the CMA environment varied from being 1/3 to only 1/9th as great as in the NaCl environment. The large differences in performance that were evident for the CMA exposed specimens suggests that potential differences in the galvanizing process may exist which could significantly (and favorably) affect the life of galvanized materials in a CMA environment.

While galvanizing specimens were also exposed for six, nine, and twelve months, results are only reported for the first three months. Difficulties in successfully removing the zinc and iron oxides without significantly affecting the remaining galvanizing proved to be too much for these later specimens to allow for quantitative results (all or most of the remaining galvanizing was inadvertently removed from these specimens during the cleaning process). Some observations can still be made however.

For all the galvanized materials in CMA, at least some of the galvanizing was still remaining after even twelve months and there was no significant rusting of the underlying base metal. This was not so for the galvanized materials in NaCl where by twelve months most or all of the galvanizing was gone and significant corrosion and/or pitting of some portions of the specimens had occurred. Rusting of the underlying base metal at the unprotected cut ends of specimens was most apparent (up to 150 mils after twelve months) with similar if not as severe of corrosion occurring where the galvanizing had been consumed (average approximately 30 to 50 mils after twelve months).

Aluminum (Fig. 16) - All aluminum specimens performed extremely well in both environments. The average corrosion in both environments was negligible, but some mild pitting did occur on all of the NaCl exposed specimens. The pitting (5 to 10 mils) was not of sufficient density or magnitude to result in any significant loss of strength but might act enough as a stress riser under tensile loading to adversely affect fatigue performance. While pit depth did not appear to increase with time, the density (or number) of pits did.

Painted Steels (Fig. 17) - No deterioration of the painted coatings was observed for either environment. The few small breaks in the painted coating, which may be observed in the photographs, are the result of mechanical contact between specimens during the cleaning process following exposure.

For the lapped surfaces that were only tack-welded some minor corrosion did occur between the lapped surfaces (a few pits of 5 to 10 mils deep), however average corrosion for these surfaces was negligible.

For the bolted surfaces, where the materials were painted prior to bolting, no corrosion was evident for either exposure environment after twelve months.

TABLE 3
CORROSION PERFORMANCE OF GALVANIZING AFTER THREE MONTHS

Specimen	Original		Weight Loss, oz/%	Average ¹ Corrosion Rate (ACR), mils/yr/surface	Ratio, ACR, NaCl / ACR, CMA	Original Thickness, mils	Weathered ² Thickness, mils	Surface Area Still Galvanized, percent
	Dimensions, in. x in. x in.	Surface Area, sq in.						
Fence Post								
CMA	Irregular	14.53	0.029/.76	1.66	8.81	5.0	2.6	100
NaCl	Irregular	14.40	0.252/6.97	14.62		5.0	1.0	25
Bridge Rail								
CMA	Irregular	16.38	0.048/.66	2.42	5.60	3.7	2.8	100
NaCl	Irregular	15.68	0.255/3.66	13.56		3.7	1.2	25
Expansion Joint								
CMA	Irregular	36.60	0.086/.49	1.95	5.28	2.7	1.7	95
NaCl	Irregular	36.50	0.451/2.76	10.30		2.7	1.9	40
Guradrail								
CMA	5.30 x 2.00 x .110	22.81	0.013/2.62	4.89	2.94	4.0	1.8	95
NaCl	5.40 x 2.05 x .110	23.78	0.041/7.62	14.37		4.0	1.4	10

¹ Based on weight loss.

² Based on change in zinc coating thickness measured by a positector.

Galvanic Couples - 1) Stainless/Galvanized. The galvanizing and underlying steel bolts proved to be especially sacrificial to the stainless nuts for both environments, but markedly worse for the NaCl environment. After twelve months there is very little left of the original fastener that was placed in the NaCl environment. Even the stainless nut has deteriorated significantly in the NaCl. While the NaCl exposure was obviously worse, this couple (for the ratio of sacrificial metal to protected metal as it exists here) would not be recommended for either environment.

2) Stainless/Aluminum. The stainless fasteners experienced negligible corrosion and the aluminum sheeting only minor pitting (roughly 5 mils after twelve months) where the two materials made contact. Corrosion performance was only slightly worse in NaCl.

CMA and NaCl Mixes

CMA/NaCl mixes always performed better than NaCl alone even when only minuscule amounts of CMA were present (0.10 percent CMA).

While mixes (especially as the CMA/NaCl ratio is reduced) matched more closely the performance of NaCl alone at the earliest exposure durations, their performance improved considerably as time went on, usually leveling off at a corrosion rate comparable to CMA alone with only a few mils more average corrosion loss having occurred.

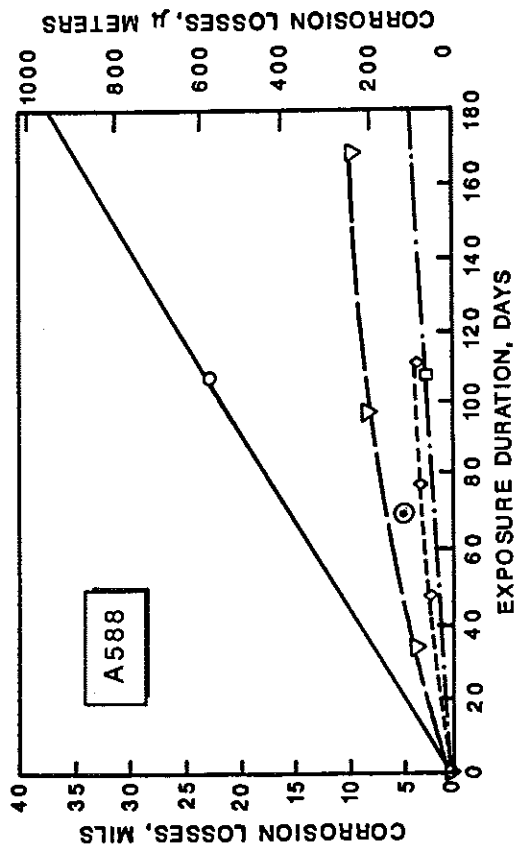
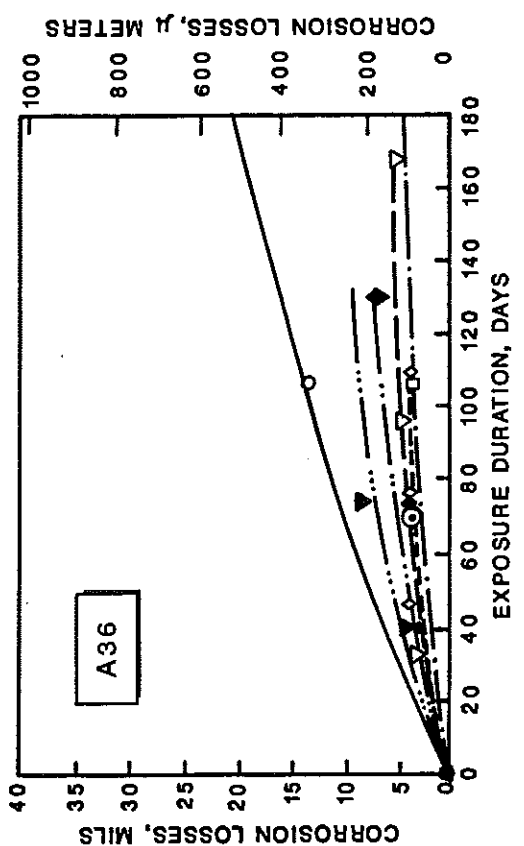
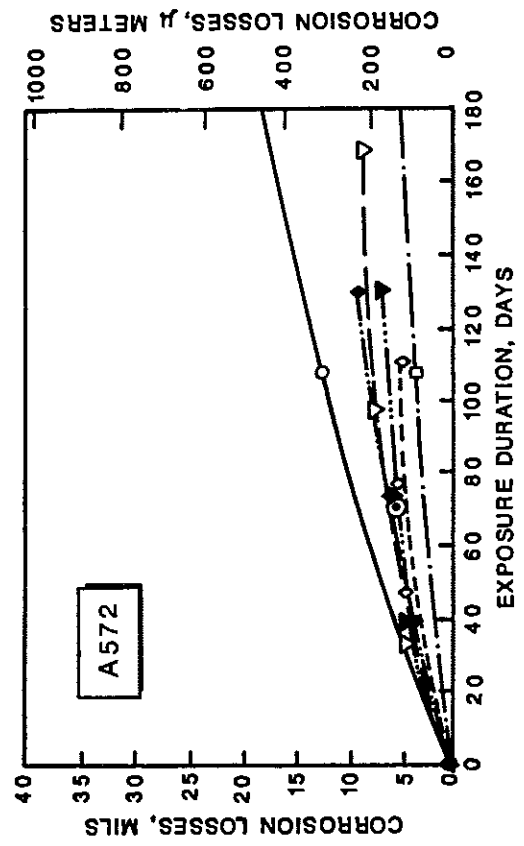
Pitting was, in general, less severe (deep) in the CMA/NaCl mixes than for NaCl alone, although there were some exceptions—most notably the freely exposed surfaces of the bridge steels (open exposure).

The performance of the 0.46 CMA/NaCl ratio (1.6 percent CMA and 3.5 percent NaCl), sometimes as bad or worse than the 0.11 CMA/NaCl ratio, is probably more related to the concentration of the CMA than to the ratio of CMA to NaCl. Other research which has examined the corrosiveness of CMA as a function of its concentration has found that at roughly this concentration CMA is more corrosive than either higher or lower concentrations (8). Since in the real world, as drying occurs, CMA can at most be at this concentration for only a very small percentage of the time, this CMA/NaCl ratio probably is not as potentially corrosive as the data might otherwise indicate.

Bridge Steels (Figs. 18 through 22) - Even for the lower CMA/NaCl ratios average corrosion performance remains close to that of CMA alone for an open exposure but starts to degrade becoming closer to that of NaCl alone for more sheltered exposures.

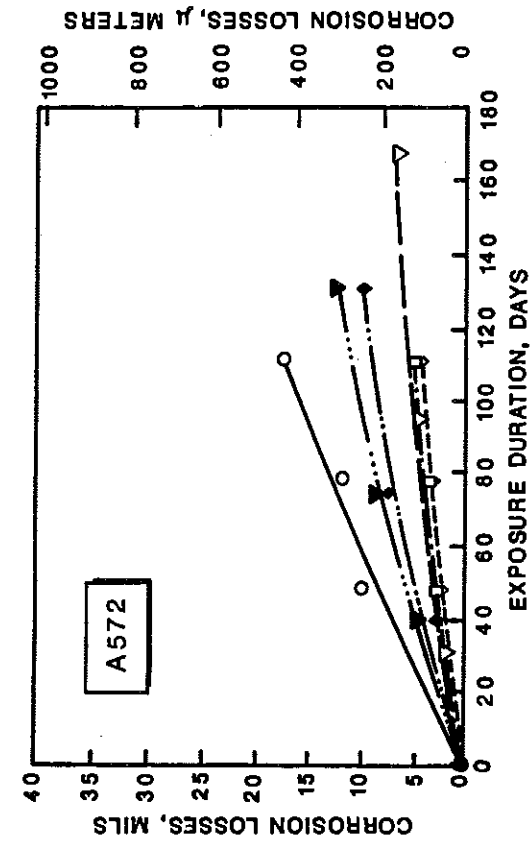
For the higher CMA/NaCl ratios average corrosion performance was actually better in a sheltered exposure than an open one.

Differences between higher and lower CMA/NaCl ratios are most evident for the average and effective cross-sections of the sheltered tensile specimens. Even the lowest CMA/NaCl ratio tested, however, had



- LEGEND**
- — NaCl, 3 1/2%
 - — CMA, 6 1/8%
 - ◇ — 6 1/6% 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 18. Average corrosion losses of bridge steels in CMA and NaCl 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

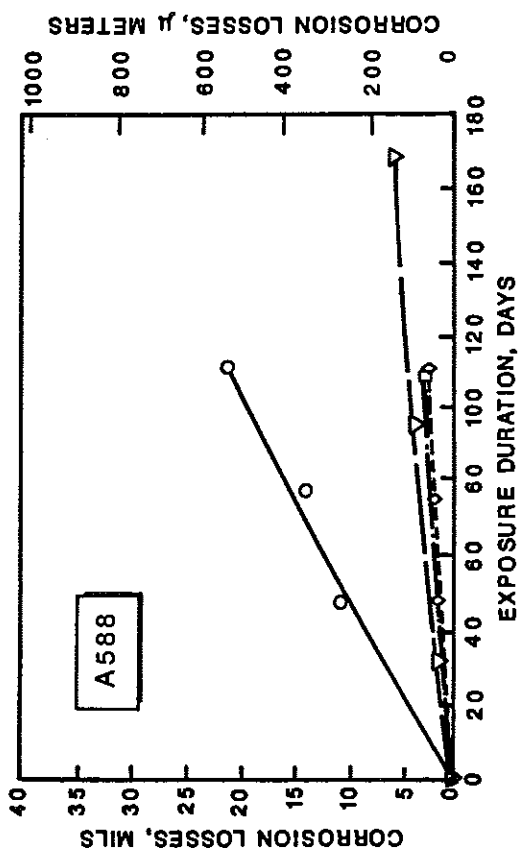
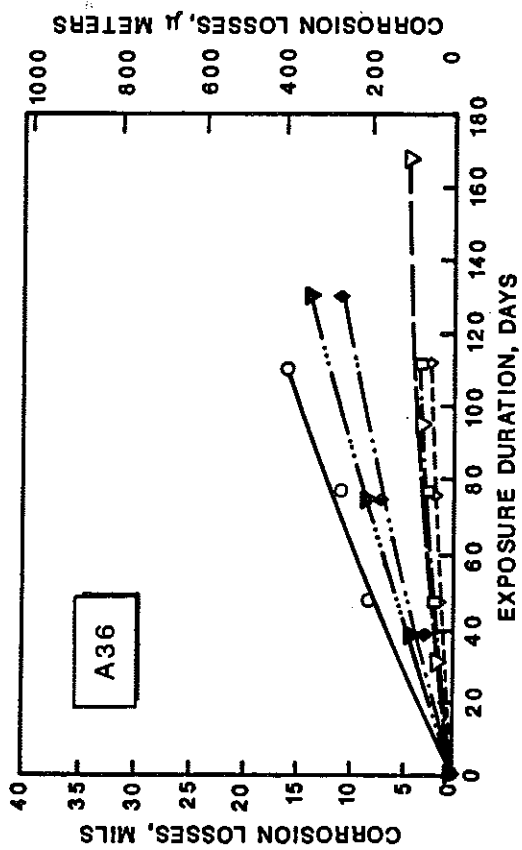
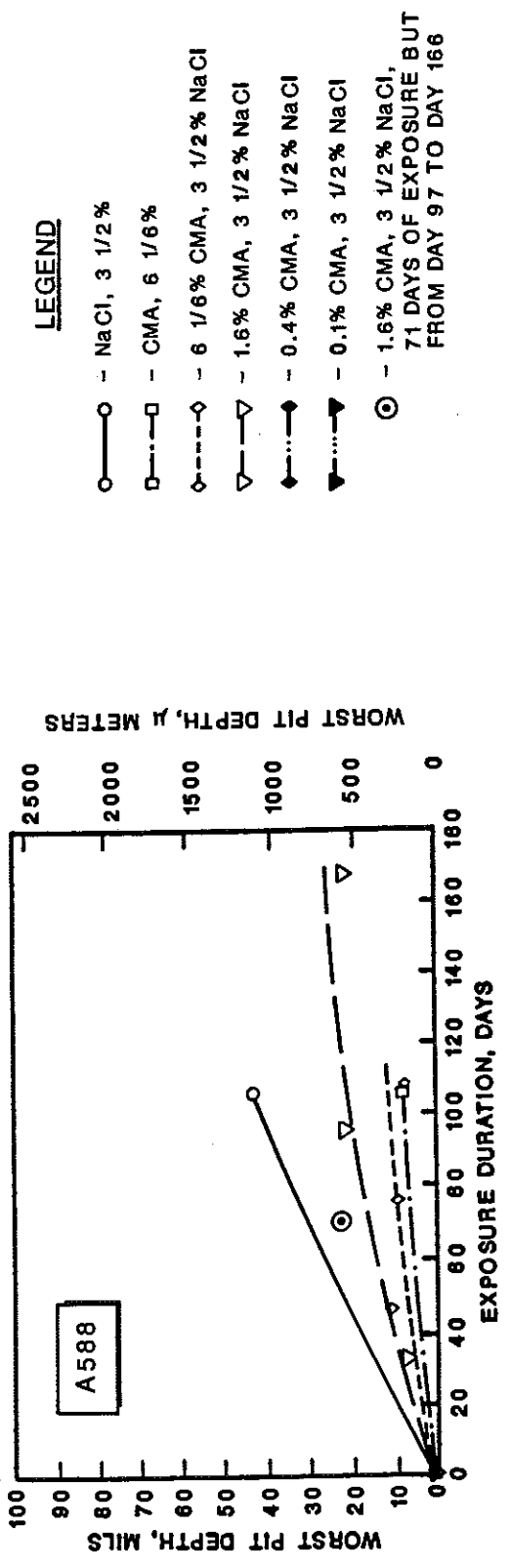
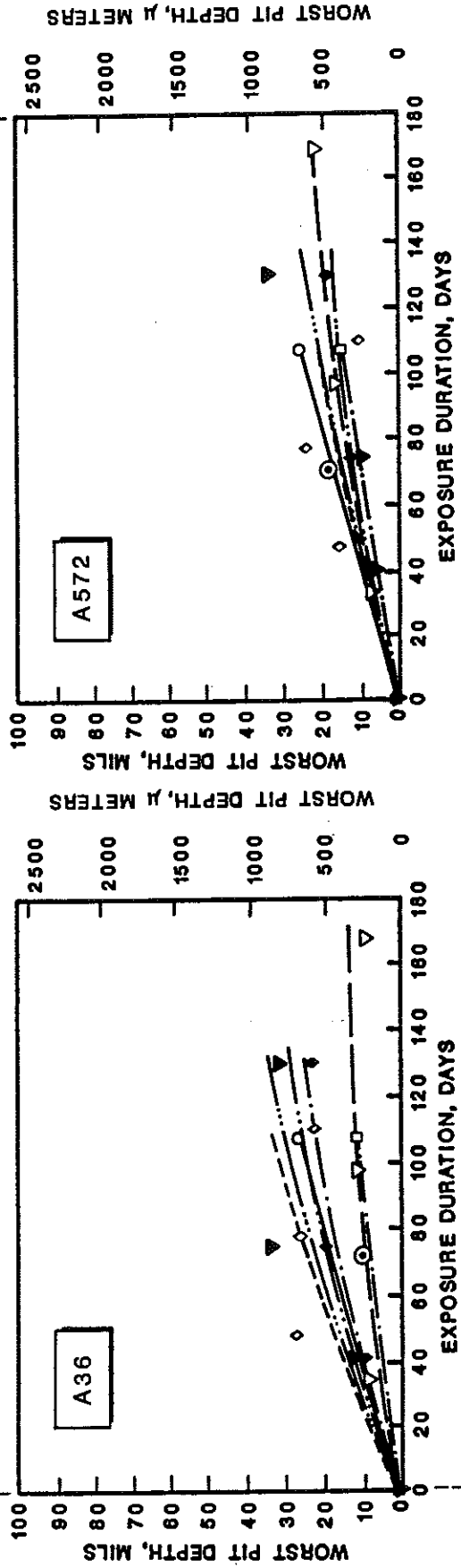


Figure 19. Average corrosion losses of bridge steel tensiles in CMA and NaCl mixes (sheltered exposure).

