

**CORROSION OF STEEL IN**  
**CALCIUM-MAGNESIUM-ACETATE (CMA) DEICER**

FINAL REPORT

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## FOREWORD

Chloride salts are used to melt ice on roads throughout the United States as a public safety measure. It has been found, however, that corrosion and pollution damages associated with chloride salt applications may generate long term costs as much as 10-15 times the initial amount required to purchase and apply the deicing chemicals themselves. Calcium Magnesium Acetate (CMA) has been recently identified as a possible alternative to chloride salts which is relatively free from damage-associated secondary costs. The Alaska Department of Transportation and Public Facilities (DOT&PF) has funded several research projects examining the feasibility of producing and utilizing CMA as a chloride salt replacement throughout the state's highway system.

DOT&PF commissioned this research study in order to verify positive, although mostly qualitative, literature findings regarding the low corrosion potential of CMA. This was done in preparation for large scale field testing of the material. Quantitative results described in this report justify use of CMA based on standard laboratory testing procedures. The tests were conducted within a temperature range of interest to Alaskan engineers and vehicle owners.

In non-acidic solutions it appears that CMA is less corrosive than sodium chloride by a factor of 10 or more. The reader is cautioned, however, that this conclusion is based on the limited sample types and the specific test methods employed in this research effort.

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## **IMPLEMENTATION**

Vehicle owners and others may be concerned with the chemical nature and safety of CMA. This report will be used as a resource for responding to such concerns. Findings of this study will be incorporated into any environmental impact statement required for further field applications of CMA.

## ABSTRACT

The corrosiveness of a new road deicer, Calcium Magnesium Acetate (CMA), was determined under various conditions of temperature, pH, and concentration. The corrosion rates of steel in CMA solutions were generally found to be of the order of 2 mils per year (mpy). In comparison, for the currently used chloride salt deicers the corrosion rates can range from 25-80 mpy.

CMA is generally found to be a non-corrosive medium compared to sodium and calcium chloride. Although this preliminary corrosion research indicates that CMA is less corrosive to steels than salts, further work is necessary to confirm the corrosion characteristics of CMA on other materials. Additional studies should be performed on environmental and aesthetic aspects before widespread application of CMA as a road deicer.

## **ACKNOWLEDGMENTS**

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## TABLE OF CONTENTS

	PAGE
ABSTRACT .....	iii
ACKNOWLEDGMENTS .....	iv
LIST OF TABLES .....	vi
LIST OF FIGURES .....	vii
I. INTRODUCTION .....	1
II. PREVIOUS WORK .....	3
III. EXPERIMENTAL WORK .....	4
1. CMA Solution Preparation .....	4
2. Testing Variables .....	4
3. Recorded Information .....	5
4. Sample Preparation .....	5
5. Exposure Technique .....	6
6. Sample Cleaning .....	9
7. Measuring and Weighing .....	10
IV. RESULTS AND DISCUSSIONS .....	11
1. High Temperature (150°F - (66°C)) .....	11
2. Room Temperature (70°F - (22°C)) .....	12
3. Low Temperature (20°F - (-7°C)) .....	12
4. Problems with CMA .....	13
V. CONCLUSIONS .....	27
VI. RECOMMENDATIONS FOR FUTURE WORK .....	28
VII. REFERENCES .....	29

**LIST OF TABLES**

	PAGE
Table 1: Corrosion Rates of Steel-1 in CMA (100 day tests) .....	14
Table 2: Corrosion Rates of Steel-2 in CMA (100 day tests) .....	15
Table 3: Corrosion Rates of Steel-1 in CMA (30 day tests) .....	16
Table 4: Corrosion Rates of Steel-2 in CMA (30 day tests) .....	17

## LIST OF FIGURES

		PAGE
FIGURE 1:	Photograph Showing Sample Cleaning Procedure . . . . .	7
FIGURE 2:	Photograph Showing Samples Arranged in Corrosion Medium . . . . .	8
FIGURE 3:	Corrosion Rate vs pH at 150°F for Steel 1 (30 day test) . . . . .	18
FIGURE 4:	Corrosion Rate vs pH at 150°F for Steel 2 (30 day test) . . . . .	18
FIGURE 5:	Corrosion Rate vs pH at 150°F for Steel 1 (100 day test) . . . . .	18
FIGURE 6:	Corrosion Rate vs pH at 150°F for Steel 2 (100 day test) . . . . .	18
FIGURE 7:	Corrosion Rate vs Percent CMA at 150°F for Steel 1 (30 day test) . . . . .	19
FIGURE 8:	Corrosion Rate vs Percent CMA at 150°F for Steel 2 (100 day test) . . . . .	19
FIGURE 9:	Corrosion Rate vs Percent CMA at 150°F for Steel 1 (100 day test) . . . . .	19
FIGURE 10:	Corrosion Rate vs Percent CMA at 150°F for Steel 2 (100 day test) . . . . .	19
FIGURE 11:	Corrosion Rate vs pH 30 Day Test at 70°F for Steel 1 (30 day test) . . . . .	20
FIGURE 12:	Corrosion Rate vs pH at 70°F for Steel 2 (30 day test) . . . . .	20
FIGURE 13:	Corrosion Rate vs pH at 70°F for Steel 1 (100 day test) . . . . .	20
FIGURE 14:	Corrosion Rate vs pH at 70°F for Steel 2 (100 day test) . . . . .	20
FIGURE 15:	Corrosion Rate vs Percent CMA at 70°F for Steel 1 (30 day test) . . . . .	21
FIGURE 16:	Corrosion Rate vs Percent CMA at 70°F for Steel 2 (30 day test) . . . . .	21
FIGURE 17:	Corrosion Rate vs Percent CMA at 70°F for Steel 1 (100 day test) . . . . .	21



