

MICHIGAN DEPARTMENT OF TRANSPORTATION
M•DOT
EVALUATION OF UNITED SALT'S CORROSION
INHIBITOR INTENDED FOR USE WITH SODIUM
CHLORIDE DEICING SALT

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Research Laboratory Section
Materials and Technology Division
Research Project 89 G-271
Research Report No. R-1313

Michigan Transportation Commission
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Lansing, August 1991

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ACTION PLAN

1. Materials and Technology Division

A. Distribute copies of report to Maintenance and districts with cover letter indicating how this shows that field corrosion performance of alternate deicers may not be as good as the laboratory results that most manufacturers use to declare their product a 'proven' success. Also mention that, based on our field results, this product is not recommended for further testing or use.

B. Close project.

2. Engineering Operations Committee.

A. No action necessary upon approval of this report.

ABSTRACT

This study documents the performance of United Salt's corrosion inhibitor mixed with sodium chloride (NaCl) deicing salt in the following areas:

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

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

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

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

INTRODUCTION

Sodium chloride (NaCl) has long been used as a deicing agent for highways, due to its availability, low initial cost, and superb performance as a deicer. NaCl, however, produces a highly corrosive environment for all metals used in the highway system, has a deleterious effect on concrete that is exposed to repeated freezing and thawing, and in large enough quantities can pose environmental problems.