FREELY EXPOSED SURFACES

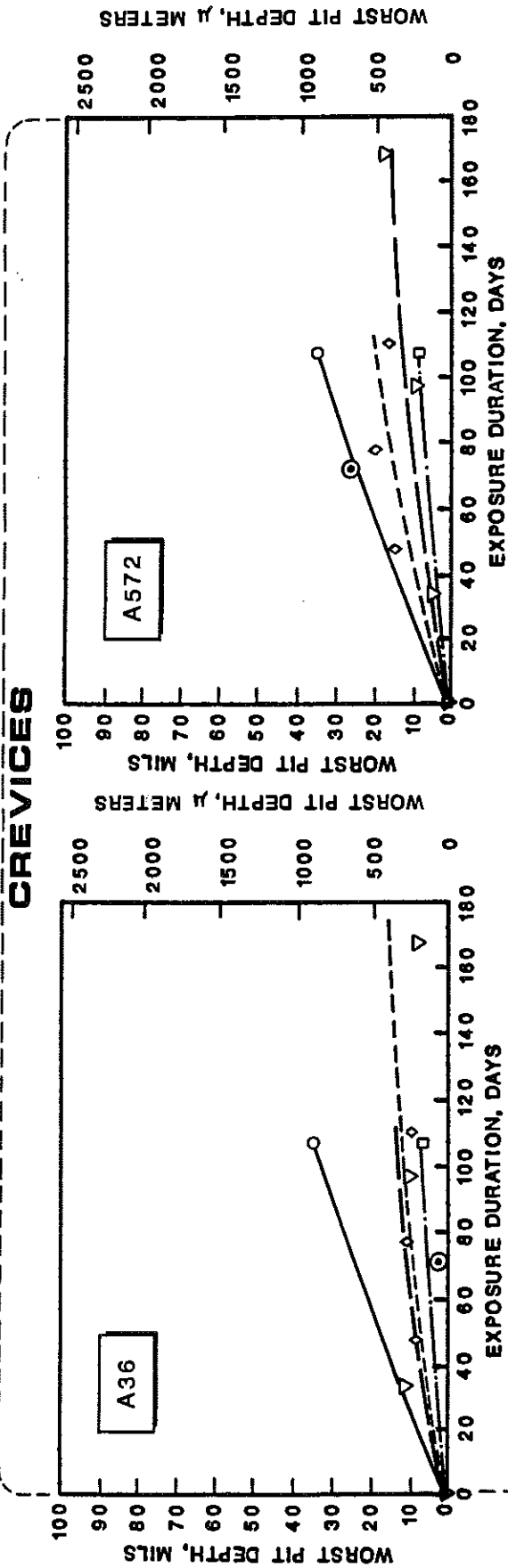


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/6%
- ◇ — 6 1/6% 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 166

Figure 20. Worst pit depth of bridge steels in CMA and NaCl mixes for both freely exposed surfaces and crevices (open exposure).

CREVICES

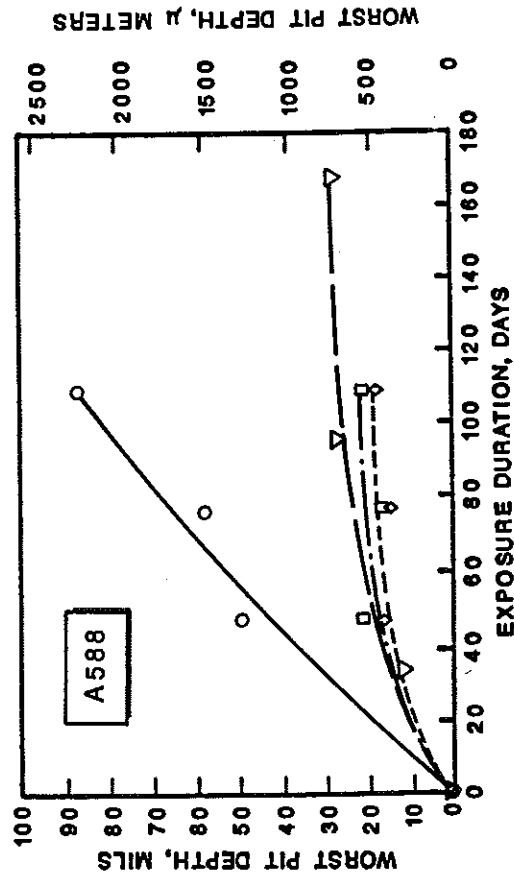
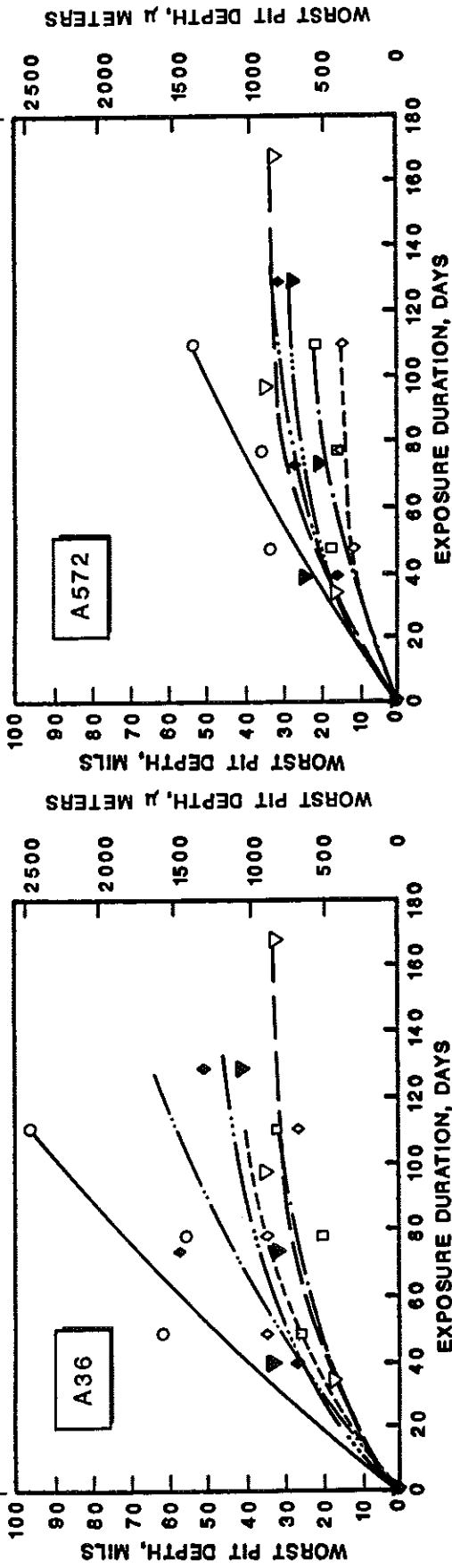


LEGEND

- NaCl, 3 1/2%
- -□- - CMA, 6 1/6%
- · · · ·◇· · · · · 1/8% CMA, 3 1/2% NaCl
- · - · -△- · 1.6% CMA, 3 1/2% NaCl
- ⊙ 1.6% CMA, 3 1/2% NaCl, 71 DAYS OF EXPOSURE BUT FROM DAY 97 TO DAY 166

Figure 20 (cont). Worst pit depth of bridge steels in CMA and NaCl mixes for both freely exposed surfaces and crevices (open exposure).

FREELY EXPOSED SURFACES



LEGEND

- - NaCl, 3 1/2%
- - CMA, 6 1/8%
- ◇ - 6 1/6% 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 21. Worst pit depth of bridge steels in CMA and NaCl mixes for both freely exposed surfaces and crevices (sheltered exposure).

CREVICES

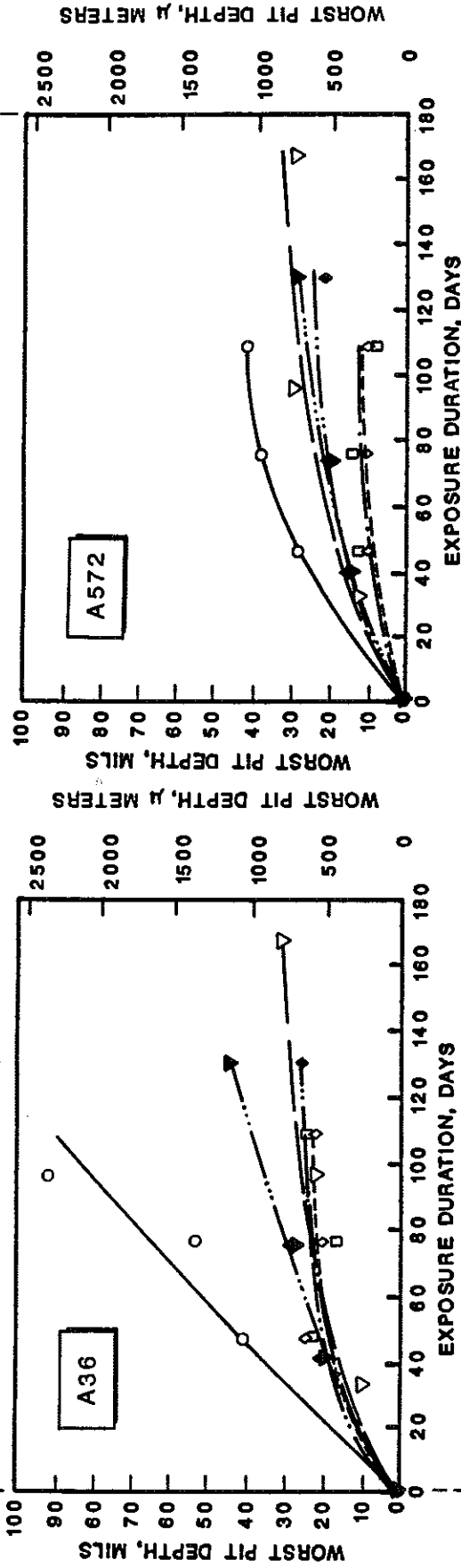
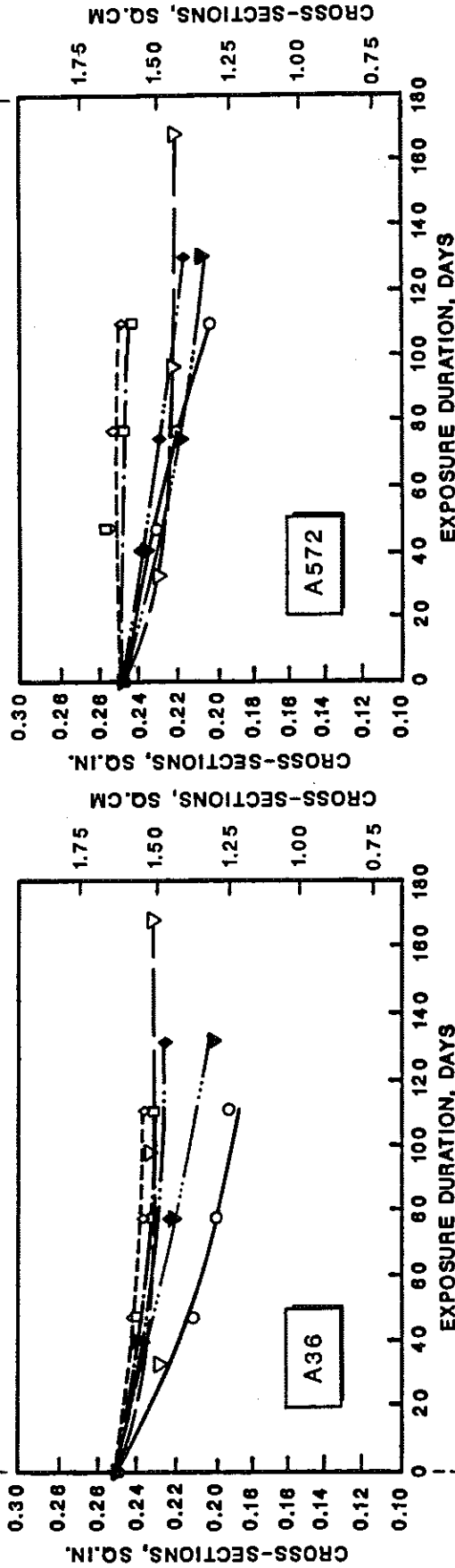


Figure 21 (cont). Worst pit depth of bridge steels in CMA and NaCl mixes for both freely exposed surfaces and crevices (sheltered exposure).

EFFECTIVE

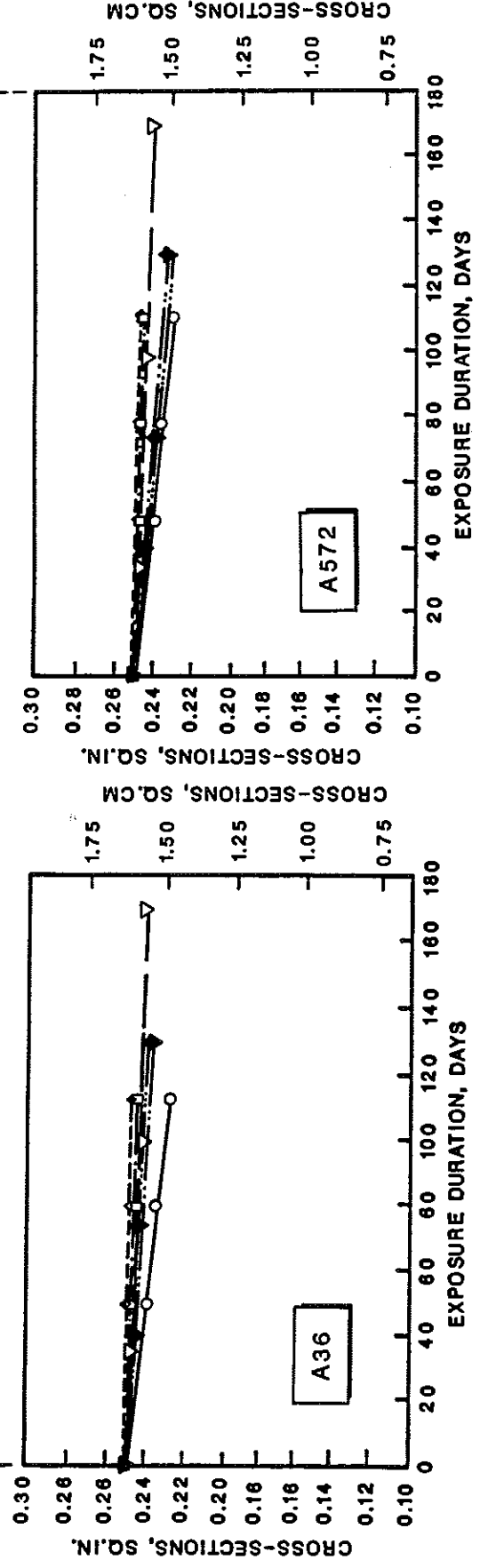


LEGEND

- - NaCl, 3 1/2%
- - CMA, 6 1/8%
- ◇ - 8 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 22. Effective and average cross-sections of bridge steel tensiles in CMA and NaCl 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

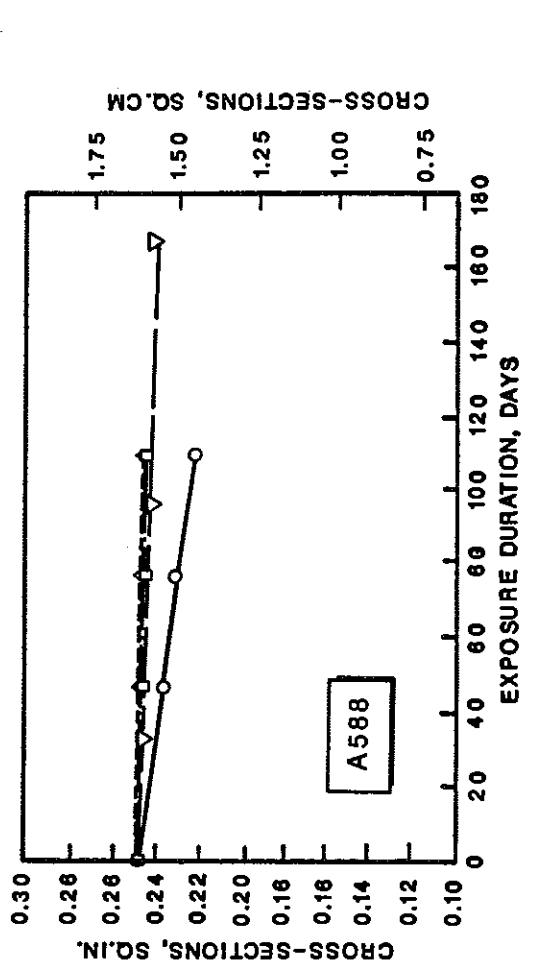


Figure 22 (cont). Effective and average cross-sections of bridge steel tensiles in CMA and NaCl mixes (sheltered exposure).

markedly better corrosion performance than NaCl alone at the longest exposure durations.

Guardrail (Figs. 23 and 24) - Average corrosion rates of the higher mix ratios are slightly better than the lower mix ratios for both the weathering steel and galvanized guardrail although the quantitative differences are much smaller for the galvanized guardrail. Worst pit depth measurements for the higher CMA/NaCl ratios appear to more closely resemble the performance of CMA alone as exposure duration increases than do the lower ratios.

Steel Reinforcement for Concrete (Fig. 25) - All of the steel reinforcements, epoxy coated or uncoated, performed noticeably better in all of the CMA/NaCl mixes than in NaCl alone.

Prestressing Strand - Although prestressing strand was included in all of the various solutions tested, only the NaCl and CMA exposures had pieces long enough to allow actual performance (tensile) testing. For the other solutions the likely performance can be approximated by figuring that strength losses will be directly proportional to the worst pit depth for the environment (sheltered, crevice) and exposure solution in question. This seems an appropriate means of estimating performance since the overall tensile performance of the strand will be dictated by the smallest remaining cross-section of its weakest member, which for the small dimension of an individual strand wire will in turn be related to the maximum pit depth.

None of the mixes generated anywhere near as severe of corrosion as occurred in NaCl alone. For even the lowest CMA/NaCl ratio tested pitting is relatively uniform and it is difficult to find a pit which is more than 5 mils deeper than the adjacent surface.

Aluminum - Only very minor pitting occurred on the freely exposed surface for all combinations of CMA/NaCl. For the two lower CMA/NaCl ratios, however, crevice corrosion of approximately 5 mils depth occurred for almost half of the lapped surfaces after three months exposure.

Distilled Water and Simulated Acid Rain

In almost all instances both the distilled water and the acid rain produced slightly less corrosion than CMA alone with the acid rain, naturally, being slightly more corrosive, in general, than the distilled water alone.

While acid rain is noted for accelerating corrosion, the effect is apparently small compared to that produced by NaCl in concentrations such as those used for deicing highways.

Bridge Steels (Figs. 26 through 30) - In general, average corrosion is less in both the distilled water and the simulated acid rain than in CMA alone for both open and sheltered exposures. The simulated acid rain

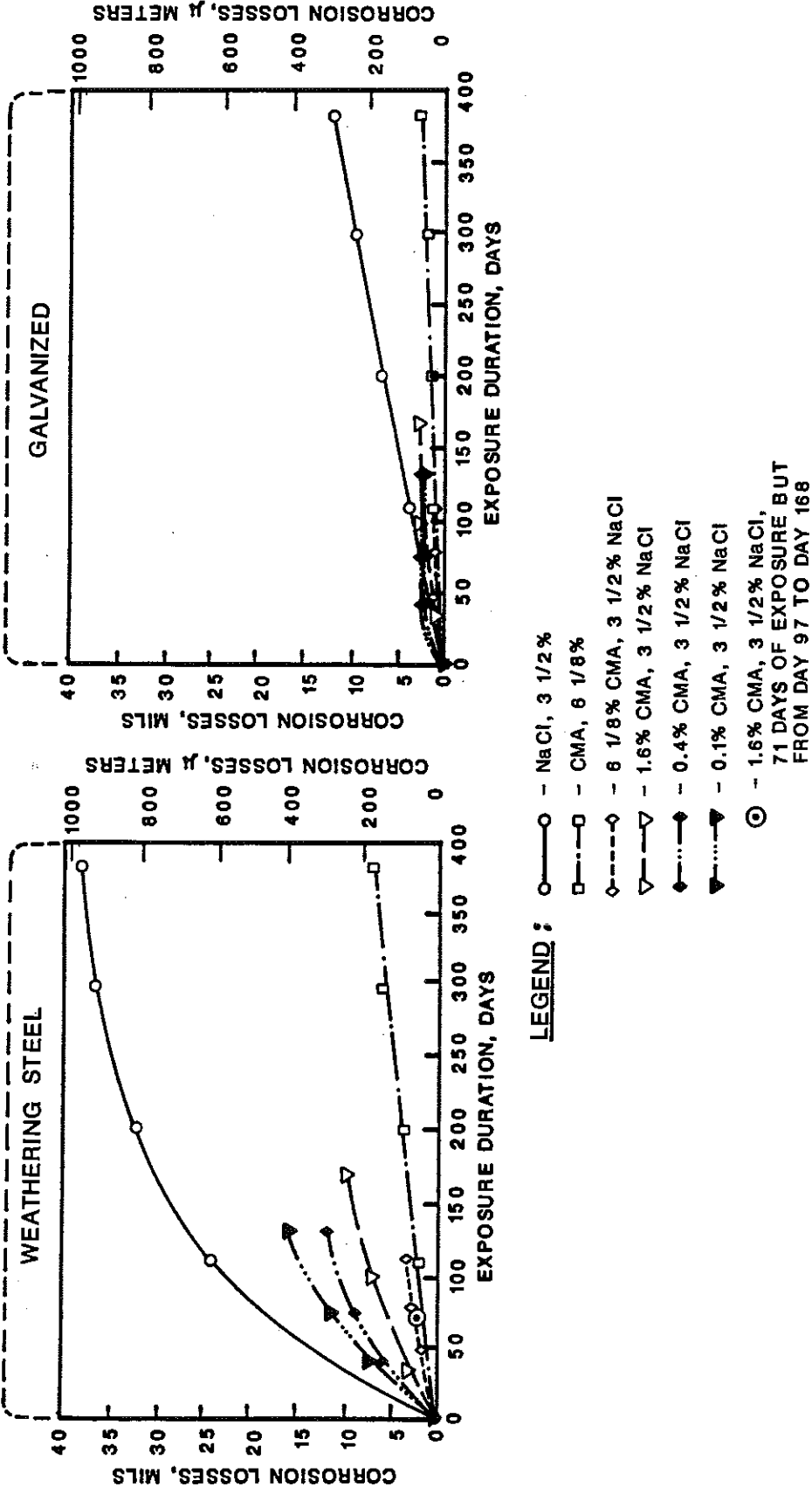


Figure 23. Average corrosion losses of weathering steel and galvanized guardrail in CMA and NaCl mixes (open exposure).