FIGURE 18:	Corrosion Rate vs Percent CMA at 70°F for Steel 2 (100 day test) .....	21
FIGURE 19:	Corrosion Rate vs pH at 20°F for Steel 1 (30 day test) .....	22
FIGURE 20:	Corrosion Rate vs pH at 20°F for Steel 2 (30 day test) .....	22
FIGURE 21:	Corrosion Rate vs pH at 20°F for Steel 1 (100 day test) .....	22
FIGURE 22:	Corrosion Rate vs Percent CMA at 20°F for Steel 2 (100 day test) .....	22
FIGURE 23:	Corrosion Rate vs Percent CMA at 20°F for Steel 1 (30 day test) .....	23
FIGURE 24:	Corrosion Rate vs Percent CMA at 20°F for Steel 2 (30 day test) .....	23
FIGURE 25:	Corrosion Rate vs Percent CMA at 20°F for Steel 1 (100 day test) .....	23
FIGURE 26:	Corrosion Rate vs pH at 20°F for Steel 2 (100 day test) .....	23
FIGURE 27:	Photograph Showing some Pitting of Steel due to Corrosion in CMA at 150°F .....	24
FIGURE 28:	CMA Crystallization due to Dehydration at Higher Temperature .....	25
FIGURE 29:	Deposits of CMA on Samples that Persisted Even After Thorough Cleaning .....	26

## I. INTRODUCTION

Highway departments everywhere should make safety their number one priority. Sand, gravel, and salts have been used in the past to minimize unsafe winter driving conditions on U.S. roads.<sup>1,2</sup> Salts are used to melt ice, while sand and gravel are used to provide traction.

The use of sodium and calcium chloride as deicing compounds will continue until a viable alternative is found. These compounds give good deicing results above 20°F (-7°C), but they become less effective below this temperature. Salt usage in Arctic regions is therefore often ineffective and uneconomical. Although salt sometimes works well as a deicer in Alaska, both the public and government agencies dislike its use due to corrosion damages and other side effects. The harmful effects of salt include corrosion of automobile parts and buried material, damage to highway structures, ground water contamination, and vegetation damage.<sup>3</sup> Corrosion of automobile parts and buried materials are considered in this report.

Corrosion damages and environmental pollution offset the deicing benefits of salts.

"With the exception of real property, the monetary investment in the automobile in the United States is perhaps greater than any other item of capital equipment. Approximately 20% of United States steel production is devoted to the automobile, and the automobile is used by all sectors of the economy. It is not surprising, therefore, that the cost of corrosion in terms of vehicle damage is great. A report by the National Bureau of Standards and Battelle Columbus Laboratories estimates that the total cost of automobile corrosion in 1975 in the United States was about \$16 billion and is ever increasing. This amounted to approximately 20% of the then total cost of corrosion in the U.S. Corrosion in automobile fuel systems, radiators, exhaust systems, and the exterior chassies and body have been a problem for all manufacturers for many years."<sup>4</sup>

It has been recognized that salt is the main culprit in reducing the aesthetic value of the automobile particularly in the northern tier of the United States. Here salt is used in enormous amounts to facilitate winter driving. It is estimated that some ten million tons are used each year.

To eliminate many of the harmful effects of salts, much work has been done to find an alternative road deicer. Calcium Magnesium Acetate (CMA) has been considered as a viable alternative to deicing salts. Limited laboratory study has indicated that CMA is less corrosive to steel than chloride salts. It is also an effective deicing agent, even at lower temperatures.<sup>5</sup> CMA may be relatively inexpensive if corrosion and environmental damages are included in the economic analysis. Further, CMA has also been found to be a safe, non-toxic substance with respect to animal and plant life.

The purpose of this report is to determine some long term (100 day) corrosive characteristics of Calcium Magnesium Acetate (CMA) with respect to steel and compare these to the corrosive characteristics of a currently used road deicer, sodium chloride.