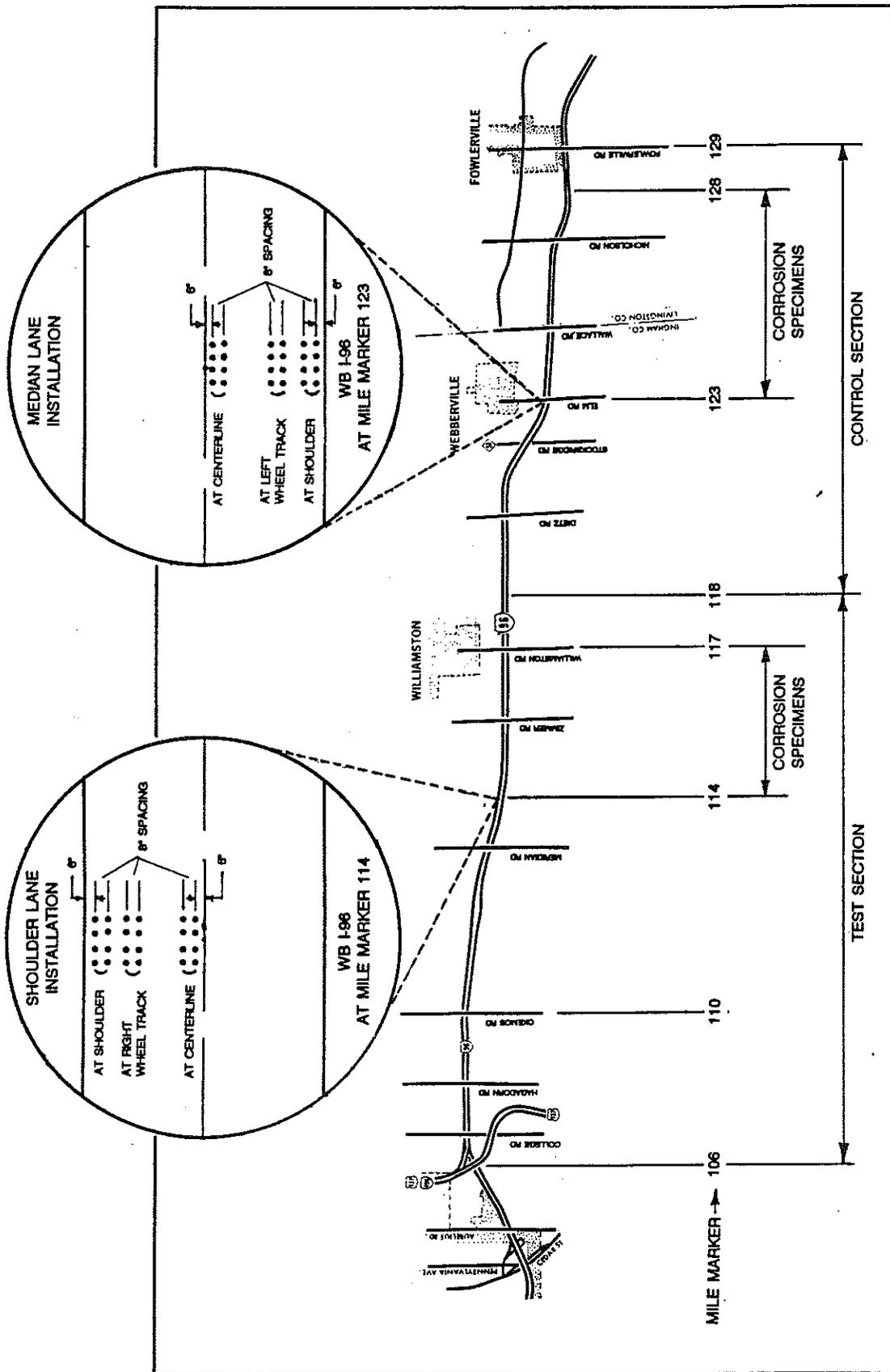


Figure 1. Section of I 96 West of Lansing where corrosion specimens were originally installed (blow-ups show detail of typical installation sites). Specimens were installed at each of the mile marker numbers listed.

Studies performed in the mid-seventies estimated that the cost of using salt was somewhere between six (1) to twenty (2) times the cost of the salt itself. Due to the rise in the cost of those things damaged by salt (and the repair labor) relative to the cost of salt, this estimate in today's market is probably closer to 12 to 40 times the initial cost of salt (3). The high cost of the damage done by salt has prompted interest in alternate deicing agents and corrosion inhibitors for salt, that might lower the effective long term cost of using a deicer.

United Salt Corporation's corrosion inhibitor, composed primarily of a buffered organic fertilizer, is intended to deposit a barrier coating on steel surfaces in the form of an insoluble 'precipitate.' Since the phosphate is only soluble for a short period of time it does not appear to represent a serious environmental problem. Independent laboratory testing (4) has also been performed confirming the inhibitor's performance in reducing corrosion (under laboratory conditions). However, further testing is necessary to confirm the corrosion performance of this inhibitor in a real highway environment. Performance of corrosion inhibitors has traditionally varied considerably, for the worse, from that predicted by laboratory evaluations.

Additional testing (concrete freeze-thaw) has been performed to determine whether or not the corrosion inhibitor might actually be detrimental or possibly have added benefits in other areas of performance.

PROCEDURE

Subjective Observations

Maintenance personnel kept a record of the times and rate of application of both the treated and untreated salt on the test area.

Drivers on the experimental route filled out forms to record their observations of the performance of the treated salt versus their experience with regular deicing salt.

Observations of the drivers were also transmitted during several scheduled meetings between Research Laboratory and Maintenance personnel.

Corrosion of Reinforcing Steel

Using uncoated, deformed reinforcing steel (ASTM A706 or Grade 60 of either A615, A616, or A617) 216 samples of 4-in. length and 3/4-in. diameter were prepared. The samples were sandblasted, degreased, weighed, and installed at sites on I 96 east of the laboratory (Fig. 1). Eight sites were originally selected for installing the specimens—four sites for exposure to the corrosion inhibitor (experimental) and four sites for exposure to regular deicing salt (control). Two sites were added to the control group, however, after two of the original sites were scheduled for

resurfacing. The control and experimental sites were separated by roughly six miles to minimize possible carryover effects.

For each of the original eight sites, twenty-four 2-in. diameter holes were drilled to a depth of approximately 4-1/2 in. At each site the holes were divided into three equal sets with one set located near the center-line, one near the right outside wheel track, and one near the outside shoulder. The specimens were placed in the holes, and fixed with epoxy at the bottom to ensure that freeze-thaw action would not dislodge them. The tops of the specimens were typically 1/4 to 1/2-in. below the surface of the roadway.