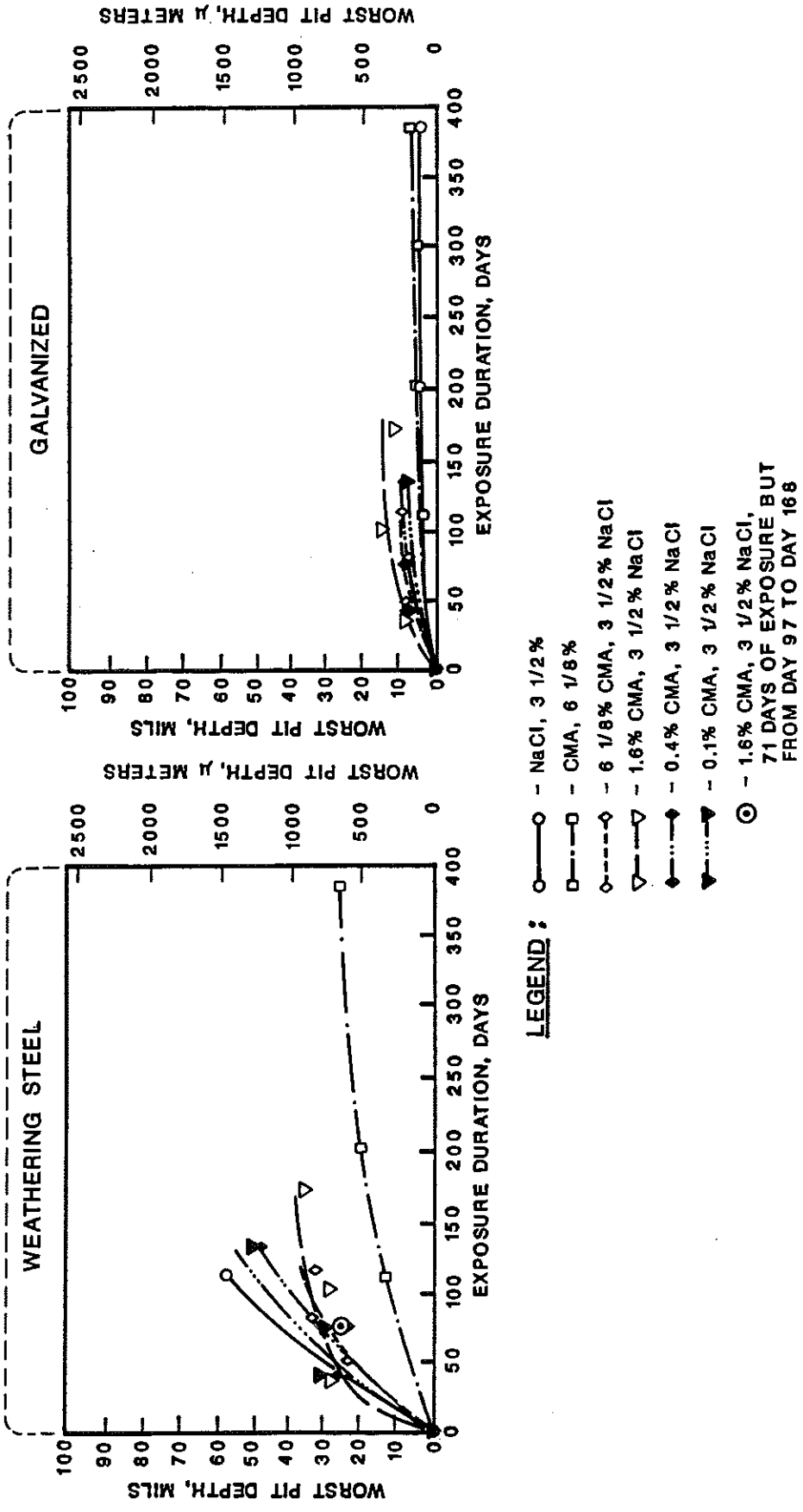
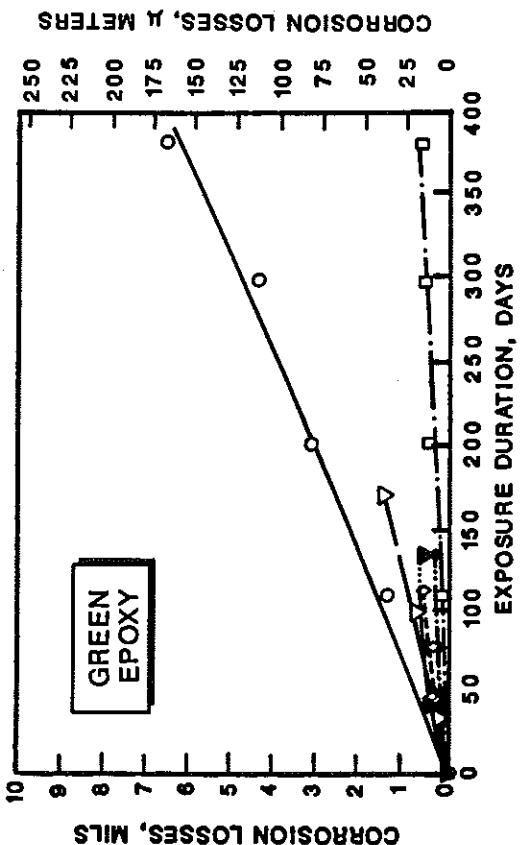
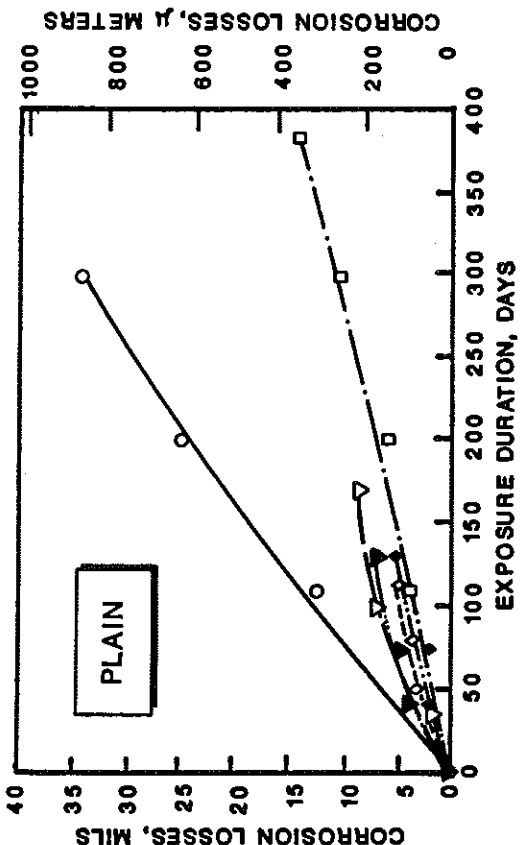
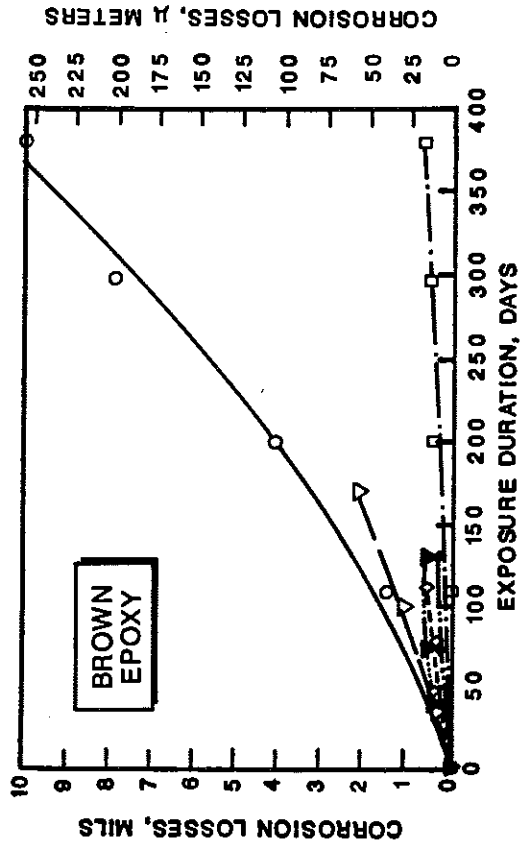
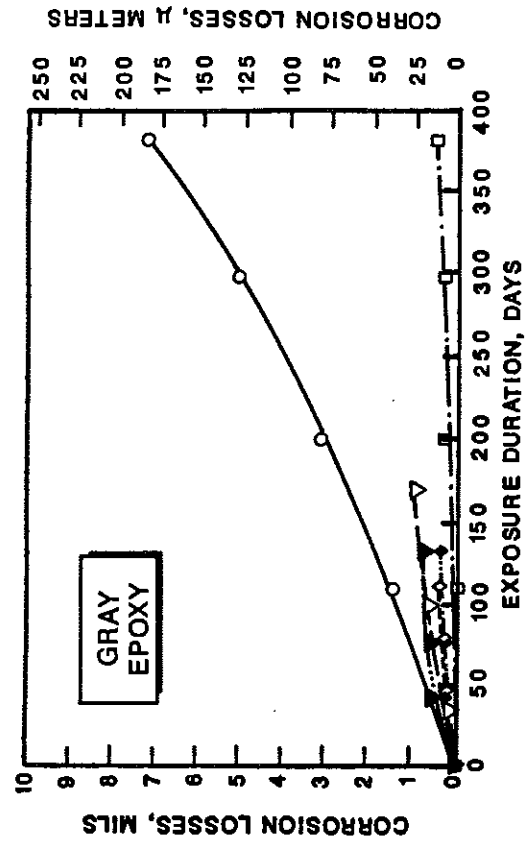
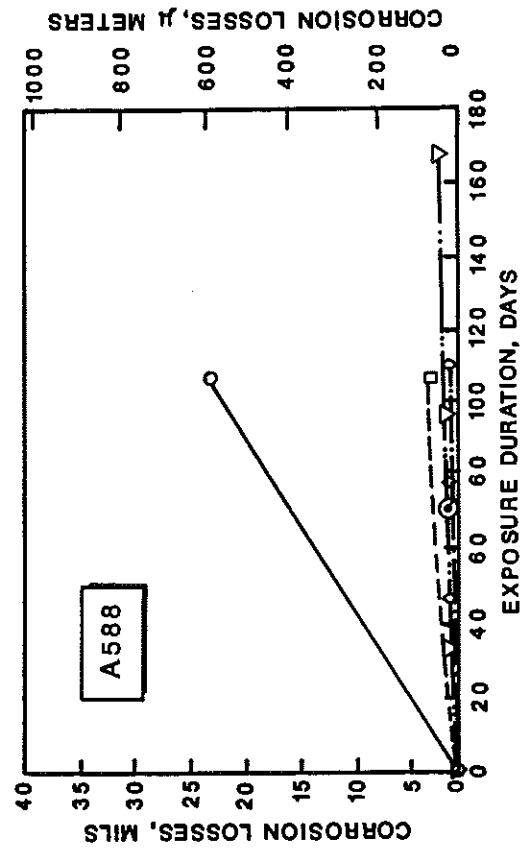
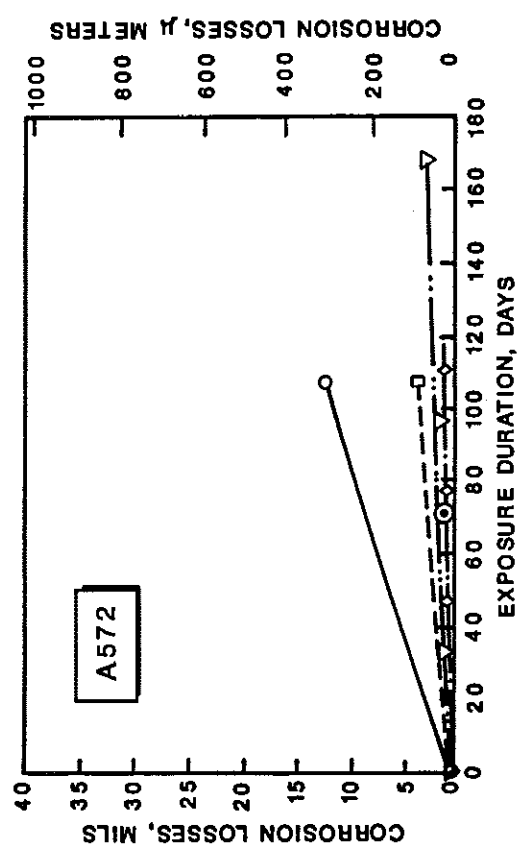
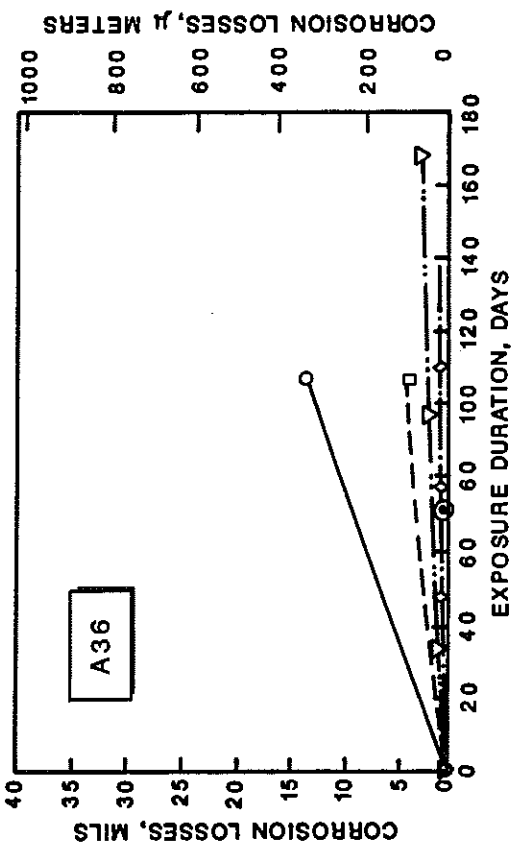


Figure 24. Worst pit depths for weathering steel and galvanized guardrail in CMA and NaCl mixes—freely exposed surface (open exposure).



- LEGEND :**
- — NaCl, 3 1/2%
 - — CMA, 6 1/6%
 - ◇ — 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

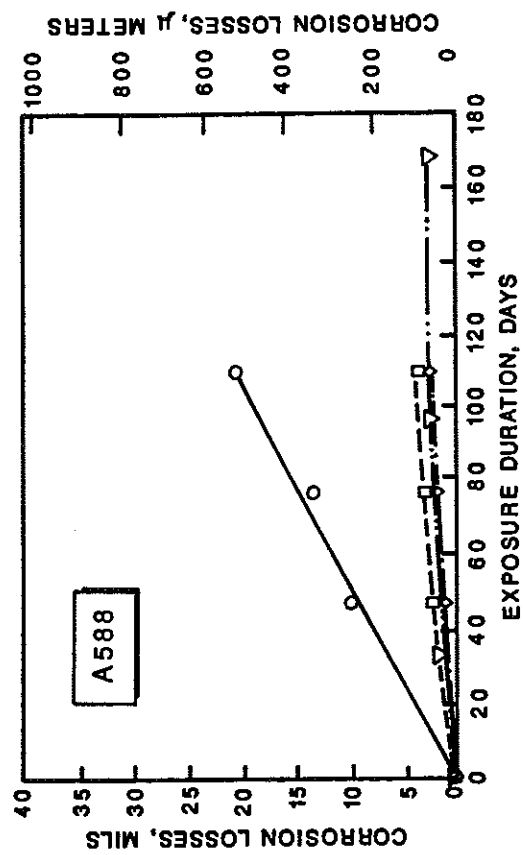
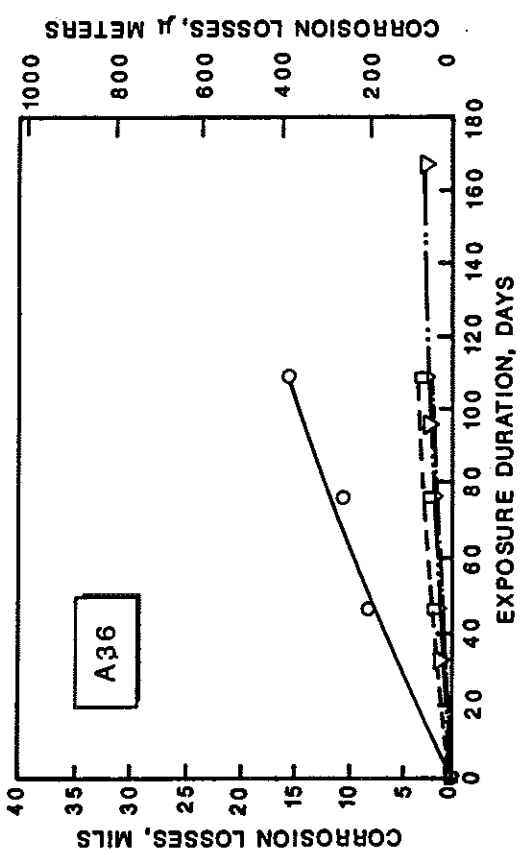
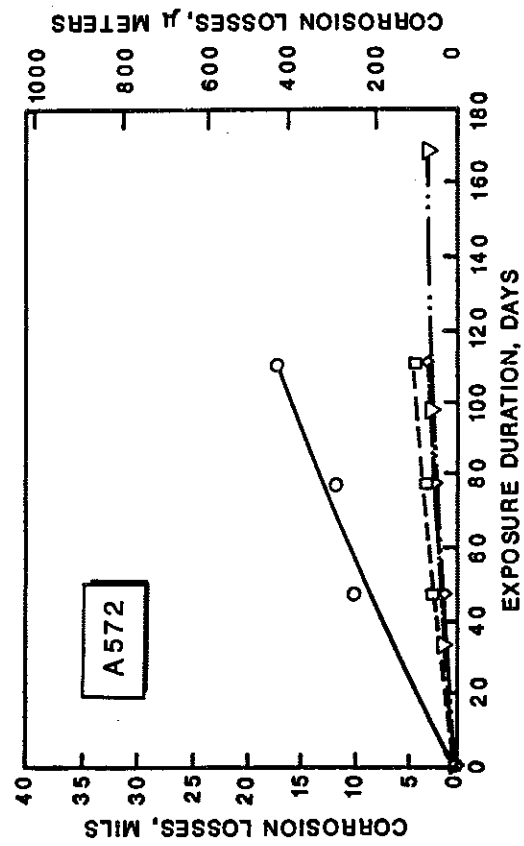
Figure 25. Average corrosion losses of steel reinforcement for concrete in CMA and NaCl mixes (open exposure).



LEGEND

- - NaCl, 3 1/2%
- - CMA, 6 1/8%
- ◇ - DISTILLED WATER
- ▽ - ACID RAIN
- ⊙ - ACID RAIN, 71 DAYS OF EXPOSURE BUT FROM DAY 97 TO DAY 168

Figure 26. 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 27. Average corrosion losses of bridge steel tensiles in distilled water and acid rain (sheltered exposure).