## II. PREVIOUS WORK

It is generally recognized that salt solutions corrode steel. This is especially true of sodium chloride solutions (sea water for example). Research and experience have indicated that both stagnant and moving salt solutions are detrimental to steel surfaces. The higher the relative motion of the metal substrate or the solution, the higher the corrosion rate.<sup>6-12</sup>

Corrosion damage is expressed in terms of the rate of penetration into the metal through surface deterioration. This is commonly given as mils per year (mpy). One mpy corrosion corresponds to one thousandth of an inch reduction in thickness of a sample over the entire exposed surface in one year due to corrosion.

In general, the corrosion rates of steel in aqueous salt solutions can range from 25 to over 80 mils per year (mpy)<sup>6-13</sup> and in some cases much more depending upon the temperature. For example, the corrosion rates of steels can be as high as 10,000 mpy in non-stagnant salt solutions at 150°F.<sup>10</sup> In the case of Calcium Magnesium Acetate, limited work has been done to characterize the corrosion rate quantitatively. Qualitatively, the conclusion from this limited work is that the corrosion rate of steel in CMA is low.<sup>5</sup> These results, however, cannot be compared quantitatively with the corrosion rates determined for salt solutions.

An experimental project was undertaken to determine the corrosion resistance of steel in CMA solution and to compare the results to the corrosion resistance of steel in salt solutions. In any corrosion experiment, choosing the various parameters is very important. Three variables were considered important for the current project: temperature, pH and CMA concentration in water.

### **III. EXPERIMENTAL WORK**

This project is mainly concerned with the corrosive aspects of CMA on steel. Two types of steel samples - rebar steel (Steel 1) and structural/automotive (Steel 2) grade mild steel\* - were used in this study. Steel 1 used is the common 40 ksi grade rebar steel and Steel 2 is the A-36 type structural steel.

The effect of temperature is perhaps the most important single factor in corrosion studies. Accordingly, it is very important to identify the surface temperature of the specimens. In these experiments the temperature of the enclosing apparatus was recorded as the specimen temperature. This measurement is sufficiently accurate, since the experiments were long enough to achieve equilibrium temperature conditions between specimens, corrosive mediums, and their enclosure.

#### **1. CMA Solution Preparation**

Different batches of corrosive solution were made with the various concentrations and pH values indicated. CMA as normally prepared is neutral, corresponding to a pH of 7.0. The pH was adjusted to values below 7.0 using glacial acetic acid. For values above 7.0, calcium hydroxide was used as per standard test techniques. This technique was used to minimize the introduction of other corrosive substances into the solution. Prepared steel samples were then immersed in glass containers containing the above solutions at predetermined CMA concentrations. These specimens were kept at the desired temperatures.

#### **2. Testing Variables**

The range of the parameters studied were:

- pH (6.0, 7.0, 8.5)

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\* For brevity "Steel 1" and Steel 2" are used to identify the samples, especially in figures and tables.

- Concentration\* (10%, 50%, 100%)
- Temperature (150°F (66°C), 70°F(22°C), 20°F(-7°C))

There are 27 combinations of these variables. Three samples of each of the two types of steel were made for each combination. Thus a total of 162 separate tests were performed.

All the samples were coded with a color, number, and letter for identification purposes.

### **3. Recorded Information**

Information that was regularly recorded throughout the experiment included temperature, solution pH, and any observations that were unusual.

### **4. Sample Preparation**

As received rebar (Steel 1) and one inch wide structural steels (Steel 2) were cut into 2 inch long samples. Rebar steel was a 1/2 inch in diameter and the sheet steel was 1/8 inch thick. Ideally the surface of the test specimen should be identical with the surface of the actual equipment being represented by the test. This is not always possible. The degree of scaling or oxidation or other coatings on the metal surfaces may vary. It was appropriate in this case, because of the ease of standardization and the determination of the corrosion resistances of the metal or alloy itself, to use a clean metal surface. To do this, chemical cleaning treatments were utilized to prepare the metal surfaces. The procedure for cleaning the samples was as follows:

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\* The concentration is expressed in volume percent in terms of saturated CMA solution in water. 100% CMA concentration, therefore, corresponds to approximately 25% by weight of CMA.

Each sample was grasped with tongs and rinsed thoroughly with tap water. If the specimen had any deposits on it, it was scrubbed with a plastic brush to insure a deposit-free surface for accurate determination of metal weight. After this initial rinsing, the specimen was picked up with the tongs and stirred in a solution of 50% HCL and 50% distilled water for 10 - 15 seconds. The sample was removed from the acid solution and rinsed with tap water, then distilled water, and finally methyl alcohol. A final rinse in methyl alcohol was done to remove any water and keep the surface free from oxidation. The samples were stored in methyl alcohol until ready for drying and weighing as seen in figure 1. To dry the specimens, they were removed from the methyl alcohol with the help of a pair of tongs and placed in the oven at a temperature of 100°F (38°C). This was done in order to make certain the specimen's weight was accurately determined. Finally, the specimens were taken out of the oven with the tongs and placed on the scale to be weighed. After recording the weight, the samples were put immediately into their designated containers filled with CMA solution (see figure 2). A pair of tongs was always used to handle the samples to avoid coating of the samples with oils and sweat from handling the samples with bare hands.