Using a mixture of 100 lb of corrosion inhibitor per ton of salt, one part inhibitor to 20 parts salt (as recommended by the manufacturer), the inhibited (treated) salt was applied to the experimental section, while non-inhibited (untreated) salt was applied to the control section of the roadway. Applications occurred whenever deicing treatment was necessary for this particular stretch of road.

After approximately four months, the first winter's exposure, six specimens were removed from each of the original sites (two from each set) except for the two locations that were scheduled for resurfacing where all specimens were removed. The specimens underwent rust removal as per ASTM Standards and were reweighed. After approximately 12 more months, the same procedure was performed for 48 additional samples.

Accelerated Freeze-Thaw Specimens

A total of 56 cubes (2 in. on a side) was prepared using concrete mortar, with no coarse aggregates, following the example of Dr. Peter Hudec (5) of the University of Windsor (Windsor, Ontario).

Half of the cubes were air-entrained, and half were non-air-entrained. The air-entrained concrete was prepared identically to the non-air-entrained concrete except air-entrainment was added at the rate of 3/4 oz per 100 lb of cement. This gave the air-entrained concrete a total air content of 8.1 percent as measured by an Acme Air Meter versus 4.3 percent for the non-air-entrained concrete.

The cubes were separated into seven sets of eight cubes each, with each set having four air-entrained samples, and four non-air-entrained samples. During freeze-thaw cycling, each set of cubes was exposed to a unique solution.

One set was exposed to a 3.5 percent NaCl solution, three sets were exposed to solutions of NaCl and varying concentrations of the corrosion inhibitor, two sets were exposed to solutions of NaCl and varying concentrations of CMA, and one set was exposed to CMA only. The solutions

used (made with deionized water) were as follows (concentrations are given in percent by weight):

<u>Set Number</u>	<u>Solution</u>
1	3.5% NaCl
2	3.5% NaCl, 0.175% Corrosion Inhibitor
3	3.5% NaCl, 0.0875% Corrosion Inhibitor
4	3.5% NaCl, 0.35% Corrosion Inhibitor
5	6.125% CMA
6	3.5 % NaCl, 3.5% CMA
7	3.5% NaCl, 1.25% CMA

After proper curing and air drying all of the specimens were weighed. Freeze-thaw cycling was then performed, with each set of specimens exposed to its designated solution. At a given interval of cycles (ten for air-entrained and five for non-air-entrained) the specimens were rinsed, the weakened solids were removed, and the largest remaining portions of the original specimens were air dried and reweighed. A total of 40 cycles was performed, and the results were compared.

RESULTS AND DISCUSSION

Subjective Observations

Treated and untreated salt were, in general, viewed as performing essentially the same, as far as deicing performance goes, as long as they could both be applied at the same rate. Since the treated salt is still almost 95 percent salt this result is not surprising.

Problems occurred, however, that resulted in less of the treated salt being applied in some instances which in turn resulted in reduced deicing performance for equivalent application time and effort. The treated salt had a greater tendency to cake and harden resulting in plugging of various parts of the spreader truck's salt delivery system. Spinners and chutes are mentioned most frequently as problem areas in the Driver's Reports and at least one driver verbally mentioned having problems with the auger. This particular problem was reported much more frequently as the first batch of corrosion inhibitor with a relatively smaller particle size was being applied. The second batch of corrosion inhibitor, while not being entirely problem free, did perform much closer to what is normally expected of untreated salt.

An additional problem was reported with the first batch of corrosion inhibitor. Several vehicles following closely behind the spreader trucks were reported to have their windshields caked over with a relatively insoluble coating that could not be washed off with windshield washer fluid. This phenomenon could not be duplicated, however, when Research Laboratory personnel followed one of the spreader trucks which was using

the second batch of corrosion inhibitor. The larger particle size of the second batch of corrosion inhibitor also helped to alleviate the dust problems that occurred when mixing the salt and inhibitor.

Corrosion of Reinforcing Steel

There were 16 specimens from the treated area and 39 from the control area that were available for comparison after one winter's exposure. The experimental specimens were found to have a slightly greater rate of corrosion, on average, than the control specimens. The basic results are given in Table 1.