FREELY EXPOSED SURFACES

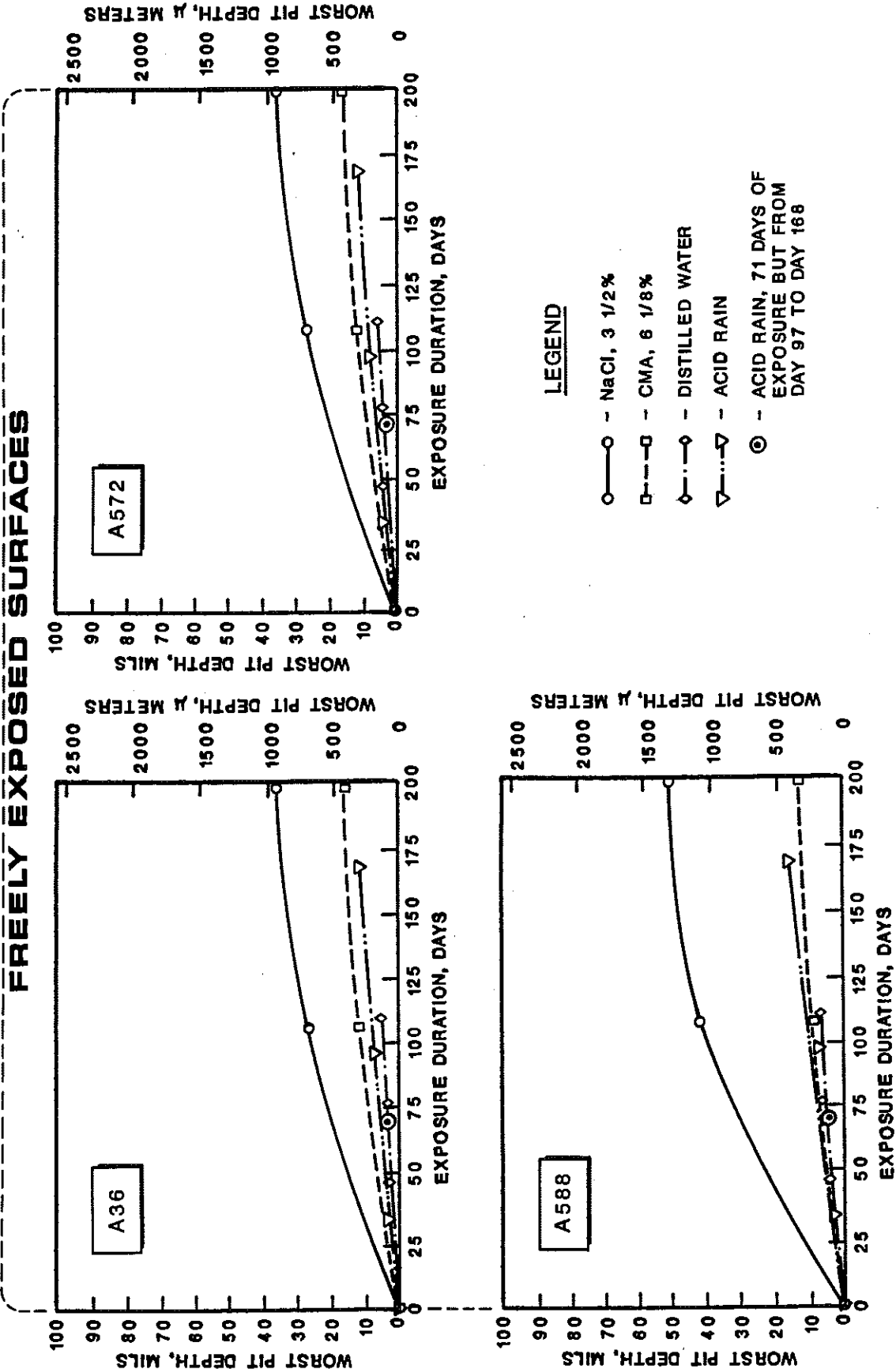
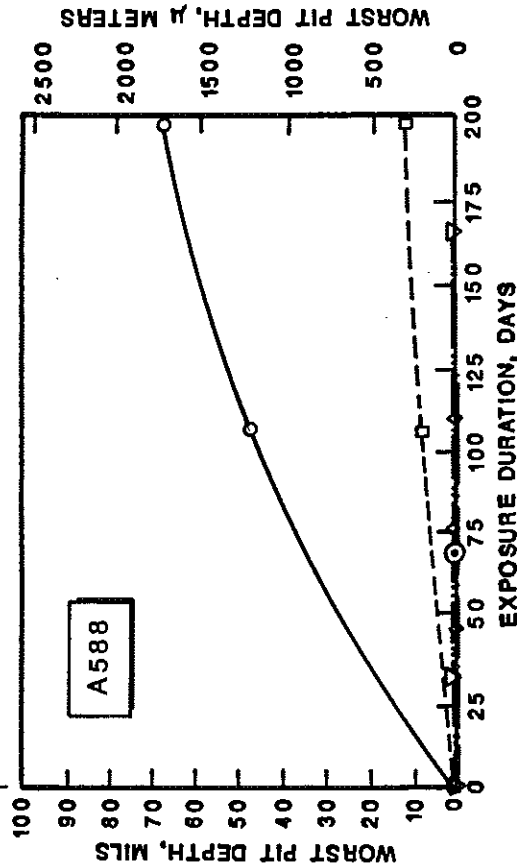
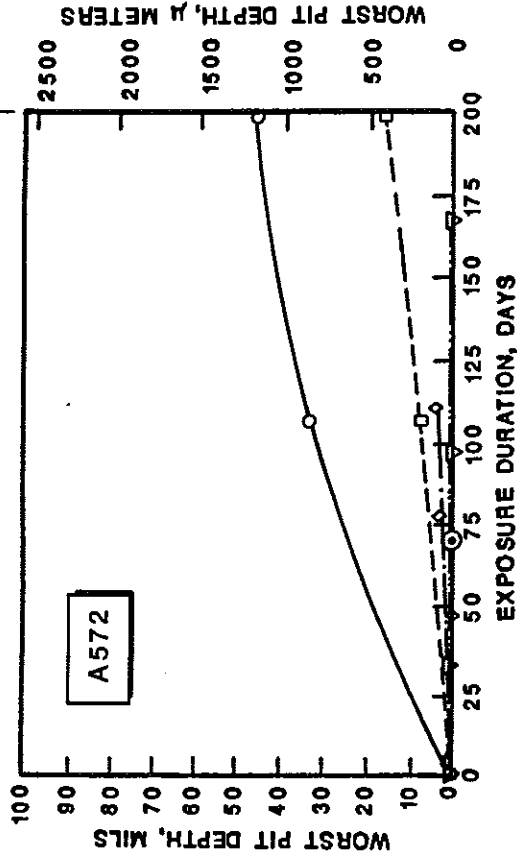
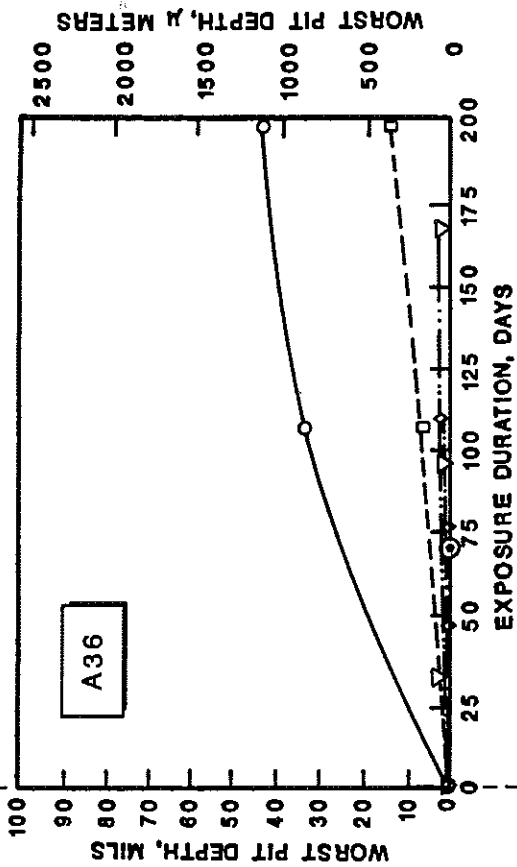


Figure 28. Worst pit depth of bridge steels in distilled water and acid rain for both freely exposed surfaces and crevices (open exposure).

CREVICES

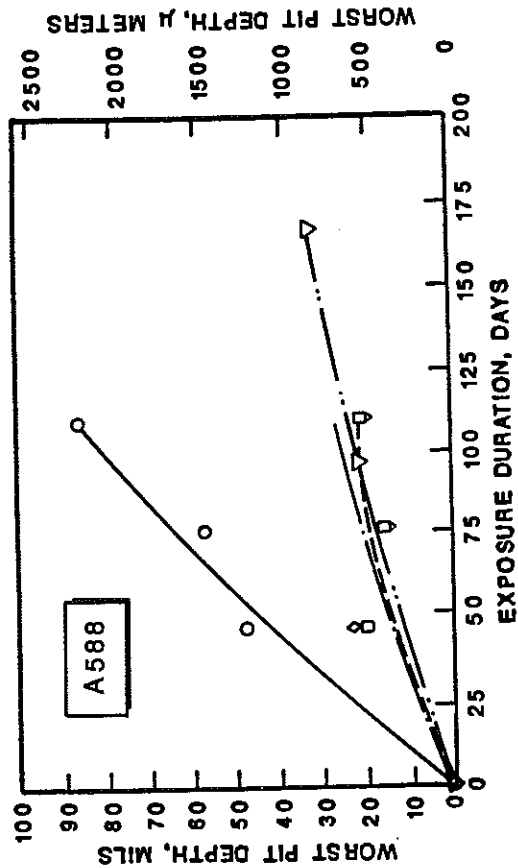
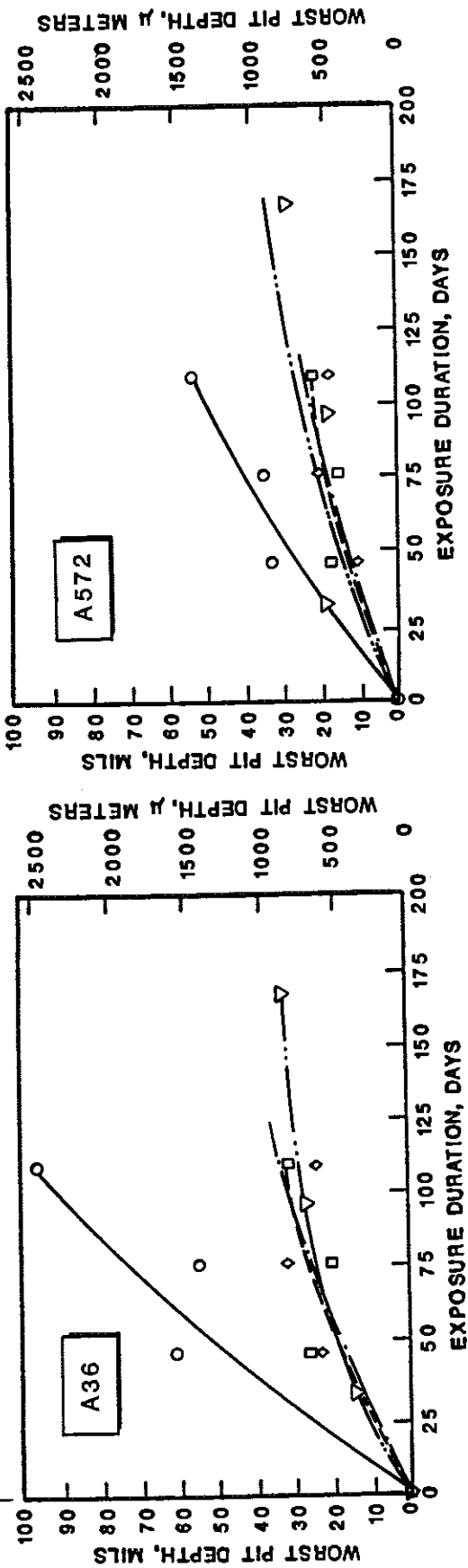


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — DISTILLED WATER
- ▽ — ACID RAIN
- ⊙ — ACID RAIN, 71 DAYS OF EXPOSURE BUT FROM DAY 97 TO DAY 188

Figure 28 (cont). Worst pit depth of bridge steels in distilled water and acid rain for both freely exposed surfaces and crevices (open exposure).

FREELY EXPOSED SURFACES

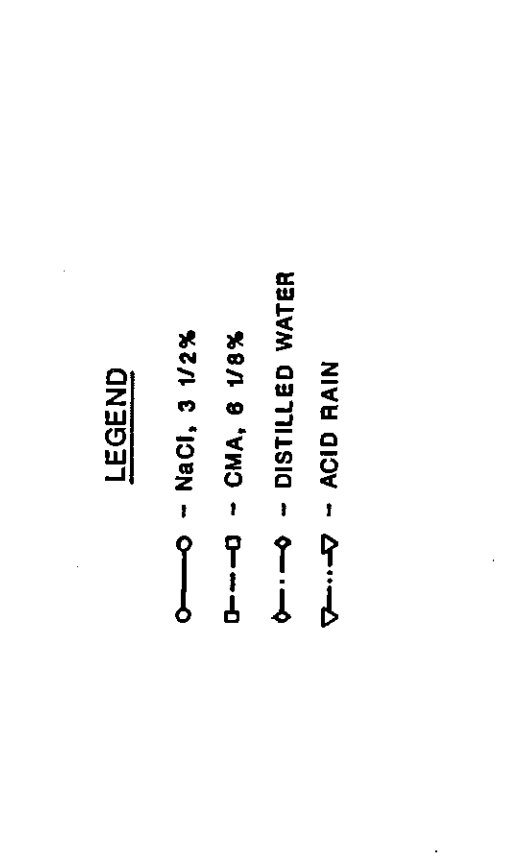
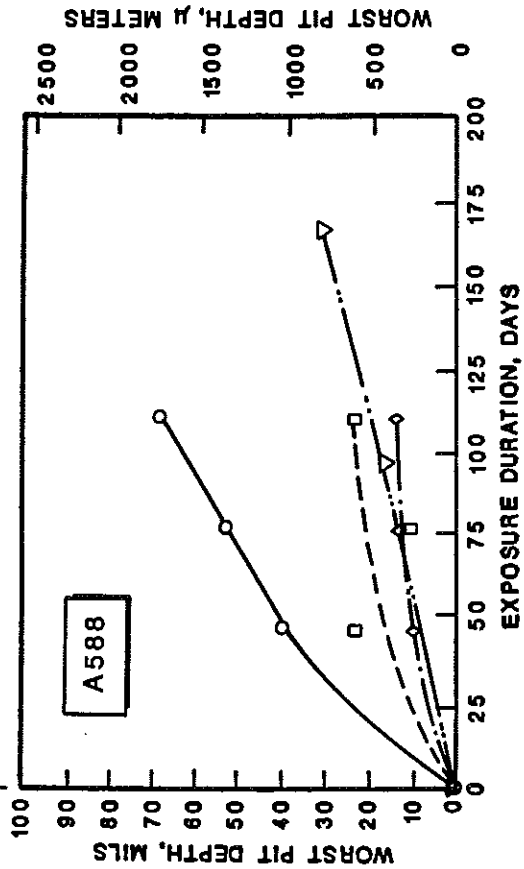
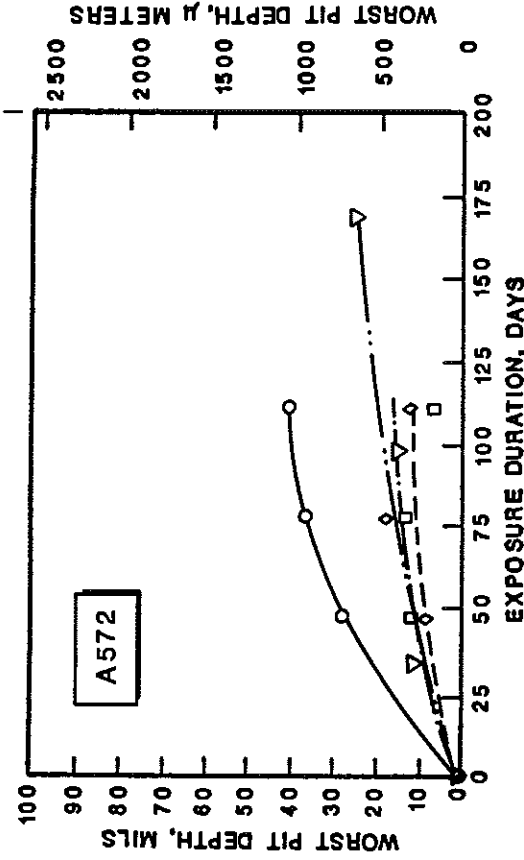
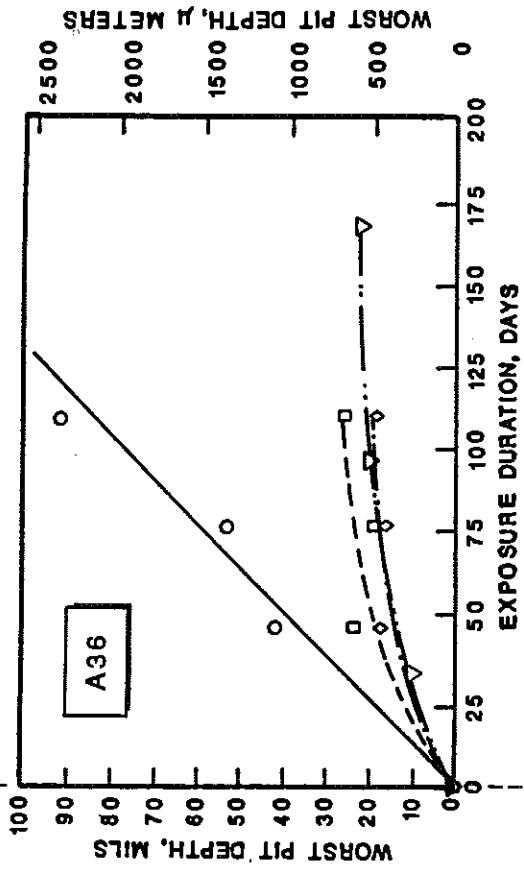


LEGEND

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

Figure 29. Worst pit depth of bridge steel tensiles in distilled water and acid rain for both freely exposed surfaces and crevices (sheltered exposure).

CREVICES

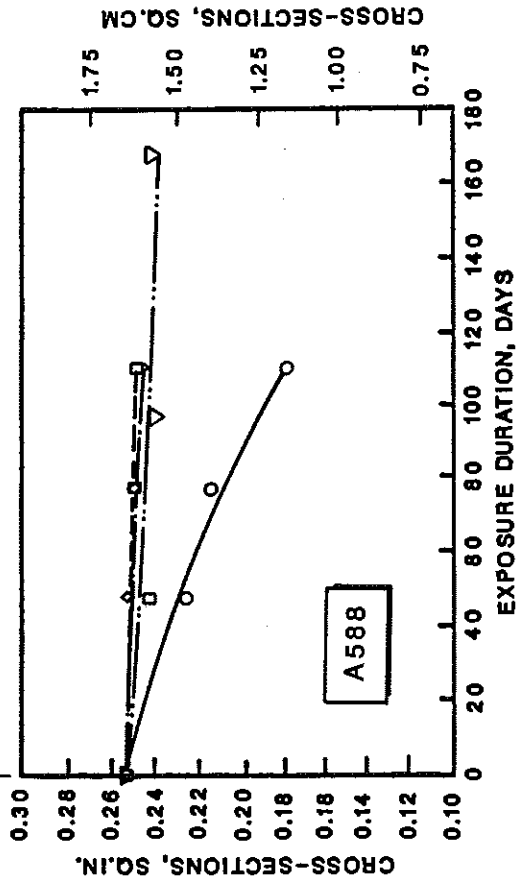
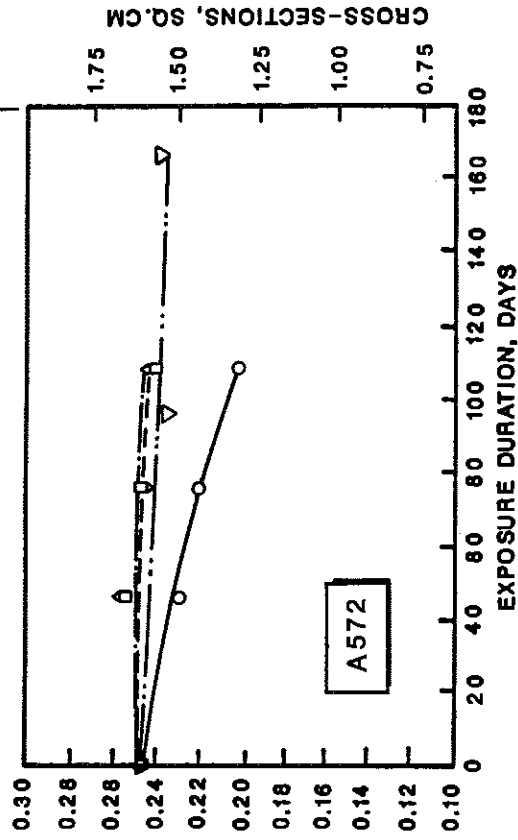
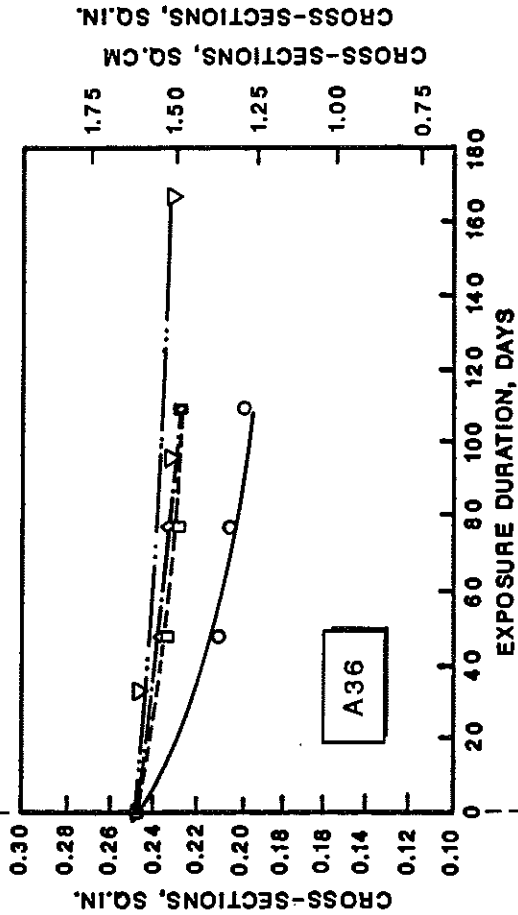


LEGEND

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

Figure 29 (cont). Worst pit depth of bridge steel tensiles in distilled water and acid rain for both freely exposed surfaces and crevices (sheltered exposure).