## 5. Exposure Technique

Important considerations concerning exposure of the specimens are:

1. the corrosive medium should have easy access to the specimen;
2. specimens should be insulated or isolated electrically from contact with any other metal;
3. the specimen should be properly positioned for complete immersion; and
4. the specimens should be as readily accessible as possible.

Proper selection of time and number of periods of exposure are important.

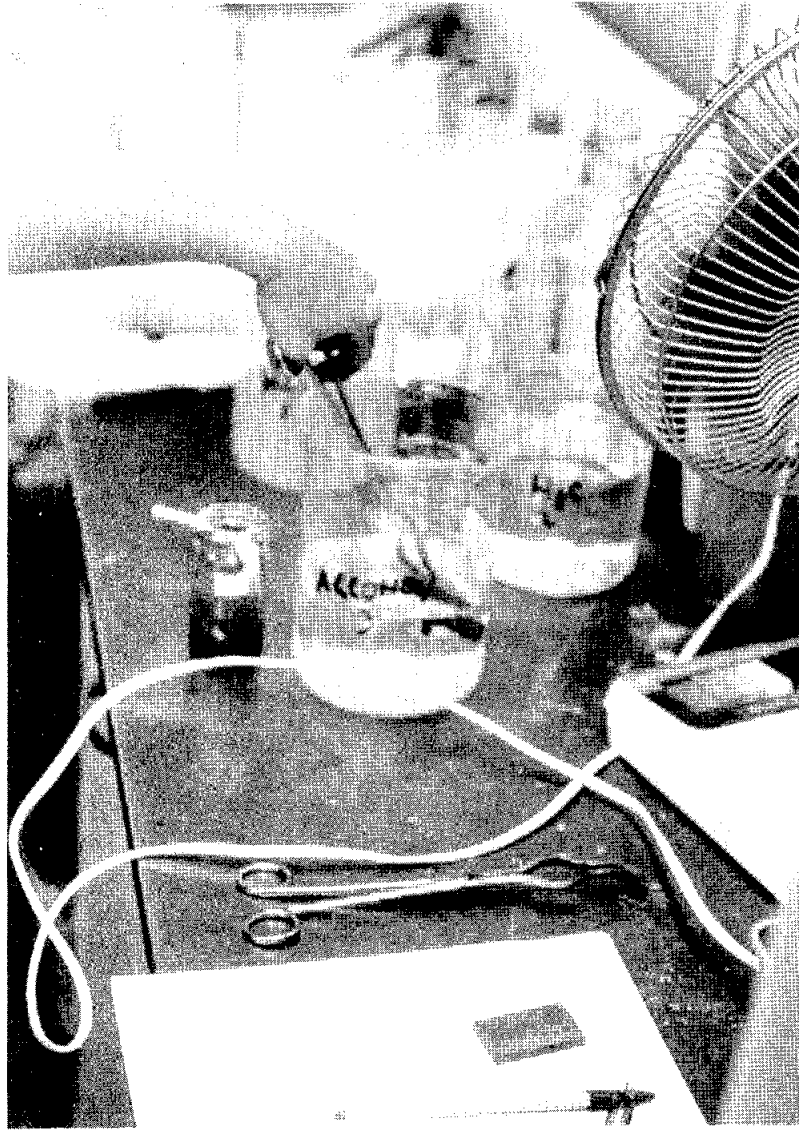


FIGURE 1: Photograph showing sample cleaning procedure



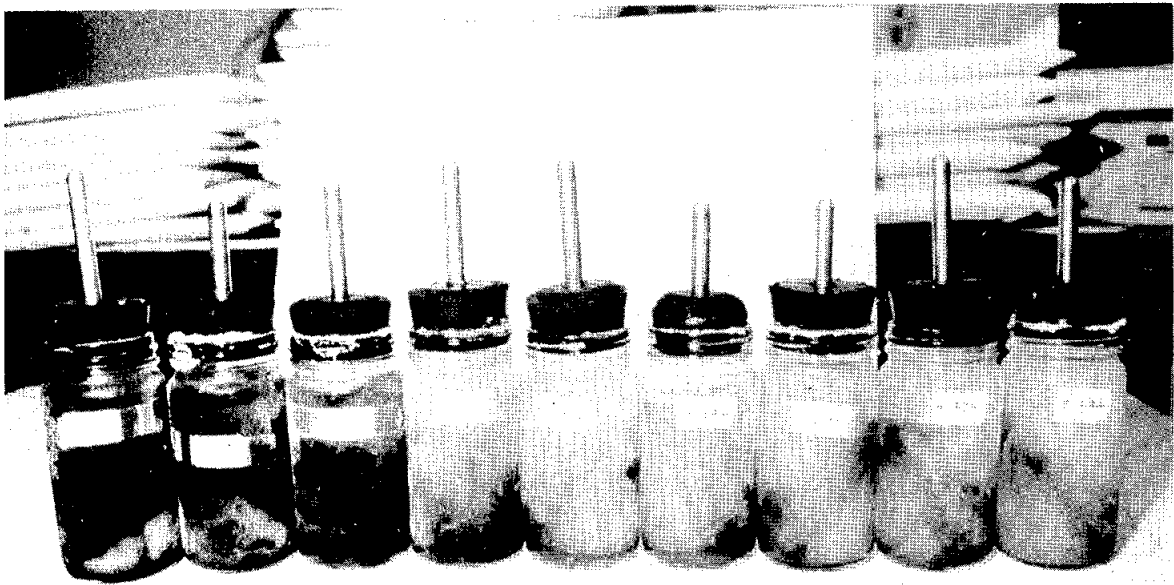


FIGURE 2: Photograph showing samples arranged in corrosive medium

Misleading results may be obtained if these factors are not considered. At least two time periods should be used. In this current project two standard test duration periods were chosen; 30 days and 100 days.

In these tests, the samples were kept in small glass containers. The bottles were agitated every two days in order to ensure that the corrosive medium was uniformly attacking the specimen surfaces.

The samples were checked every day to ensure that the specimens were completely immersed. Distilled water was added when necessary to make up the solution level and to ensure that the pH of the solution did not change.

There were some unforeseen problems with the samples at higher temperatures. After about 40 days, most of the container lids were sealed tight because the CMA crystallized around the top of the containers. In order to complete the test these samples were left in the containers but were regularly agitated.

## **6. Sample Cleaning**

This is one of the most important steps in corrosion studies and proper procedures must be used. In many cases, visual observation of the specimens on completion of the test provides valuable information concerning corrosion. For example, deposits or encrustations may be the cause of pitting of the metal.

Changes in weight of a specimen are most often used for calculating the corrosion rate. Accordingly, complete or incomplete removal of corrosion products is directly reflected in the calculated corrosion rate. Again a standard procedure was used to clean the specimens after exposure to the corrosive medium. This cleaning procedure was the same as the one used before exposure.

## 7. Measuring and Weighing

Since the sample weight enters into the calculation of corrosion rate, the results are only as accurate as the weight measurements. After the samples were prepared the specimens were weighed to the nearest .001 gram. Before initial weighing, the dimensions of the specimens were measured and recorded.