TABLE 1
AVERAGE CORROSION RATE AFTER FOUR MONTHS EXPOSURE

	Average Loss, mils/year	Number of Samples	Standard Deviation
With Inhibitor	2.83	16	1.01
Without Inhibitor	2.75	39	1.07

The differences for the one winter exposure specimens are not statistically significant; in fact, the two populations are almost identical. In other words, there is no significant difference in performance between those specimens from the experimental/treated area and those from the control/untreated area.

There were 24 specimens from the 'treated' area and 23 from the control area that were available for comparison after 16 months of exposure (i.e., two winters exposure but with corrosion inhibitor being used only during the first winter). The average corrosion rate of the experimental specimens was again greater than that for the control specimens. The basic results are given in Table 2.

TABLE 2
AVERAGE CORROSION RATE AFTER 16 MONTHS EXPOSURE

	Average Loss, mils/year	Number of Samples	Standard Deviation
With Inhibitor	2.33	24	0.507
Without Inhibitor	2.05	23	0.325

Worth noting are the reductions in corrosion rate for this longer exposure duration. As normal rust (i.e., iron oxide) builds up on steel, it acts to some extent as a barrier helping to prevent further corrosion. Here, though, the natural oxide layer appears to be performing better as a barrier than the 'insoluble precipitate' that is supposed to have formed on the specimens exposed to the treated salt.

Also significant is the greater rate of corrosion occurring for the specimens exposed to the treated salt. Analysis of variance for these data indicates that the two populations (experimental and control specimens) are different and the differences are statistically significant at the $p = 0.05$ level. This means that there is only a 5 percent or less chance that the differences seen here might be attributable to the normal variations in corrosion rate that can occur among different specimen in the same environment.

If an appreciable amount of functioning (i.e., acting as a barrier), insoluble precipitate had formed on the specimens during the first winter, its effects should have been even more apparent during the longer 16-month exposure duration. This would be expected since the cumulative effect of the repeated (i.e., with each application) formation of an insoluble precipitate barrier layer would be allowed to act over a much greater period of time.

The previously mentioned independent laboratory test results (4) suggest that this material can function as a corrosion inhibitor, at least under ideal (laboratory) conditions. Several possible problems may be adversely affecting the performance of the treated salt in our 'real' highway environment.

The instances of windshield and spreading equipment fouling with caked and hardened material suggest that the 'precipitate' may be forming much earlier than would be desirable and precipitating out on almost everything but the steel specimens. The larger particle size of the second batch of corrosion inhibitor probably functioned better in this respect, but most of the winter deicing (approximately 80 percent) was done before this batch was received and used.

The larger particle size, by itself, might not be sufficient to ensure that enough of the 'precipitate' can make its way to the metal surfaces that require corrosion protection. Debris and dirt, which are always going to exist in a real highway environment, touching the metal may get much of the 'precipitate' barrier protection that was intended for the metal.

This type of phenomenon may help to explain the greater corrosion rate for the treated specimens. Rust undercutting of the probably small portions of the barrier coating that directly contact the metal, and/or release of the precipitated coated debris/dirt from the metal surface via rain washing, thermal expansion and contraction, or other action may create crevices that can accelerate corrosion.

Premixing of the salt and inhibitor up to several weeks in advance as was done for some of the treated salt may allow the inhibitor to form its precipitate before the salt is actually spread if sufficient water is available (i.e., high humidity or otherwise).