EFFECTIVE

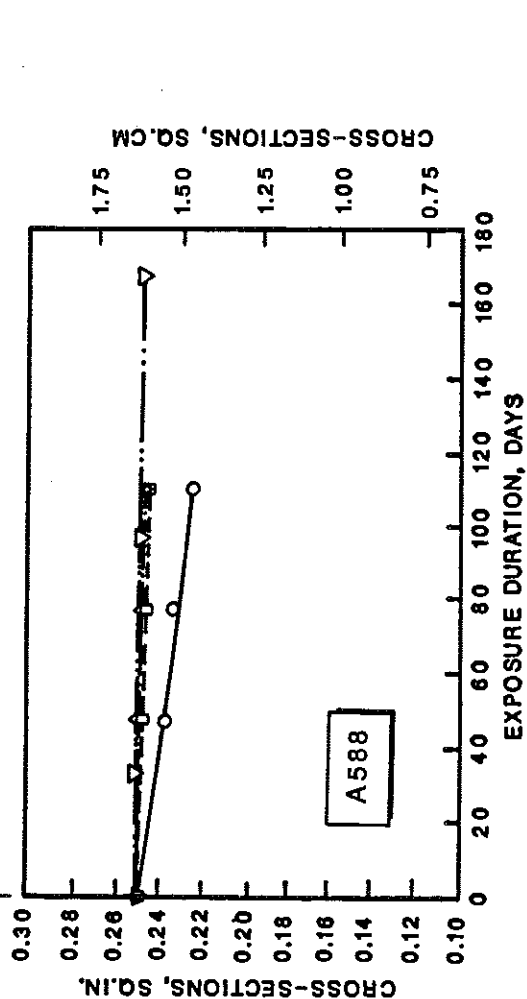
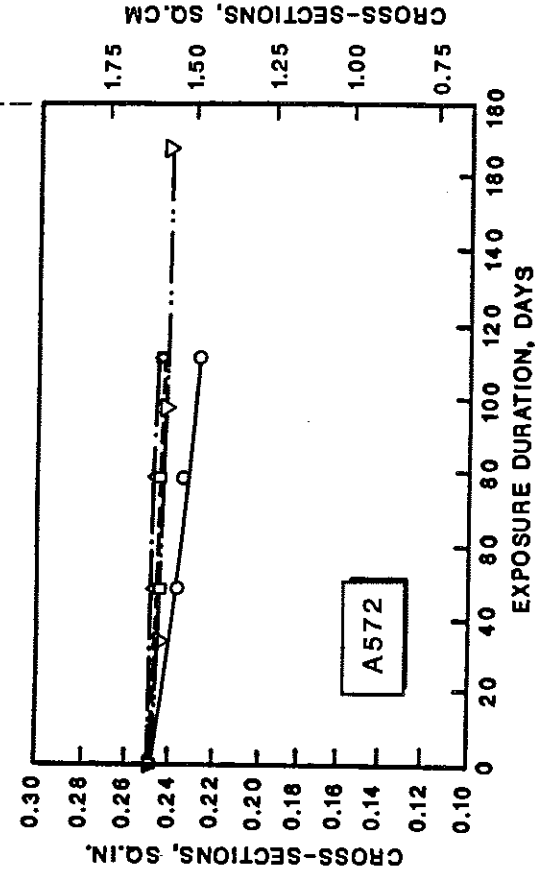
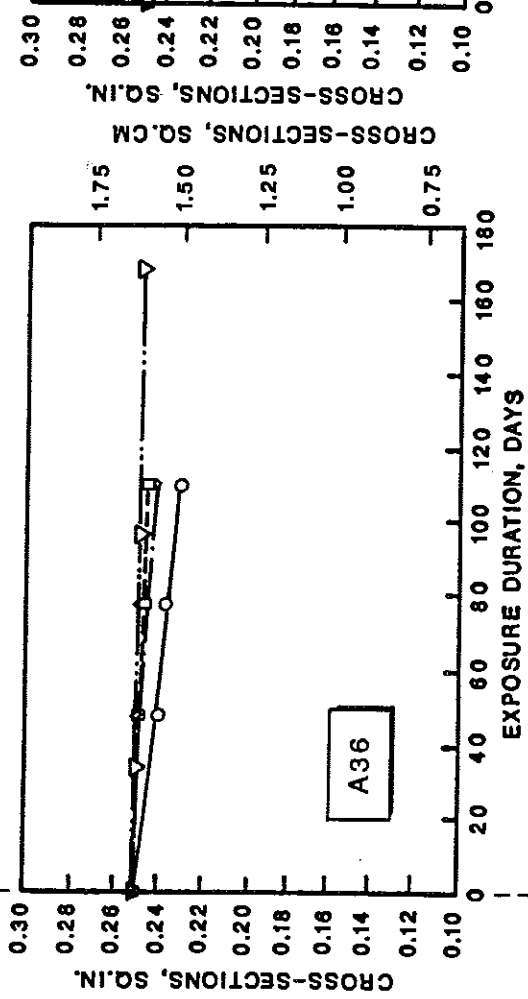


LEGEND

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

Figure 30. Effective and average cross-sections of bridge steel tensiles in distilled water and acid rain (sheltered exposure).

AVERAGE



LEGEND

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

Figure 30 (cont). Effective and average cross-sections of bridge steel tensiles in distilled water and acid rain (sheltered exposure).

produced only slightly more average corrosion than the distilled water alone.

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 worst 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.

Guardrail (Figs. 31 and 32) - The average corrosion of both the distilled water and the simulated acid rain was less than or roughly equal to that of CMA alone with the acid rain being closer to the values of CMA alone. The average corrosion of galvanized guardrail in simulated acid rain was slightly greater than occurred in CMA alone while the average corrosion in distilled water was slightly less than occurred in CMA alone.

Worst pit depths produced in distilled water and simulated acid rain on the weathering steel guardrail are intermediate between those produced in NaCl and those produced in CMA for the earliest exposure durations but approach those of CMA alone for the later exposure durations. Worst pit depths on the galvanized guardrail were slightly greater than occurred in either CMA or NaCl alone for both the distilled water and the acid rain.

Steel Reinforcement for Concrete (Fig. 33) - In all cases, the average corrosion losses that occurred in either distilled water or simulated acid rain were less than those that occurred in CMA alone.

Prestressing Strand - See prestressing strand under CMA and NaCl mixes.

Aluminum - Only very minor pitting was evident on the freely exposed surfaces for both exposures after three months.

Rust Inhibitor with MgCl₂ and Rust Inhibitor with NaCl

In general MgCl₂ with a rust inhibitor performed slightly better and NaCl with a rust inhibitor slightly worse than CMA alone. NaCl with a rust inhibitor behaved very much like the higher ratio CMA/NaCl mixes in all respects for all of the materials tested.

Bridge Steels (Figs. 34 through 38) - In general, average corrosion losses were slightly better in MgCl₂ with a rust inhibitor and slightly worse in NaCl with a rust inhibitor than occurred in CMA alone. This was true for both open and sheltered exposures although the differences were slightly

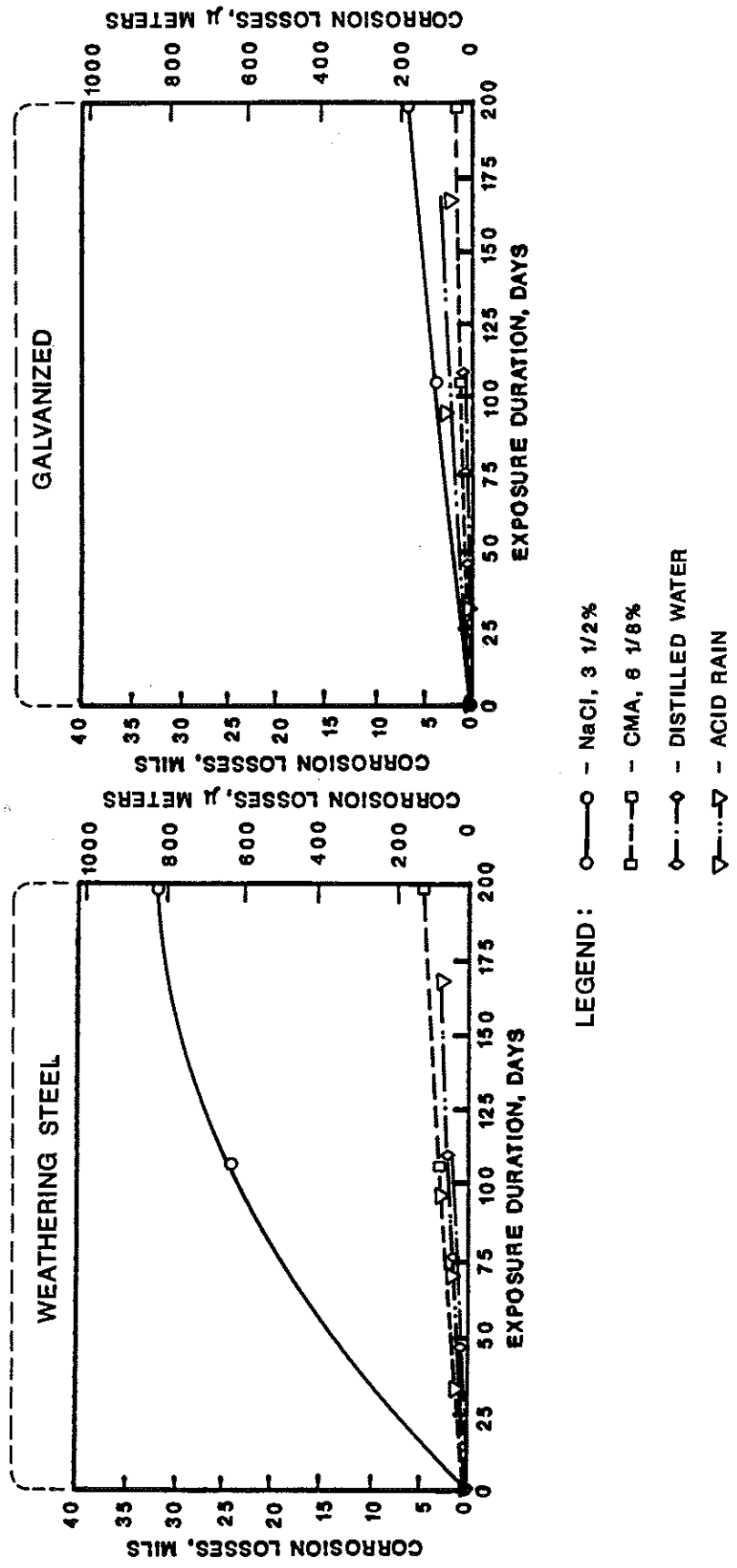


Figure 31. Average corrosion losses of weathering steel and galvanized guardrail in distilled water and acid rain (open exposure).

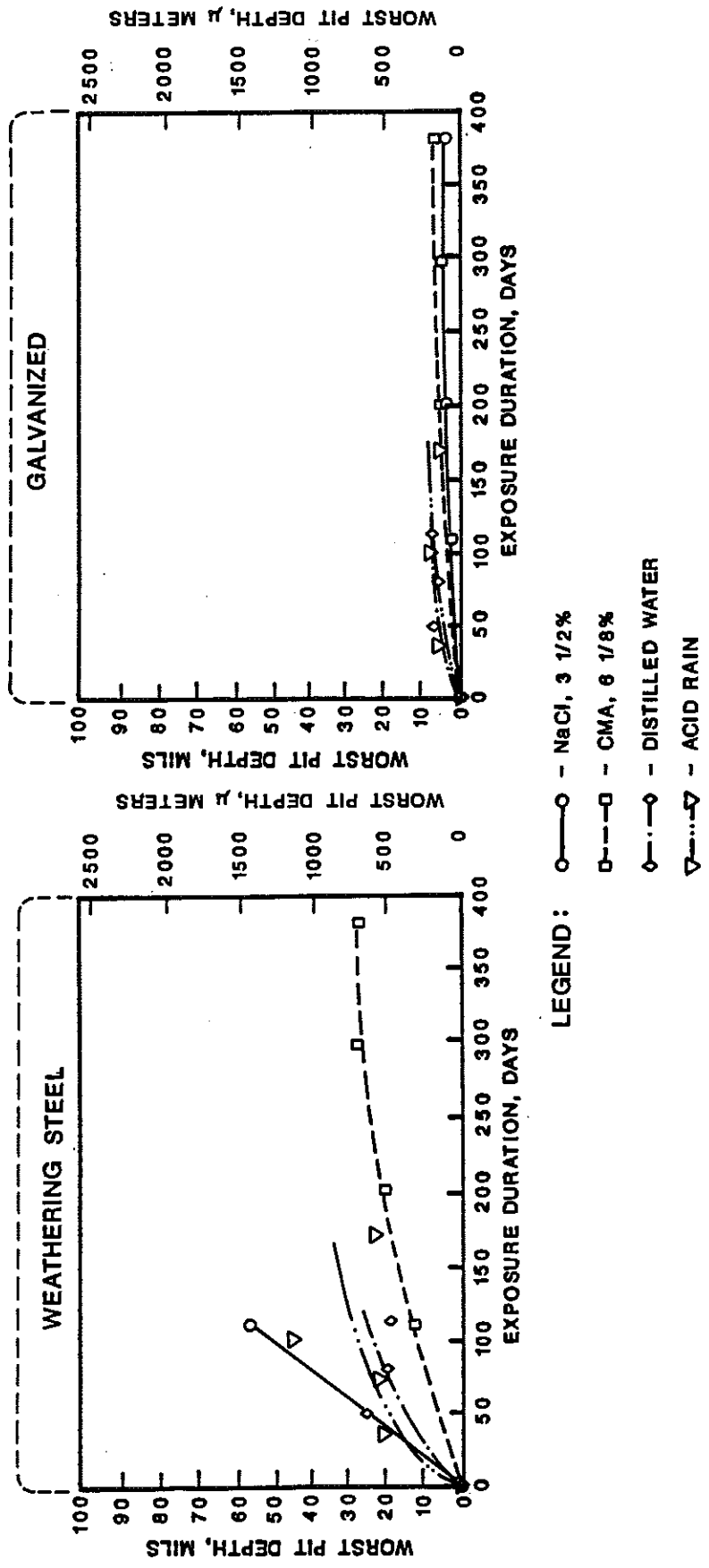
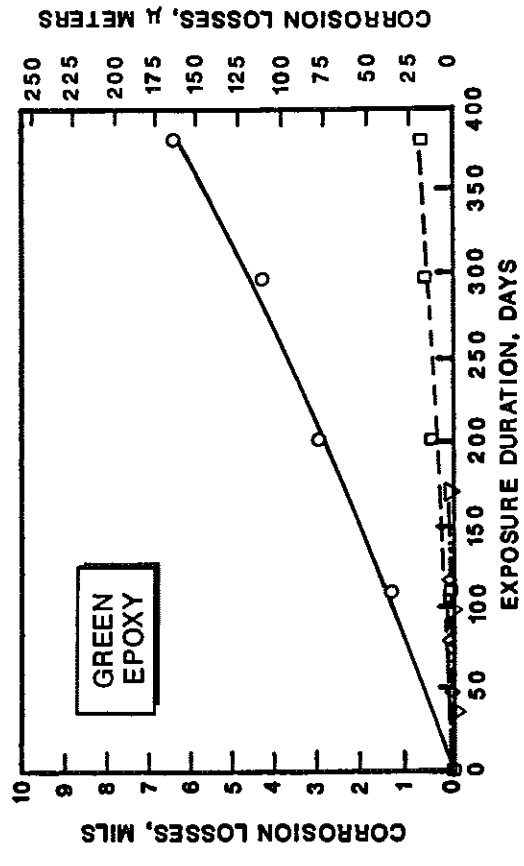
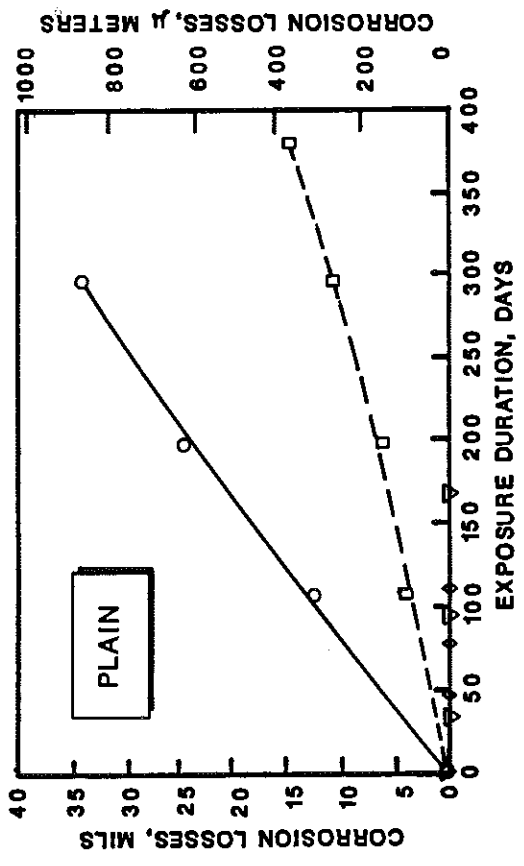
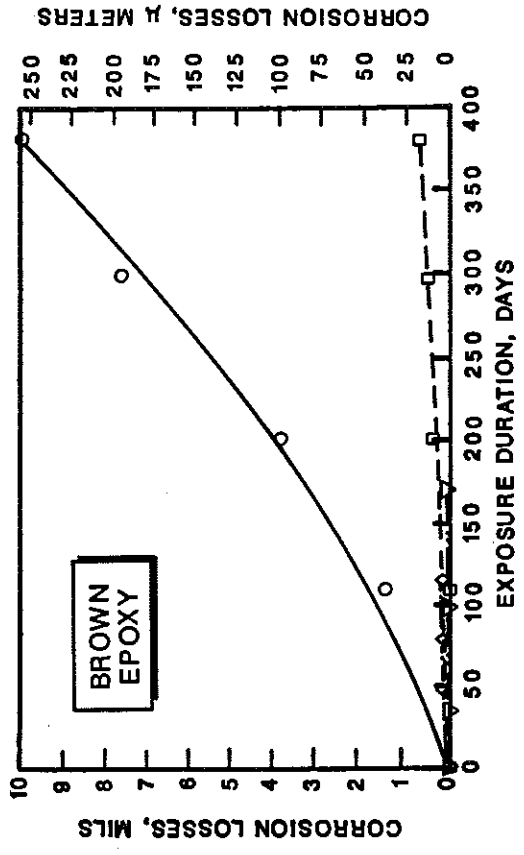
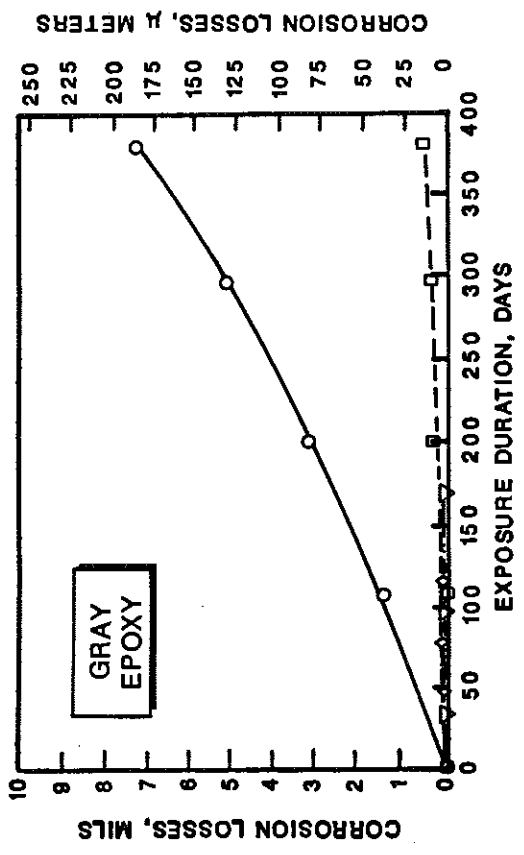
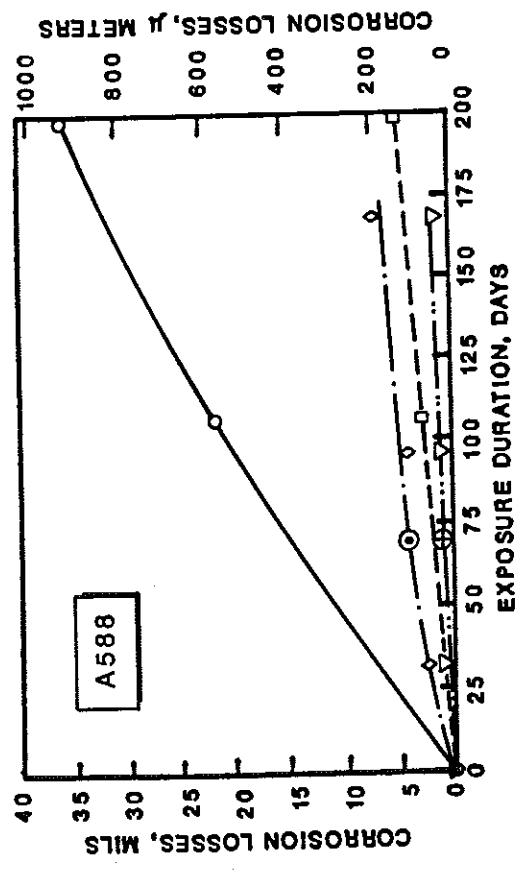
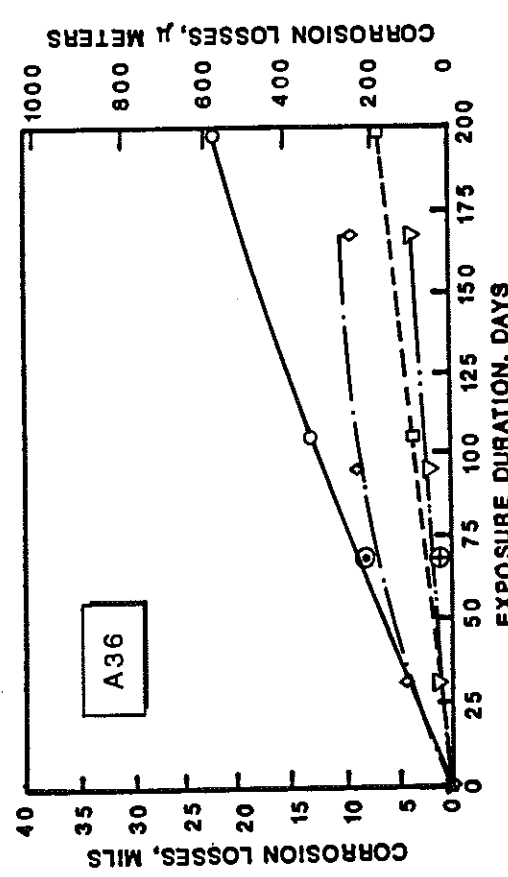
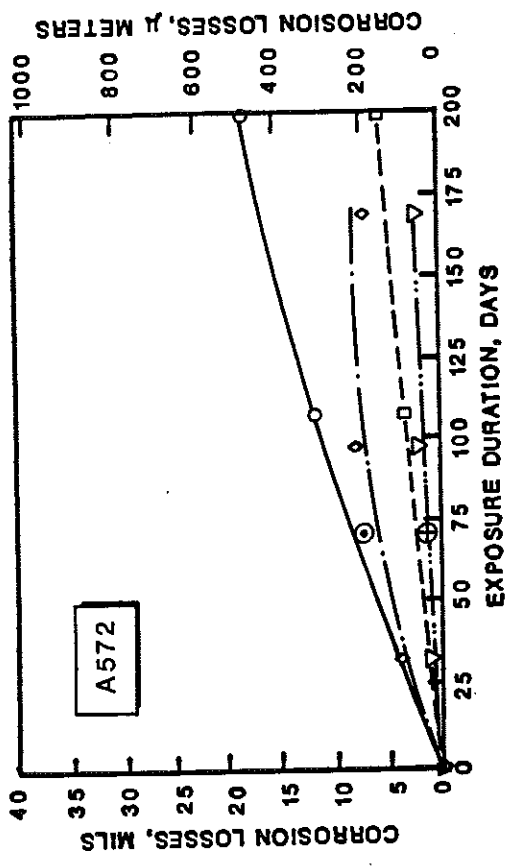