Weight loss and percent weight change of material after exposure to the corrosive environment are poor ways of expressing corrosion resistance. Results using either of these expressions will be influenced by the duration of the exposure and the shape of the exposed article. These methods also do not express the rate of penetration, or the thinning rate that a structural piece would undergo. Thus the life of a given component, which is important from an engineering design standpoint, cannot be adequately determined by these methods.

For the above reasons, the corrosion rates were calculated in units of mils per year (mpy). These units express corrosion in terms of the average loss of specimen thickness over a given period of time. The corrosion rate expressed in mpy is readily calculated from the weight loss of the metal specimen during the corrosion test using the formula<sup>14</sup>:

$$\text{mpy} = (534 * W) / (D * A * T)$$

where W = weight loss, mg

D = density of specimen, g/cm<sup>3</sup>

A = area of specimen, sq in.

T = exposure time, hr

#### IV. RESULTS AND DISCUSSIONS

The corrosion rates of steel in CMA solutions were measured in terms of mils per year. The results of the short-term (30 days) and long-term (100 days) tests are shown in Tables 1 and 3 for the rebar steel and Tables 2 and 4 for structural/automotive steel samples. These tables and figures 3 to 26 show the variations of the corrosion rates with respect to temperature, pH, and CMA concentration for the two types of steel in CMA solutions. Each data point is an average of 3 tests. Statistical analysis has not been due to small groups of data in each case. More rigorous data collection over longer period tests and a large number of experimental runs are necessary to statistically analyze the data.

These test results indicate that the corrosion rates are indeed very small. In all cases the corrosion rate was less than 10 mpy for the 100 day test and less than 15 mpy for the 30 day test. The corrosion rate increased with increased temperature in most cases. The results are discussed separately for each test temperature.

##### 1. High Temperature (150°F-(66°C))

High temperature corrosion of steel samples in CMA solutions, in general, decreased with increased pH. The corrosion rates were small (less than 15 mpy) as seen in figures 3-6. The small inconsistency that was observed may be attributed to the size and shape of the sample and the difficulties encountered in cleaning the samples. In the high temperature case there was some pitting as shown in figure 27. The corrosion rates for both types of steel were generally within a factor of two of each other under similar conditions.

The results of the 30 day and 100 day corrosion tests indicate that the corrosion rate decreased with increased concentration of CMA in solution at any given pH as can be seen in figures 7 - 11. Noting that the CMA solution was made with distilled water, increasing the CMA reduced the amount of water in the

solution. This may have decreased the corrosiveness of the solution by reducing the corrosive reaction of steel with water.