Several other variables besides presence of the corrosion inhibitor were investigated to see if other outside influences could have had an

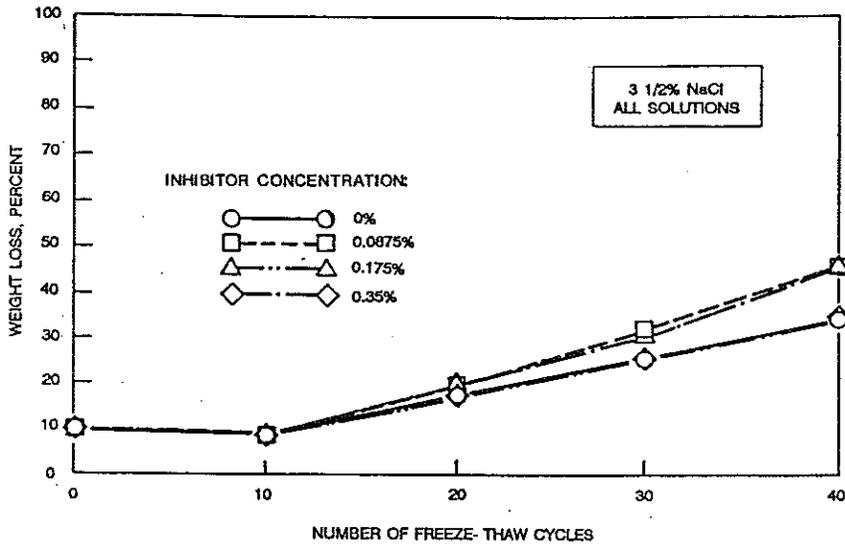


Figure 2. Weight loss vs. number of freeze-thaw cycles for air-entrained concrete.

Figure 3. Weight loss vs. number of freeze-thaw cycles for non-air-entrained concrete.

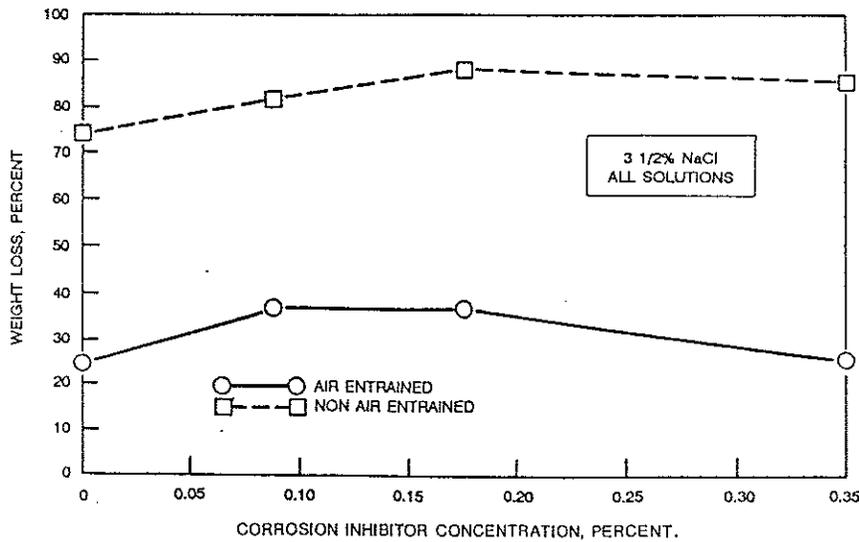
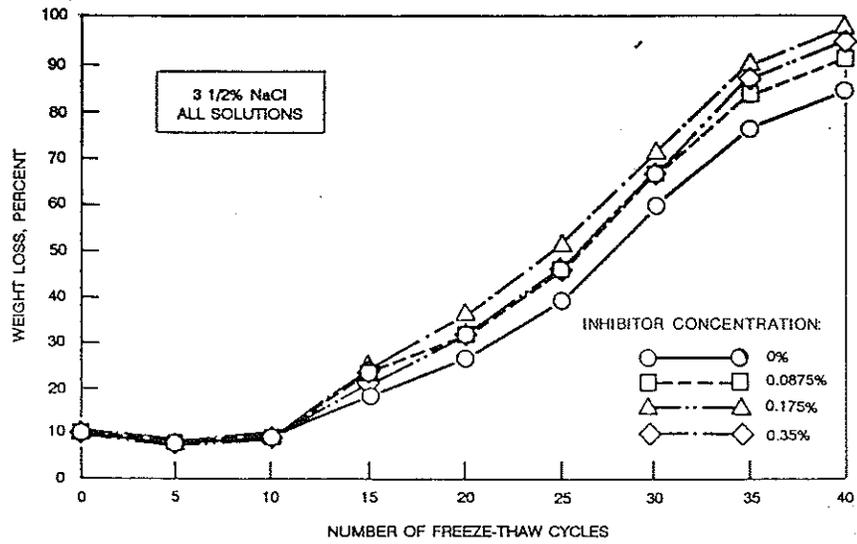