Figure 32. Worst pit depth of weathering steel and galvanized guardrail in distilled water and acid rain (open exposure).



LEGEND : ○ — NaCl, 3 1/2%
 □ — CMA, 6 1/8%
 ◇ — DISTILLED WATER
 ▽ — ACID RAIN

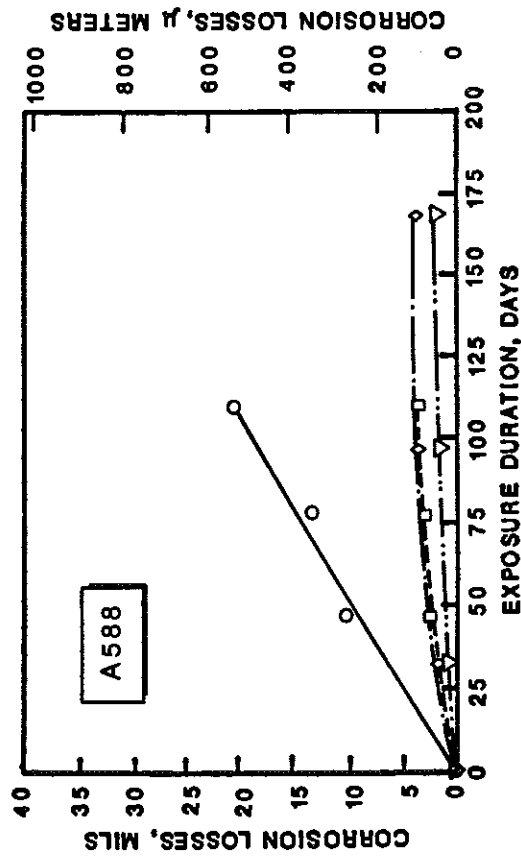
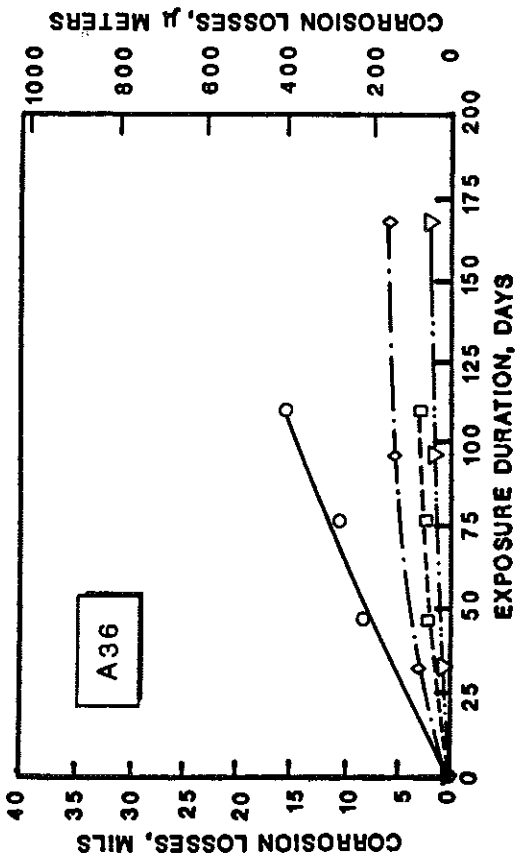
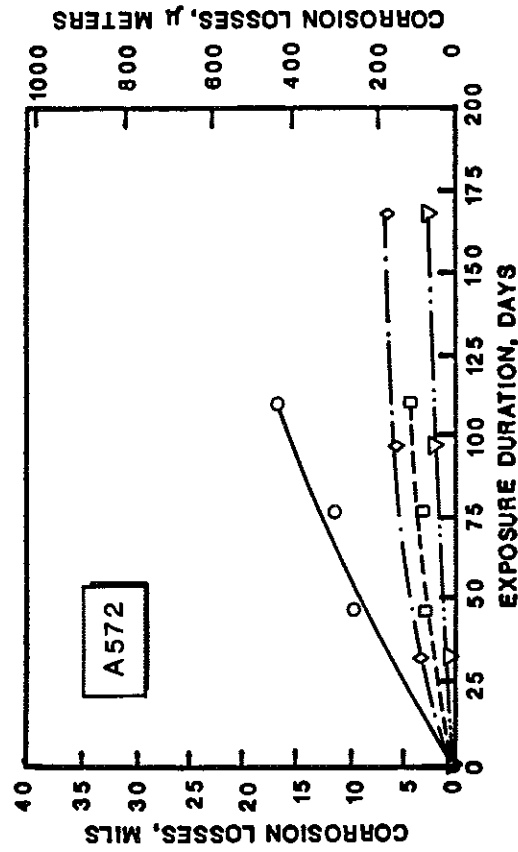
Figure 33. Average corrosion losses of steel reinforcement for concrete in distilled water and acid rain (open exposure).



LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR
- ⊙ — NaCl WITH A RUST INHIBITOR, 71 DAYS EXPOSURE FROM DAY 97 TO DAY 168
- ⊕ — MgCl₂ WITH A RUST INHIBITOR, 71 DAYS EXPOSURE FROM DAY 97 TO DAY 168

Figure 34. Average corrosion losses of bridge steels in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (open exposure).

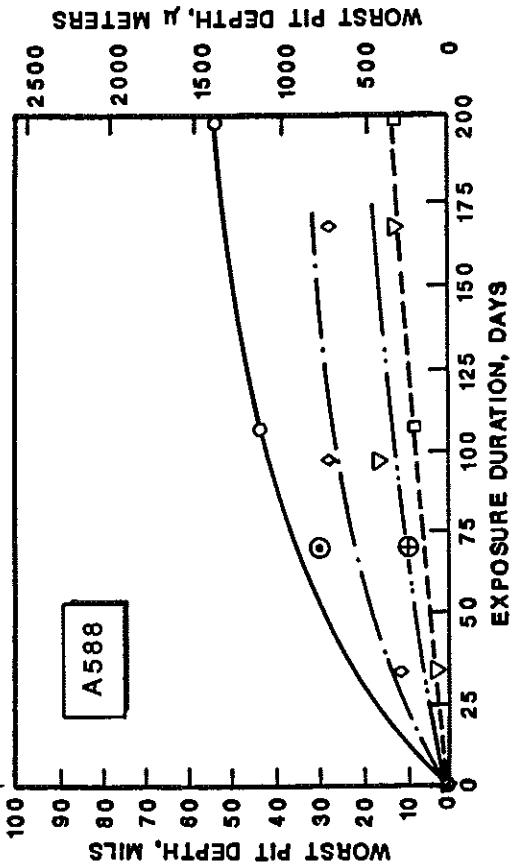
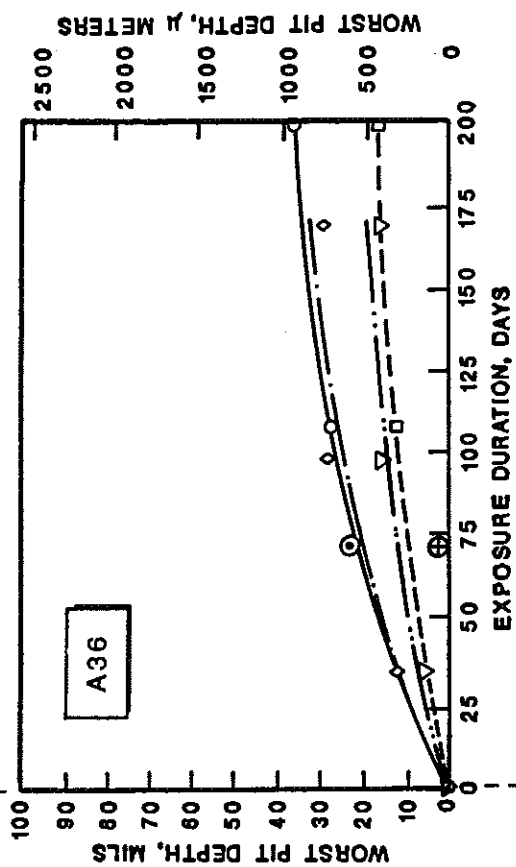
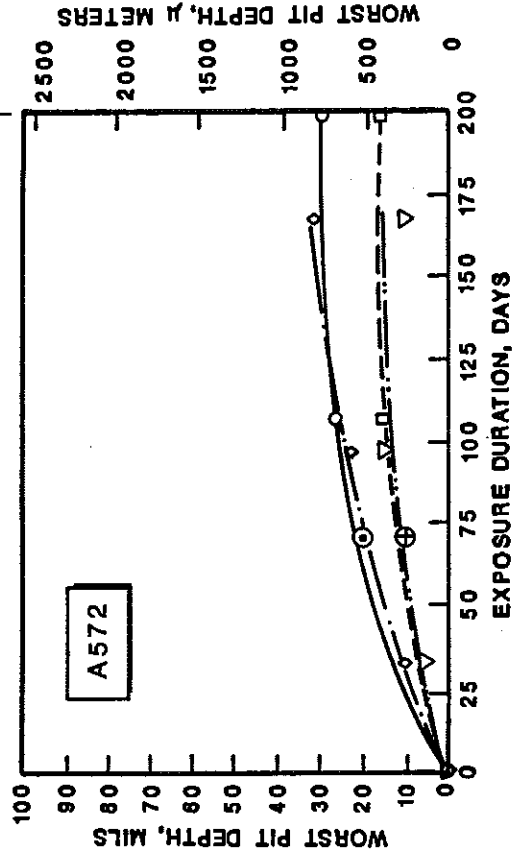


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR

Figure 35. Average corrosion losses of bridge steel tensiles in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (sheltered exposure).

FREELY EXPOSED SURFACES

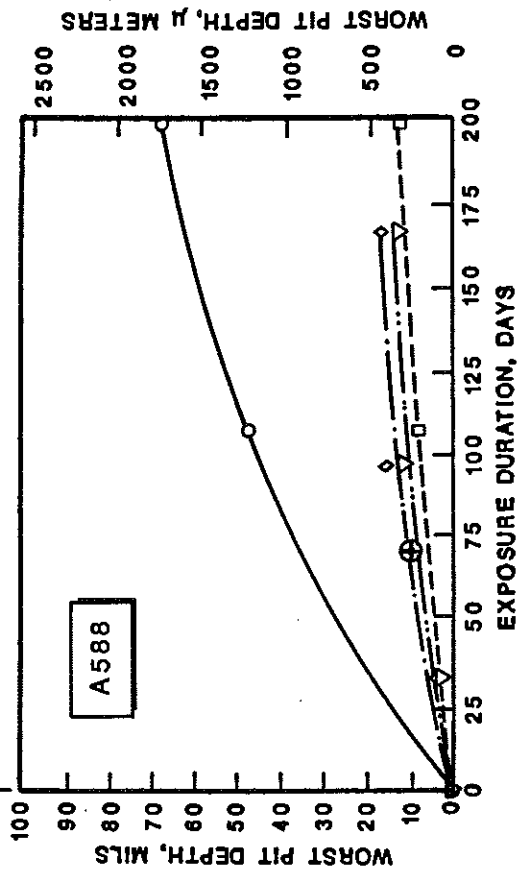
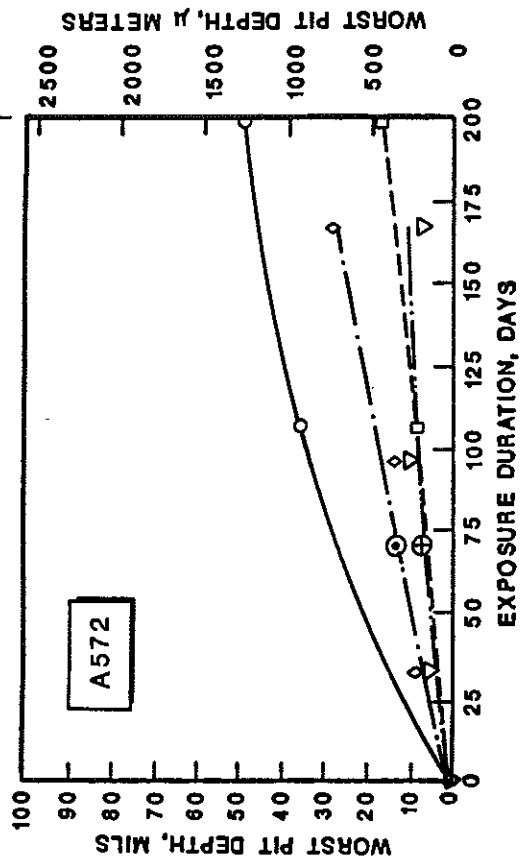
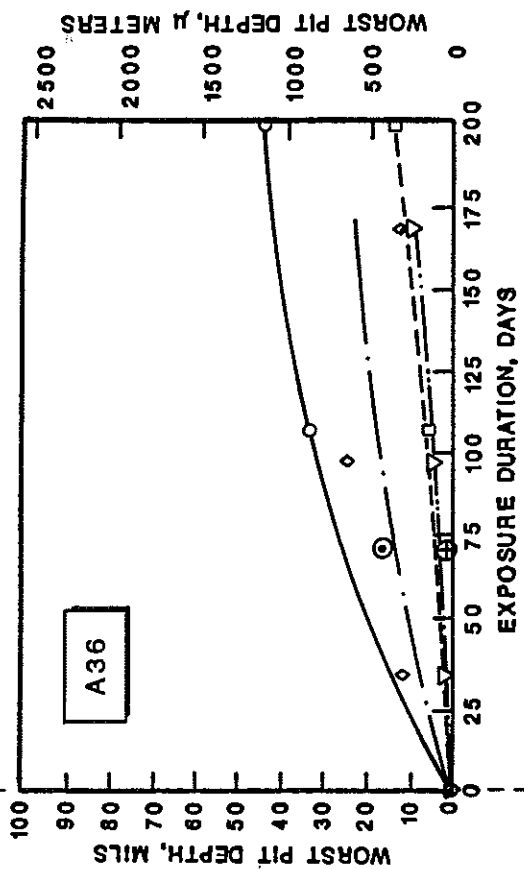


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/6%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR
- ⊙ — NaCl WITH A RUST INHIBITOR, 71 DAYS EXPOSURE FROM DAY 97 TO DAY 166
- ⊕ — MgCl₂ WITH A RUST INHIBITOR, 71 DAYS EXPOSURE FROM DAY 97 TO DAY 166

Figure 36. Worst pit depth of bridge steels in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor for both freely exposed surfaces and crevices (open exposure).