A comparison of the corrosion rates determined by the 30 day and 100 day tests indicates that corrosion rates are initially high and tend to stabilize with time.

## **2. Room Temperature (70°F (-22°C))**

Even though the data shown in figures 11-14 indicate that the corrosion rates decreased in general with increased pH, this trend seems to be insignificant, considering the very low corrosion rates of less than 1 mpy at this temperature.

The corrosion rates, as in the case of the high temperature tests, also decreased with CMA concentration at any given pH value as can be seen in figures 15-18.

## **3. Low Temperature Corrosion (20°F (-7°C))**

The results of the short term corrosion tests are shown in figures 19-26. These results show that in both types of steels the corrosion rate decreased with increased pH. The corrosion rate also decreased with increased CMA concentrations.

In the case of the long term (100 day) test there does not seem to be a general trend. The inconsistencies may be attributed to the reaction kinetics at low temperatures, as well as CMA segregation and ice formation in the solutions. Further work in this area is required before firm conclusions can be drawn.

The above results show that the corrosive characteristics of CMA solutions in general tend to decrease the corrosion rates of steels with increased pH and CMA concentration. This indicates that CMA, perhaps may have some corrosion inhibiting characteristics in distilled water.

The corrosion rates of steel in sodium chloride solutions are in general greater than 25 mpy.<sup>10</sup> An acceptable corrosion rate in the automotive industry is less than 10 mpy for the worst case.<sup>15</sup>

These results indicate that the CMA is a viable deicing alternative that can be substituted confidently for salt from the point of view of the corrosion damage. It is cautioned that the other characteristics such as traction on roads, braking distance, pollution aspects, etc. must be considered before application of CMA as a road deicer. Department of Transportation engineers are conducting research in these areas.

#### **4. Problems with CMA**

During the course of this work the following problems were observed. These problems could hinder or delay the application of CMA as a road deicer.

1. The CMA tended to crystallize at higher temperatures (see figure 28).
2. It was difficult to set up a procedure to clean the samples. Sometimes, the recrystallized CMA persistently stayed attached to the surface of the steel (see figure 29).
3. At lower temperatures a separation of CMA and water occurred, making it difficult to determine the corrosiveness of CMA in stagnant solutions.

These problems indicate that further work is required in the determination of the removal of CMA after it has been used. Cleaning of vehicles and roadsides may pose some problems, although limited field tests within and outside of Alaska have not produced any negative public comments concerning any of these questions.<sup>16</sup>

**TABLE 1: CORROSION RATES OF STEEL 1 IN CMA (100 DAY TEST)**

(Expressed in MPY)

Temperature (°F)	% CMA	pH		
		6.0	7.0	8.5
150	10	1.058	6.538	4.853
	50	1.507	.717	.742
	100	1.506	1.204	1.058
70	10	.254	.326	.139
	50	.4	.351	.185
	100	.196	.42	.29
20	10	.162	.045	.042
	50	.07	.044	.038
	100	.006	.802	.0

**TABLE 2: CORROSION RATES OF STEEL 2 (100 DAY TEST)**

(Expressed in MPY)

Temperature (°F)	% CMA	pH		
		6.0	7.0	8.5
150	10	8.997	9.28	6.997
	50	7.993	2.955	3.017
	100	6.152	1.73	1.287
70	10	.201	.512	.99
	50	.384	.481	.529
	100	.385	.353	.422
20	10	.069	.0	.221
	50	.042	.0	1.356
	100	.129	.042	.187



**TABLE 3: CORROSION RATES OF STEEL 1 IN CMA (30 DAY TEST)**

(Expressed in MPY)

Temperature (°F)	% CMA	pH		
		6.0	7.0	8.5
150	10	3.329	2.893	2.067
	50	6.274	1.665	2.348
	100	1.883	1.32	.431
70	10.0	.287	N/D	N/D
	50	N/D	N/D	N/D
	100	.241	.057	N/D
20	10	.184	.011	.0
	50	.046	.0	.0
	100	.0	.0	.0

Note (N/D): Due to technical difficulties these experiments had to be discarded. Hence no data is available for these conditions.

**TABLE 4: CORROSION RATES OF STEEL 2 (100 DAY TEST)**

(Expressed in MPY)

Temperature (°F)	% CMA	pH		
		6.0	7.0	8.5
150	10	10.364	3.239	2.515
	50	14.327	1.575	2.794
	100	2.286	1.346	.254
70	10	.0	.0	1.194
	50	3.709	.0	.254
	100	.381	.203	.279
10	10	1.143	.0	.0
	50	.127	.0	.0
	100	.0254	.0	.0