Figure 4. Weight loss vs. concentration of corrosion inhibitor after 40 freeze-thaw cycles.

effect on the corrosion performance of the test specimens. Among these were location of specimens within a given lane, location along the highway, side of highway (eastbound or westbound), and slope of pavement at specimen location. None of these parameters appeared to have any appreciable effect on corrosion rate.

Freeze-Thaw Specimens

Corrosion Inhibitors - In all cases, the specimens exposed to the corrosion inhibitor-treated NaCl suffered as much or more weight loss due to freeze-thaw deterioration of the concrete than the control specimens exposed only to NaCl. This is true for both the air-entrained and non-air-entrained specimens. The data for these cubes are plotted in Figures 2 through 4.

Although the air-entrained samples, as would be expected, suffered less loss than the non-air-entrained, the relatively adverse effect of the inhibitor is greater for the air-entrained specimens (Figs. 2 and 3).

In Figure 2, the identical behavior of the 0.35 percent corrosion inhibitor-treated salt to that of salt alone suggests that the corrosion inhibitor may have been inadvertently left out of this particular batch, although other possible explanations probably exist.

Considering the manner in which the corrosion inhibitor is intended to function (i.e., formation of an insoluble precipitate), it is not entirely surprising that salt mixes with inhibitor perform more poorly than salt alone. A likely scenario might involve the precipitate blocking 'surface' pores of the concrete trapping water inside the concrete. While such a blocking action might also have a beneficial effect in restricting future migration of salt and water into the concrete, the potential benefits are not obvious in the test environment used here.

Calcium Magnesium Acetate - In all cases, specimens that were exposed to CMA, either alone or in combination with NaCl, had significantly less weight loss than those specimens exposed to NaCl alone. Even at the lower concentration levels the presence of CMA appears to dramatically improve freeze-thaw performance. At higher concentrations freeze-thaw cycling has almost no effect. The data for these specimens are plotted in Figures 5 through 7.

The negative weight losses (i.e., weight gains) for some of the specimens are attributable to retained salt and/or moisture which weighs more than the concrete lost.

Worth noting is the performance of the non-air-entrained cubes exposed to CMA/NaCl mixes. Even the lowest CMA/NaCl ratio examined considerably improved the freeze-thaw performance compared to NaCl alone.

The results would appear to suggest that CMA, even in the presence of NaCl, may help to prevent freeze-thaw deterioration of both

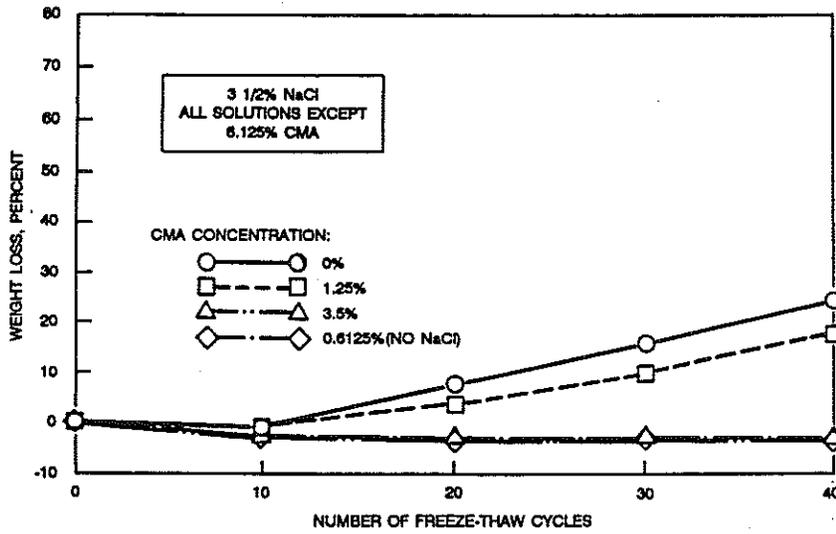


Figure 5. Weight loss vs. number of freeze-thaw cycles for air-entrained concrete.