CREVICES

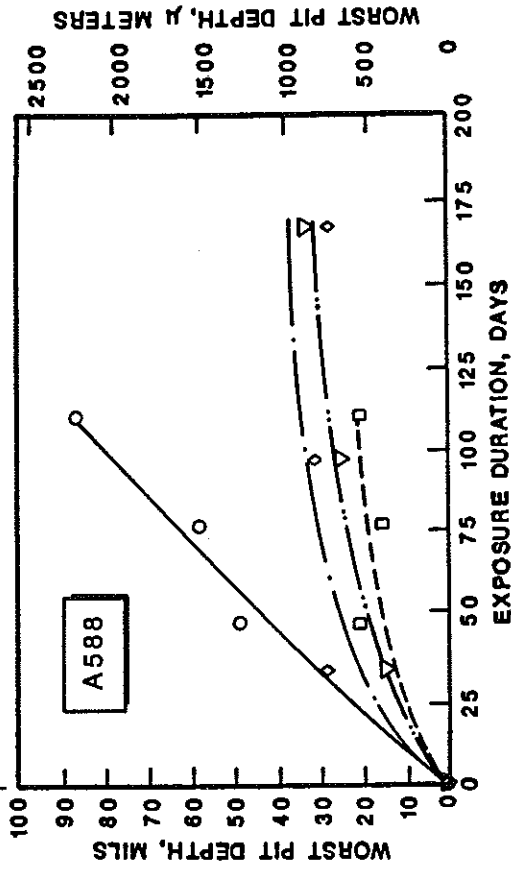
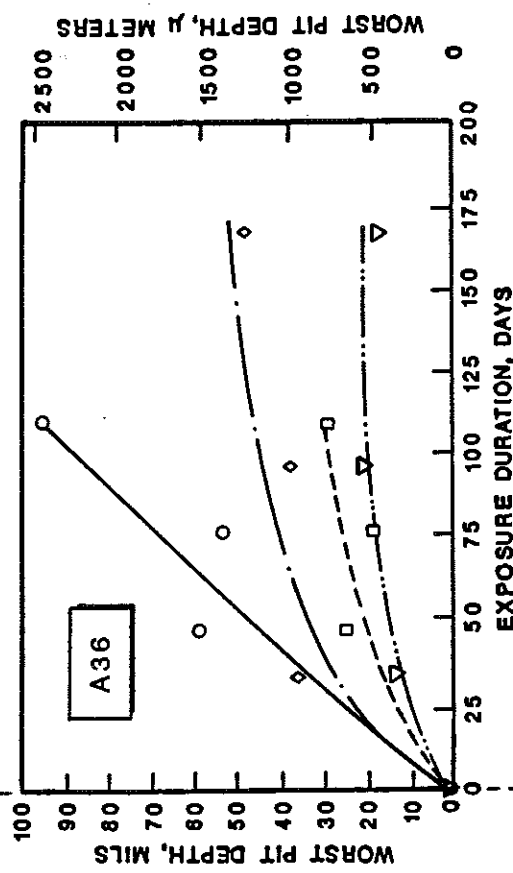
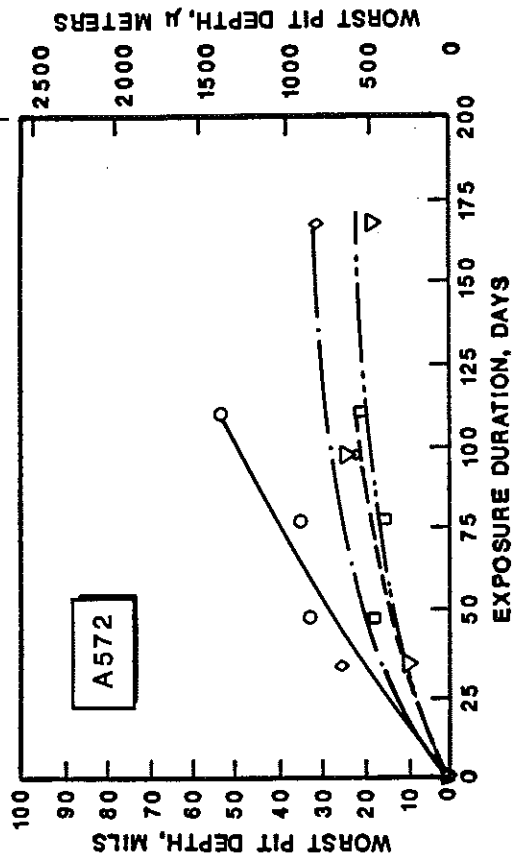


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR
- ⊙ — NaCl WITH A RUST INHIBITOR, 71 DAYS EXPOSURE FROM DAY 97 TO DAY 168
- ⊕ — MgCl₂ WITH A RUST INHIBITOR, 71 DAYS EXPOSURE FROM DAY 97 TO DAY 168

Figure 36 (cont). Worst pit depth of bridge steels in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor for both freely exposed surfaces and crevices (open exposure).

FREELY EXPOSED SURFACES

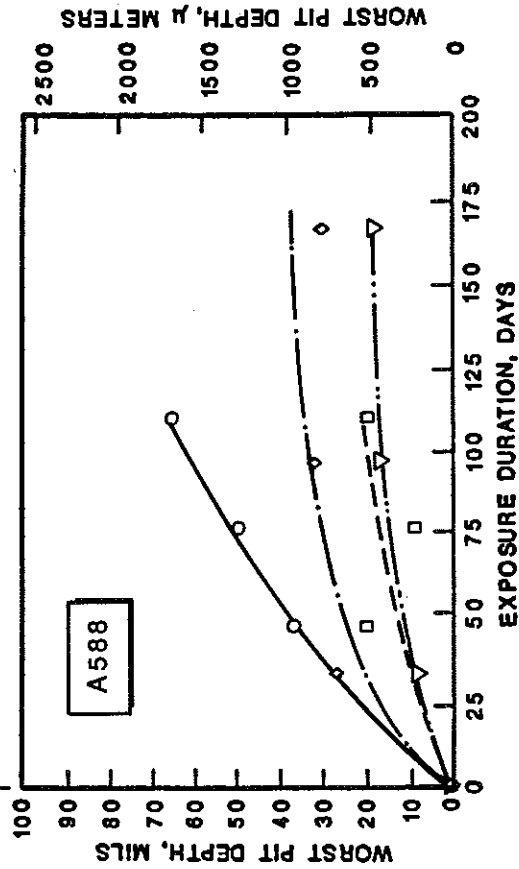
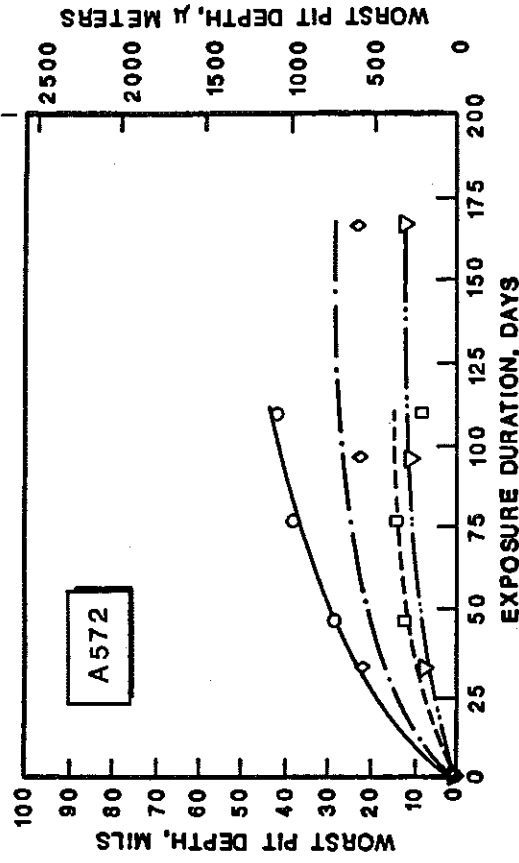
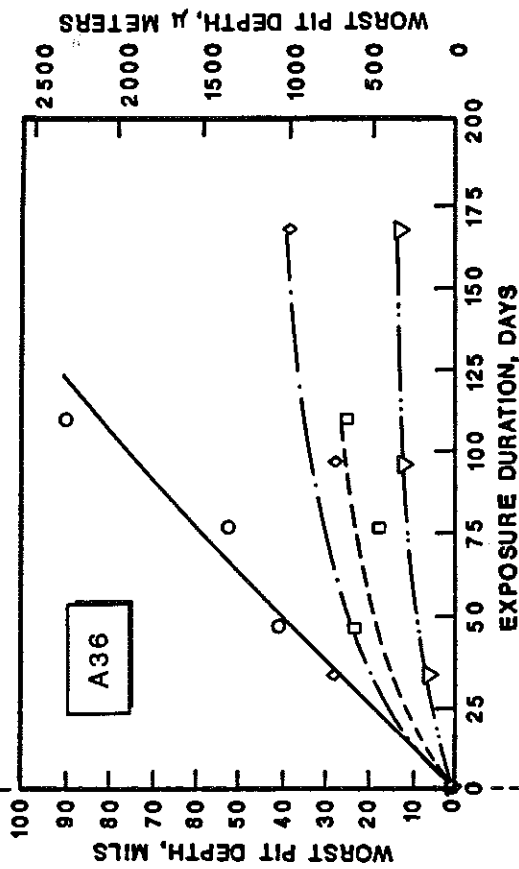


LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR

Figure 37. Worst pit depth of bridge steel tensiles in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor for both freely exposed surfaces and crevices (sheltered exposure).

CREVICES



LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl with a Rust Inhibitor
- ▽ — MgCl₂ with a Rust Inhibitor

Figure 37 (cont). Worst pit depth of bridge steel tensiles in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor for both freely exposed surfaces and crevices (sheltered exposure).

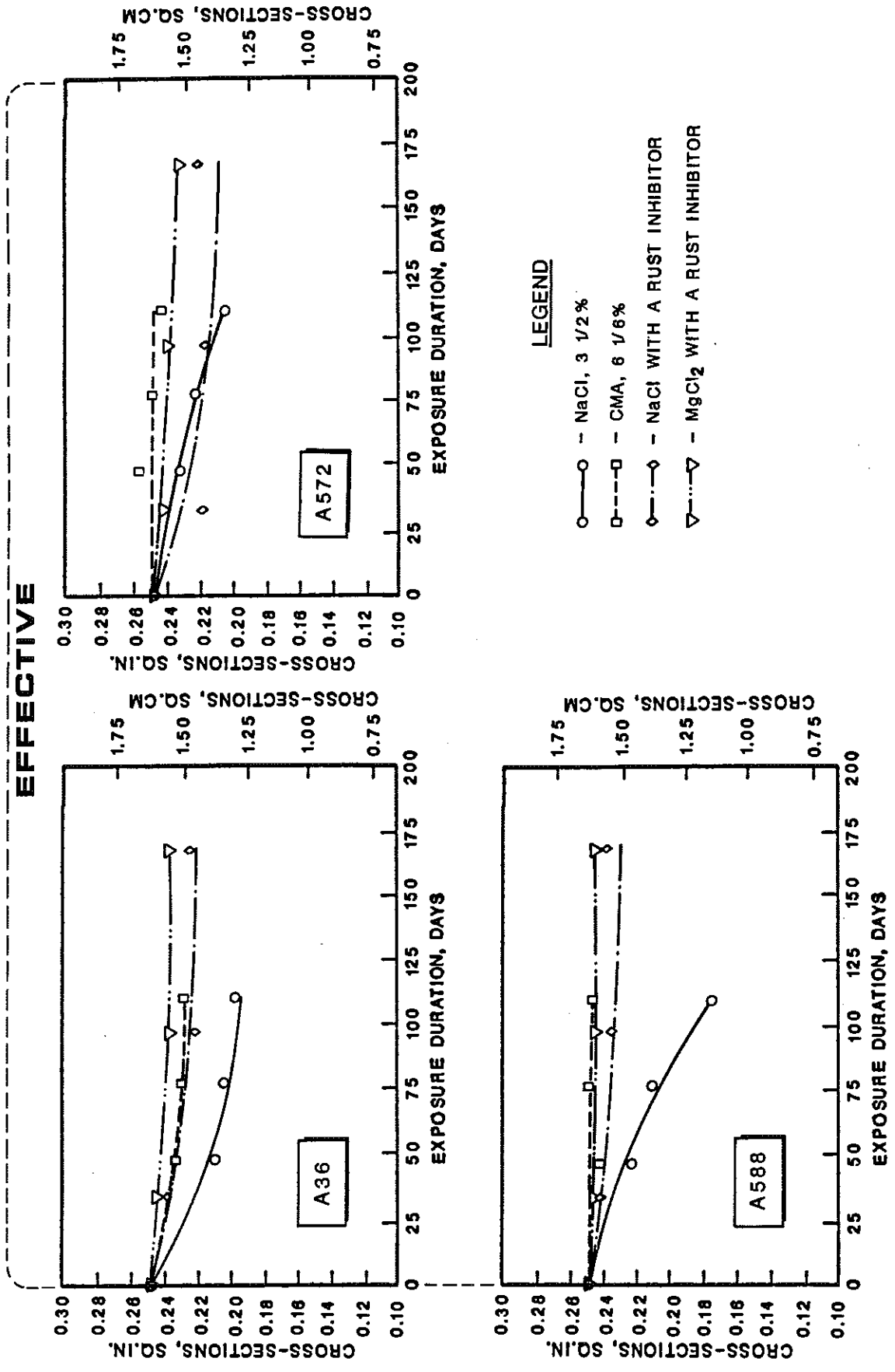
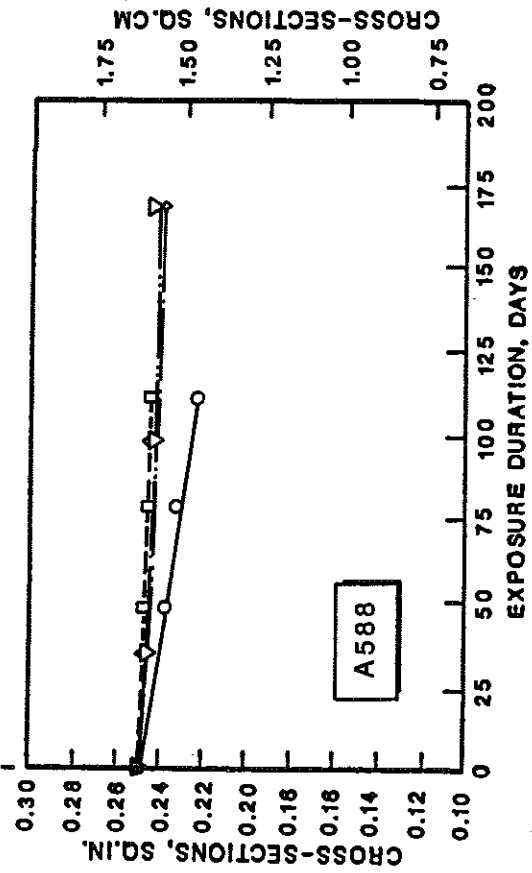
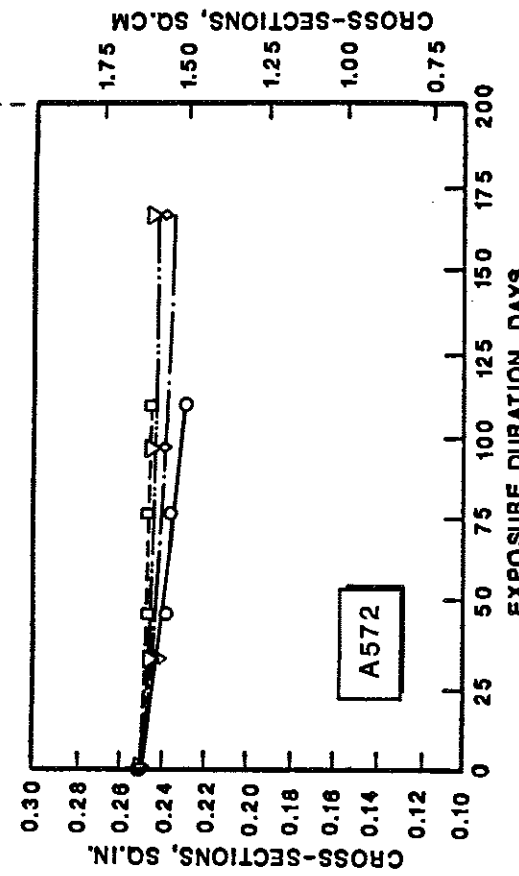
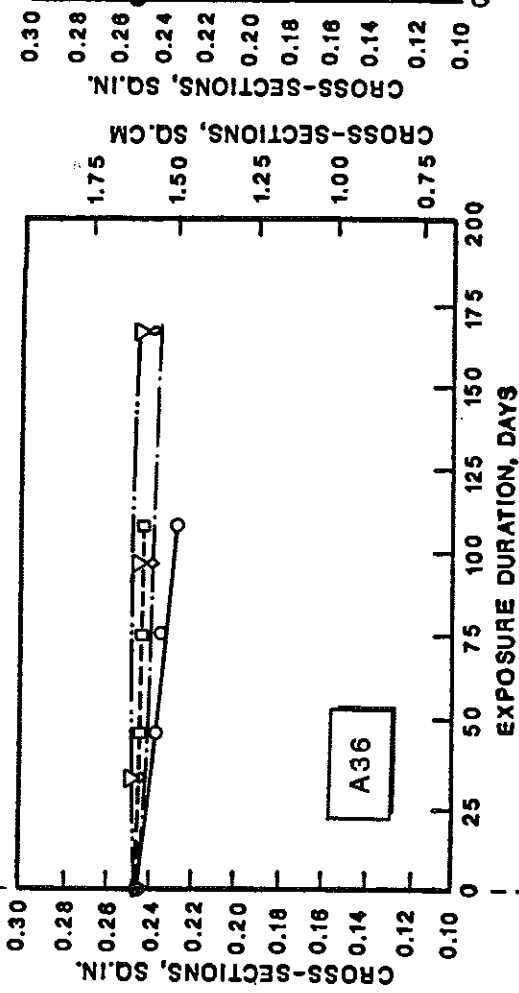


Figure 38. Effective and average cross-sections of bridge steel tensiles in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (sheltered exposure).

AVERAGE



LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR

Figure 38 (cont). Effective and average cross-sections of bridge steel tensiles in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (sheltered exposure).

less for the sheltered exposure. NaCl with a rust inhibitor had roughly the same average corrosion as CMA alone on the weathering steel ASTM A588 in the sheltered exposure.

Worst pit depths occurring in $MgCl_2$ with a rust inhibitor were, in general, slightly deeper than or roughly the same depth as those occurring in CMA alone. This was true for both freely exposed and crevice surfaces of an open exposure. Worst pit depths occurring in NaCl with a rust inhibitor were, in general, slightly shallower or roughly the same depth as those occurring in NaCl alone for the freely exposed surface but were closer to depths produced by CMA alone for the crevice surface of an open exposure.

For a sheltered exposure, worst pit depths were, in general, slightly shallower in $MgCl_2$ with a rust inhibitor and slightly deeper in NaCl with a rust inhibitor than those occurring in CMA alone. This was true for both freely exposed and crevice surfaces.

Tensile strengths of the steels exposed to $MgCl_2$ with a rust inhibitor remained close to those exposed to CMA alone while those exposed to NaCl with a rust inhibitor were slightly less than those exposed to CMA alone.

Guardrail (Figs. 39 and 40) - Average corrosion losses of $MgCl_2$ with a rust inhibitor and NaCl with a rust inhibitor were slightly better or slightly worse, respectively, than those experienced in CMA alone for the weathering steel guardrail. Average corrosion losses were roughly the same for both salt and rust inhibitor combinations on the galvanized guardrail—roughly intermediate between those for CMA and NaCl alone.

Steel Reinforcement for Concrete (Fig. 41) - For the uncoated reinforcement, the average corrosion rate of both $MgCl_2$ with a rust inhibitor and NaCl with a rust inhibitor were less than that which occurred for CMA alone with NaCl with a rust inhibitor being slightly more corrosive than $MgCl_2$ with a rust inhibitor. For the epoxy coated reinforcement the average corrosion losses of NaCl with a rust inhibitor were slightly greater and those of $MgCl_2$ slightly less than the corrosion losses occurring for CMA alone.

Prestressing Strand - See prestressing strand under CMA and NaCl mixes.

Aluminum - For both exposures, crevice corrosion interior to the lapped surfaces resulting in pitting of 10 to 20 mils depth occurred over approximately 25 percent of the contacting surfaces. While the freely exposed surfaces of the specimens in $MgCl_2$ with a rust inhibitor were relatively free of pitting, approximately 15 to 25 percent of the freely exposed surface of the specimens in NaCl with a rust inhibitor experienced pitting of roughly 5 mils depth.