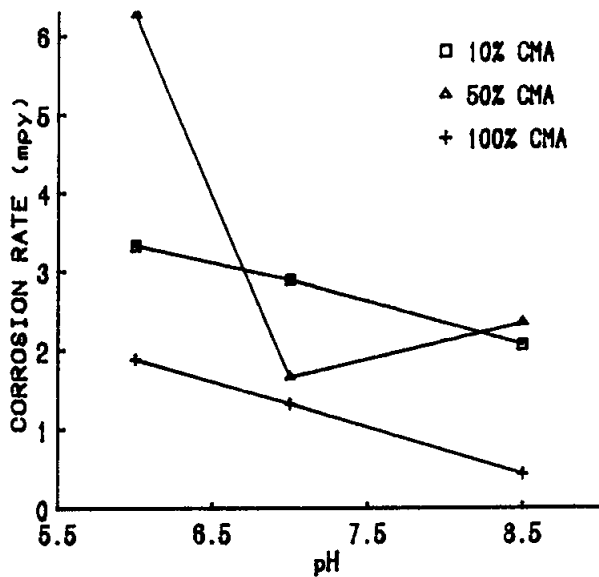


FIGURE 3: Corrosion Rate vs pH at 150°F for Steel 1 (30 day test)

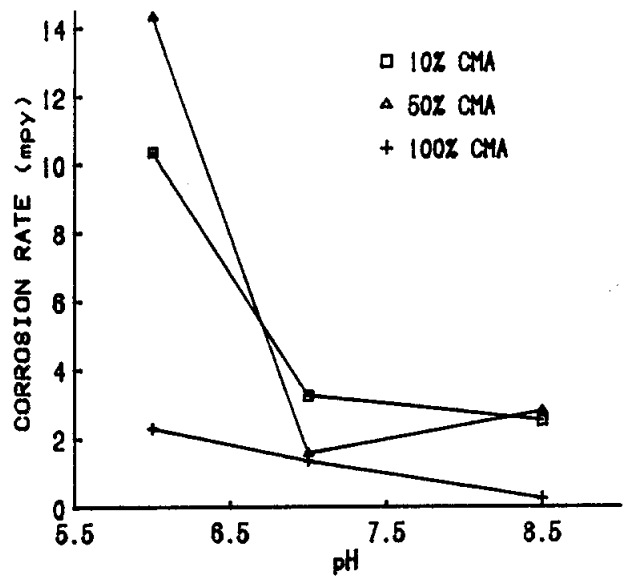


FIGURE 4: Corrosion Rate vs pH at 150°F for Steel 2 (30 day test)

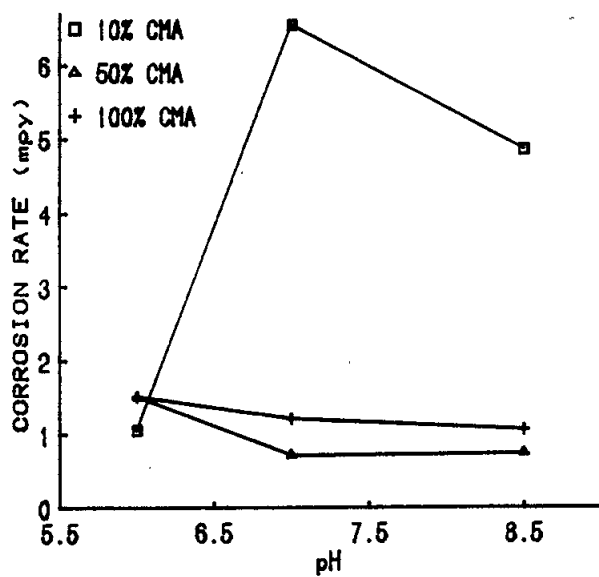


FIGURE 5: Corrosion Rate vs pH at 150°F for Steel 1 (100 day test)

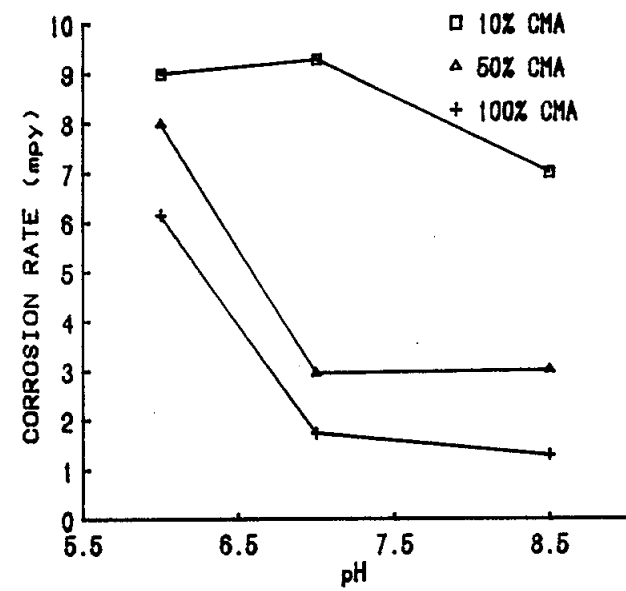


FIGURE 6: Corrosion Rate vs pH at 150°F for Steel 2 (100 day test)