Figure 6. Weight loss vs. number of freeze-thaw cycles for non-air-entrained concrete.

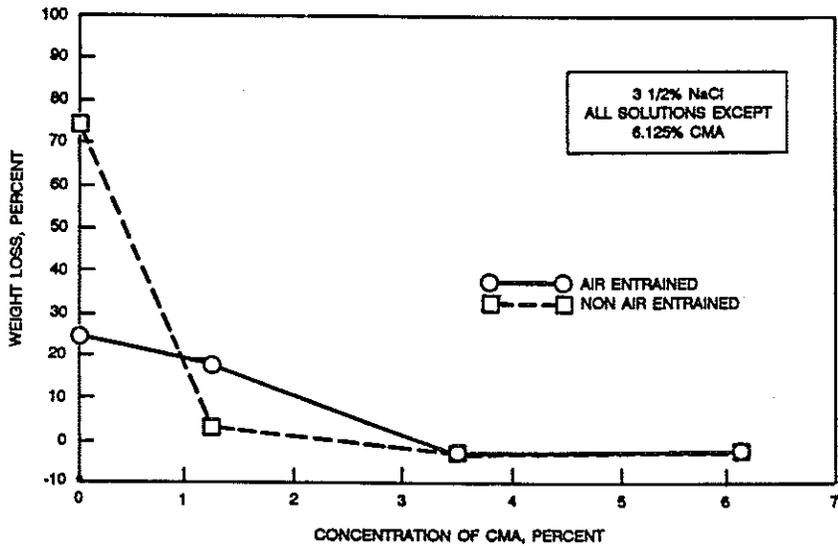
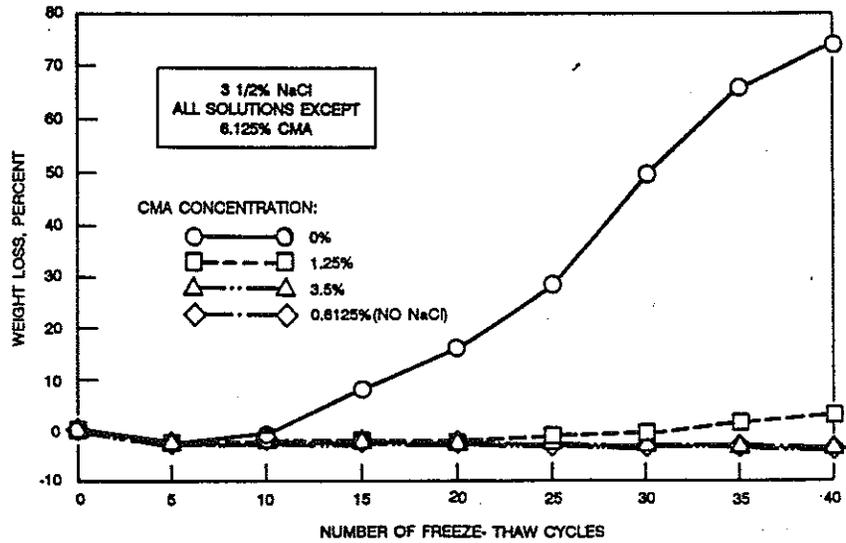


Figure 7. Weight loss vs. concentration of CMA after 40 freeze-thaw cycles.

air-entrained and non-air-entrained concrete with the non-air-entrained concrete possibly having a slight edge at lower CMA concentrations.

This is a potential added benefit which could help to counteract the relatively high cost of CMA providing field performance parallels this accelerated laboratory testing.

CONCLUSIONS

In view of the negative test results and application problems, United Salt Corporation's corrosion inhibitor, as tested in this study, does not appear to merit either current usage or further testing at this time.

CMA appears, even in the presence of NaCl, to help prevent freeze-thaw deterioration of both air-entrained and non-air-entrained concrete.

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