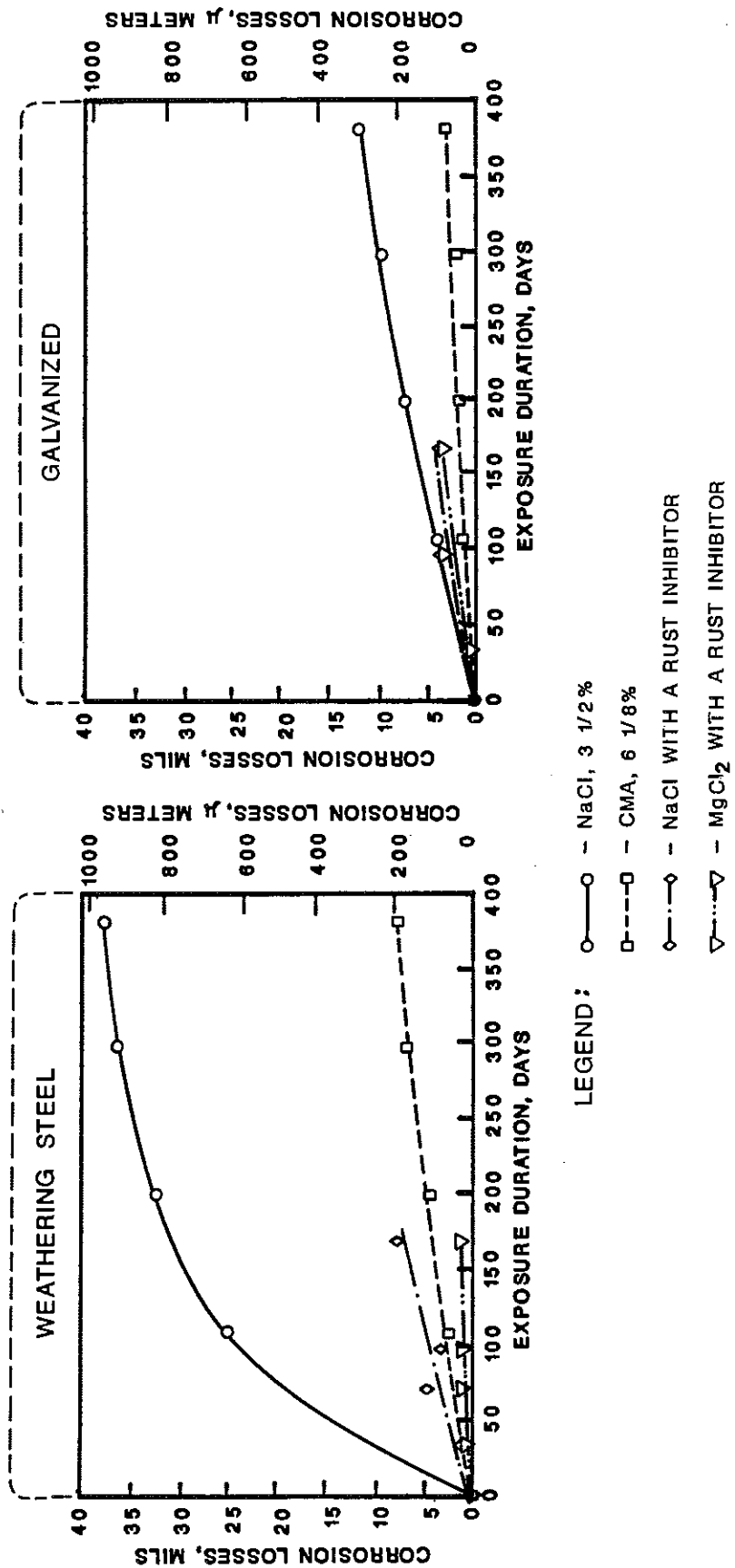


Figure 39. Average corrosion losses of weathering steel and galvanized guardrail in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (open exposure).

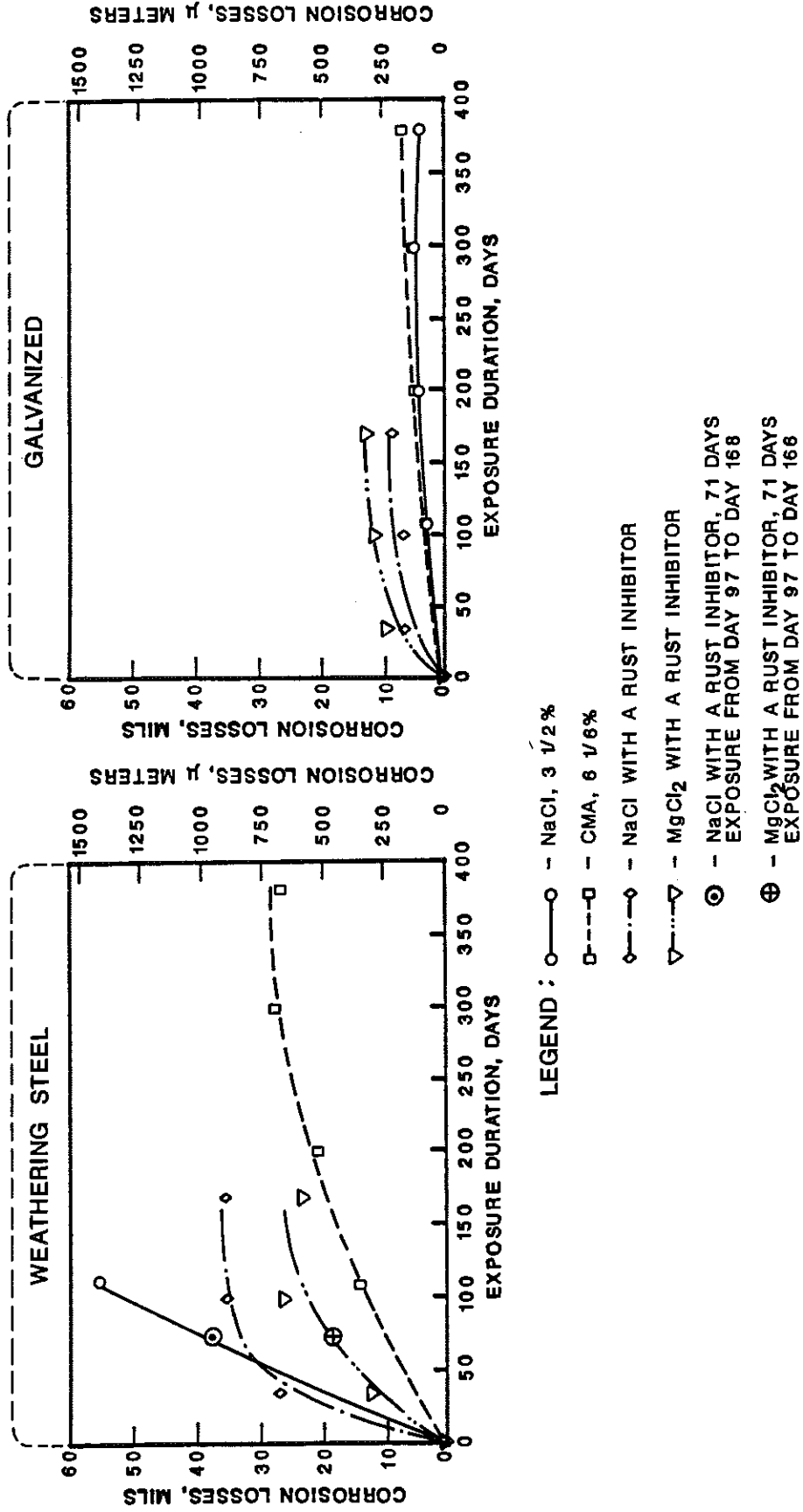
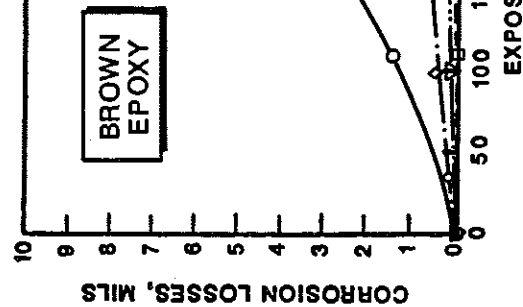
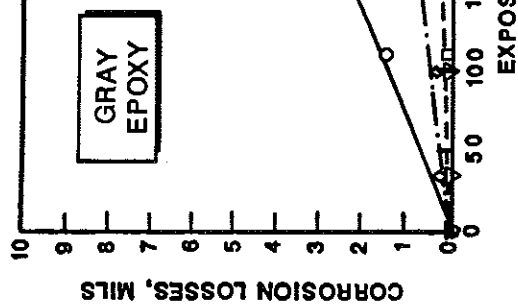
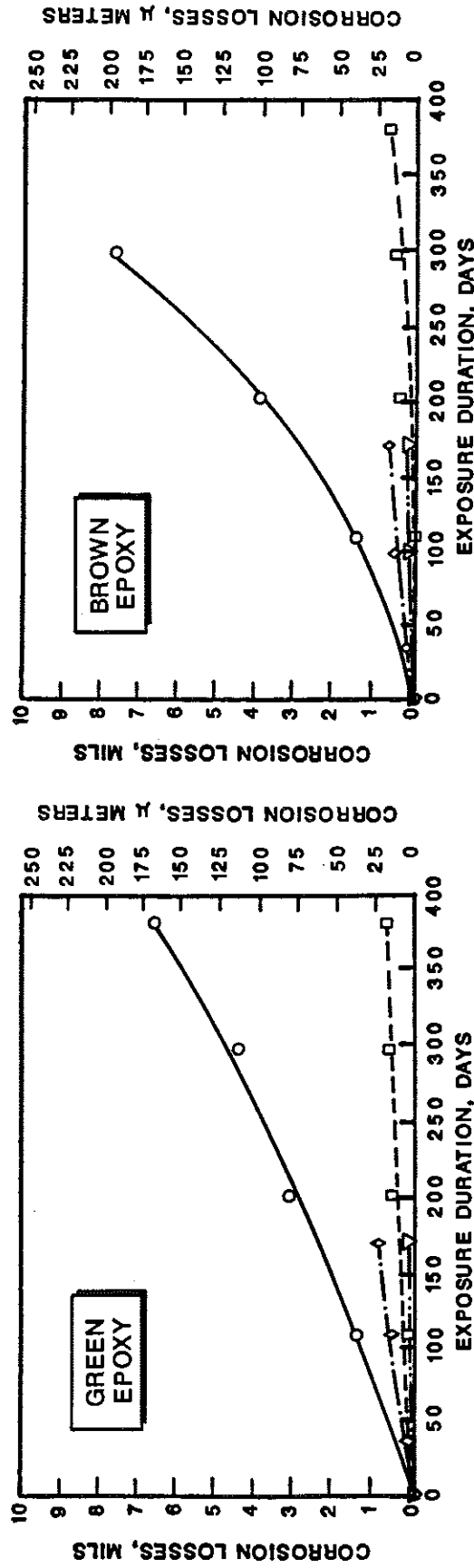
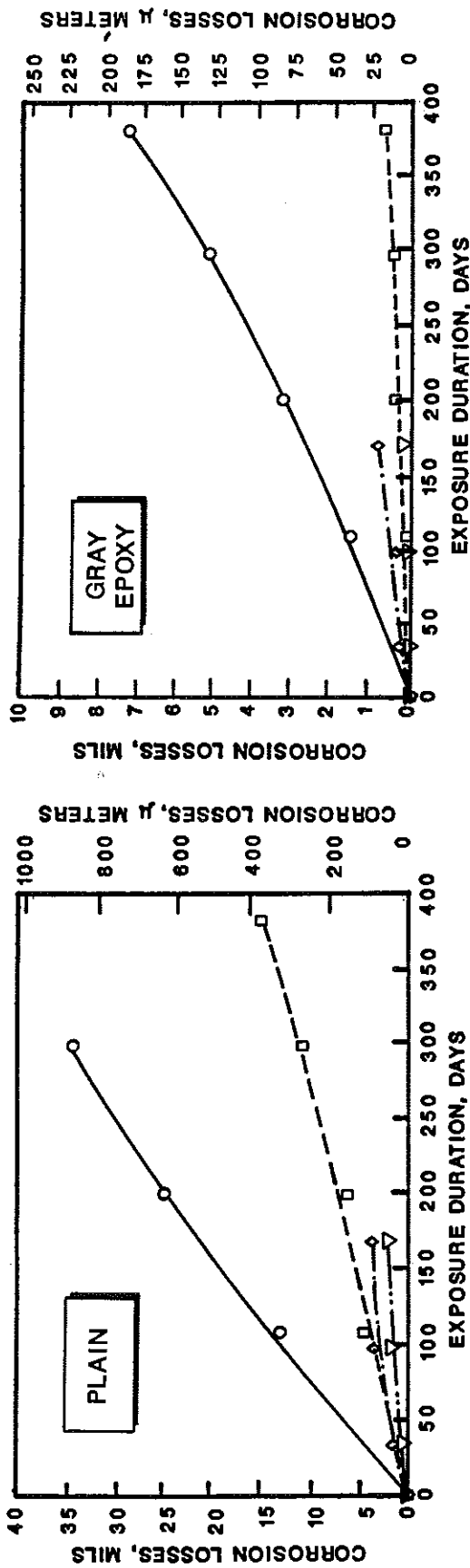


Figure 40. Worst pit depth of weathering steel and galvanized guardrail in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (open exposure).



LEGEND

- — NaCl, 3 1/2%
- — CMA, 6 1/8%
- ◇ — NaCl WITH A RUST INHIBITOR
- ▽ — MgCl₂ WITH A RUST INHIBITOR

Figure 41. Average corrosion losses of steel reinforcement for concrete in NaCl with a rust inhibitor and MgCl₂ with a rust inhibitor (open exposure).

DISCUSSION

CMA does appear to be considerably less corrosive than NaCl and only slightly more corrosive than (distilled) water alone (at least for the accelerated weathering environment in which the testing was performed). For almost all of the materials tested, the average corrosion losses in CMA were only 1/4 to 1/15th of those occurring in NaCl. Materials exposed to CMA also appear to experience more uniform pitting and, consequently, smaller reductions in original strength and probably better fatigue performance as well.

While CMA may be considerably less corrosive than NaCl, have satisfactory deicing performance (3, 9, et al), and may be environmentally safe (10), it still has a major drawback—its price. Presently pure CMA costs about \$600/ton, or about 27 times what NaCl does in Michigan for the same weight of material and approximately 1.8 times² (theoretical deicing equivalent—equiosmolar quantity) as much CMA (by weight) must be used to achieve the same deicing ability. This amounts to an effective price for CMA that is roughly 50 times what NaCl costs or roughly \$1100/ton of salt replacement. The effective cost goes even higher when one considers the difference in density of CMA and NaCl. Currently CMA has only 1/2 (loose) to 5/8th (packed) the density of NaCl. In other words, almost four times as much CMA, by volume, must be transported, stored, and applied compared to rock salt. While the final effective cost figure may be below the upper (inflated) limit of the damage done by salt (from the introduction) as well as more current estimates made by New York, Maryland, and Alaska (11) (over \$1400/ton); the difference between the two is fully realizable only if environmental problems are indeed as serious as assumed. The corrosion damage alone is only around \$360 (from the introduction)/ton even when inflation is taken into consideration.

For Michigan, the environmental aspect does not appear to be an immediate problem, but may eventually become a cause for concern. While groundwater Cl⁻ ion concentrations (which usually parallel Na⁻ ion concentrations) adjacent to our major highways are not currently at or near levels that pose a health risk and do not appear to be increasing (12), the Cl⁻ ion concentration of the Great Lakes is gradually increasing (13). For Michigan and other states in a similar situation, the use of pure CMA may not be economically sensible at the present time.

The performance of CMA and NaCl mixes suggests that there may be a cheaper alternative to using pure CMA that still retains much of the potential corrosion benefits. Current data indicate that a 0.46 CMA/NaCl ratio results in a mixture that has almost as good corrosion performance as CMA by itself and suggests that the limit may very well be

² While Chevron, currently the major producer of commercially available CMA, feels that a factor of 1.1 to 1.2 is adequate, our own Maintenance Division is using roughly 2.0 or more times as much for our current limited applications of this material.

lower (probably somewhere between a 0.46 and a 0.11 CMA/NaCl ratio.³ Even with current CMA prices such a mix would cost less than \$240/ton of rock salt equivalent (assuming no synergistic effects in the deicing ability of the mix). This price could go much lower with the introduction of new technologies for making CMA. Research aimed at producing CMA by a "single-reactor biological process" of waste feedstocks (natural carbohydrates such as pulp and paper mill sludges, cheese whey, apple and grape pomace, etc.) show promise of reducing the price by 30 to 50 percent. This would almost halve the cost of a CMA/NaCl mix. At these prices, the economics definitely favor the use of CMA/NaCl mixtures. Potential savings for Michigan alone could be as high as \$43,500,000 (current CMA prices) to \$76,500,000 (reduced CMA prices) per year taking into consideration only the reduced corrosion damage.

While such a measure might be only temporary, since part of the incentive for doing away with NaCl is the environmental damage, mixes would allow an economically sensible way for Michigan and other states to start using an alternate deicer. With an established market competition and cheaper CMA production techniques would very likely be developed much sooner than is currently expected. This could allow for either further reductions of salt in the mix for the same price or alternately a cheaper mix.

While the CMA/NaCl mix will probably have additional benefits such as deicing properties (being predominately NaCl) closer to NaCl alone and lighter weight and smaller volume (for equivalent deicing quantities) than CMA alone; there are still some potential drawbacks. There is some reason to believe that CMA may cause problems for reinforcing steel in concrete (8). Such a problem could negate any potential savings. Additionally, although the results for this accelerated weathering environment are encouraging, the same results cannot be automatically guaranteed for the real world where many additional variables will come into play. Will the CMA, being biodegradable (10), be around in a real world environment long enough to do any good in counteracting the corrosive effects of the long lasting chloride ion? Will the same passivating oxide layer be formed under changing temperatures and humidities that will, in general, be much different from the accelerated weathering environment used in testing? Only additional testing can answer these questions.

While both the $MgCl_2$ with a rust inhibitor and the NaCl with a rust inhibitor, show some definite promise as alternate deicing agents, they also have drawbacks. Since both contain Cl^- ions, there is not as much,

³ While even the 0.11 and 0.03 CMA/NaCl ratios performed well for the openly exposed specimens, their performance for the sheltered specimens suggests that they may not provide adequate protection for all areas of a structure. Such structurally important sheltered locations as guardrail splices, lamp and sign pole bases (interior), bridge cantilevered hanger plate expansion joints, and many others may corrode more than would be desirable or safe.

if any, environmental advantage to using these materials. In fact, the $MgCl_2$, for equiosmolar quantities, would produce 30 percent more Cl^- ions than $NaCl$. The rust inhibitor currently lacks the extensive environmental testing such as CMA has undergone. $MgCl_2 \cdot 6H_2O$, for equiosmolar quantities, weighs more than twice as much as $NaCl$. While performance has been very good in the test environment with optimum concentrations of the rust inhibitor, will it remain so in the real world where the rust inhibitor may be washed away leaving only the corrosive salt behind? Here again, more work remains to be done.

In view of the tremendous potential savings, Michigan is planning further work with these deicing alternatives to evaluate their corrosion performance in real highway environments. This work will involve corrosion measurements on simulated bridge deck slabs and on atmospheric exposures of representative highway metals exposed periodically to the various potential deicers.

CONCLUSIONS

For the accelerated weathering environment used in this testing, CMA was definitely less corrosive than $NaCl$ and only slightly more corrosive than distilled water alone. These results held true for all of the materials (i.e., bridge steels, guardrail, steel reinforcement for concrete, aluminum, steel prestressing strand, galvanizing, and galvanic couples) tested.⁴ This implies that CMA may (barring any possible problems with corrosion of steel in concrete) provide most, if not all of the potential corrosion savings that could result from the total elimination of $NaCl$.

The results for CMA/ $NaCl$ mixes are similar to CMA alone at the longer exposure durations although shorter exposures are closer in performance to $NaCl$ alone. With faster earlier corrosion, the mixes resulted in slightly more total corrosion than CMA alone even though the corrosion rates appeared to end up at rates close to those of CMA alone. This was true for mixes down to at least the 0.46 CMA/ $NaCl$ weight ratio and may be good for even lower weight ratios (somewhere between 0.46 and 0.11). This implies that a much cheaper CMA/ $NaCl$ mix may provide most of the corrosion savings that could be realized from the use of pure CMA as well as eliminate some $NaCl$. These potential savings are partly dependent on the ability of biodegradable CMA to remain with the corrosive $NaCl$ in the actual highway environment.

The $MgCl_2$ and rust inhibitor mix provided superior corrosion performance to distilled water alone. This suggests that this material may provide more corrosion savings than could be realized from the complete

⁴This comparison uses average corrosion rate, maximum pit depth, crevice accelerated corrosion rate, maximum crevice pit depth, and loss of tensile strength—effective cross-sectional area reduction as measures of corrosion damage.

elimination of NaCl. Possible drawbacks include approximately 30 percent more Cl^- ions and more than twice the weight for deicing ability equivalent to NaCl. The potential savings are partly dependent on the ability of the rust inhibitor to remain with the corrosive MgCl_2 in the actual highway environment.

The NaCl and rust inhibitor mix provided corrosion performance similar to that of CMA/NaCl mixes. This suggests that this material may provide the same or almost the same potential corrosion savings as a CMA/NaCl mix. While current price projections suggest that this alternative might be almost as cheap as a CMA/NaCl mix, this option does not eliminate any NaCl. The potential savings are also partly dependent on the ability of the rust inhibitor to remain in the actual highway environment.

While CMA, CMA/NaCl mixes, MgCl_2 with rust inhibitor, and NaCl with a rust inhibitor all show much promise of being deicing salt alternatives that may provide reduced highway maintenance costs and, in some cases, improve environmental safety, more work remains to be done in evaluating these alternatives.

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APPENDIX

Chemical Analysis of Deicing Salts

CMA*

	<u>Mean, Percent</u>	<u>Standard Deviation, Percent</u>
Acetate	72.4	+ 3.5
Calcium	11.8	- .8
Magnesium	8.9	.6
Water Insoluble	2.4	1.8
Moisture	1.3	.5
Chloride	.4	.1

NaCl

	<u>Percent</u>
Sodium Chloride	98.06
Water Insoluble	1.04
Calcium Sulfate	.63
Moisture	.16
Calcium Chloride	.05
Magnesium Chloride	.05

*Analysis of CMA 'produced for field tests' furnished by FHWA.