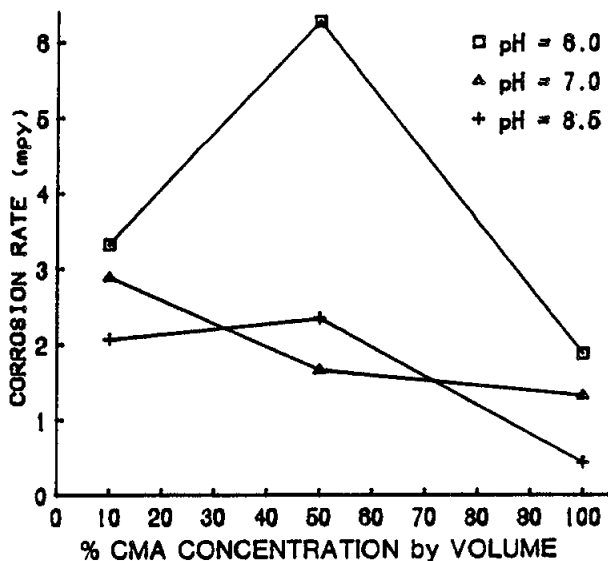


FIGURE 7: Corrosion Rate vs Percent CMA at 150°F for Steel 1 (30 day test)

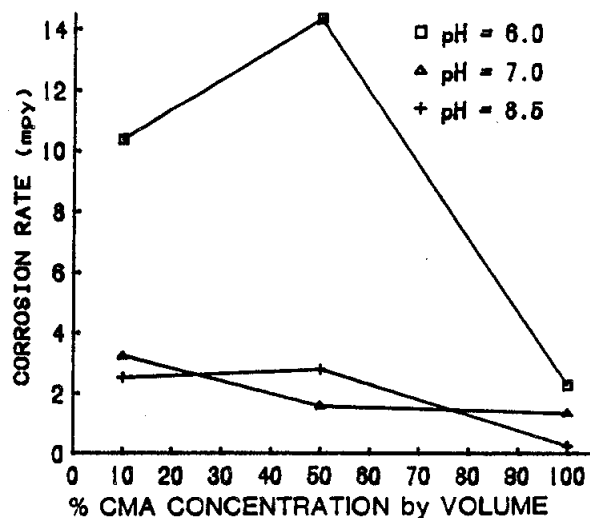


FIGURE 8: Corrosion Rate vs Percent CMA at 150°F for Steel 2 (100 day test)

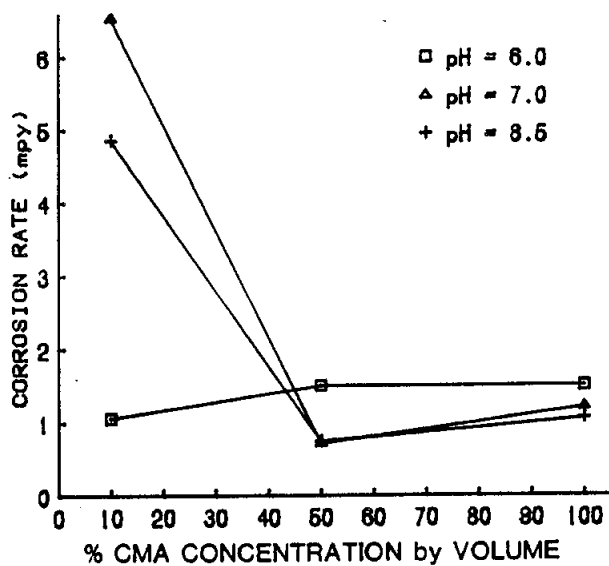


FIGURE 9: Corrosion Rate vs Percent CMA at 150°F for Steel 1 (100 day test)

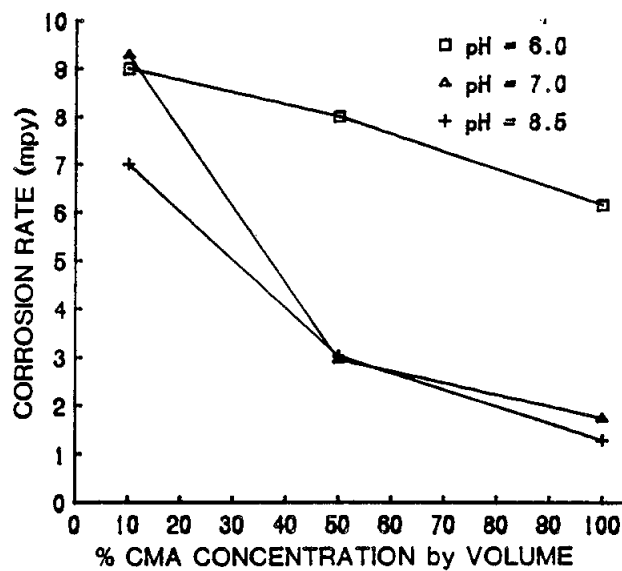


FIGURE 10: Corrosion Rate vs Percent CMA at 150°F for Steel 2 (100 day test)

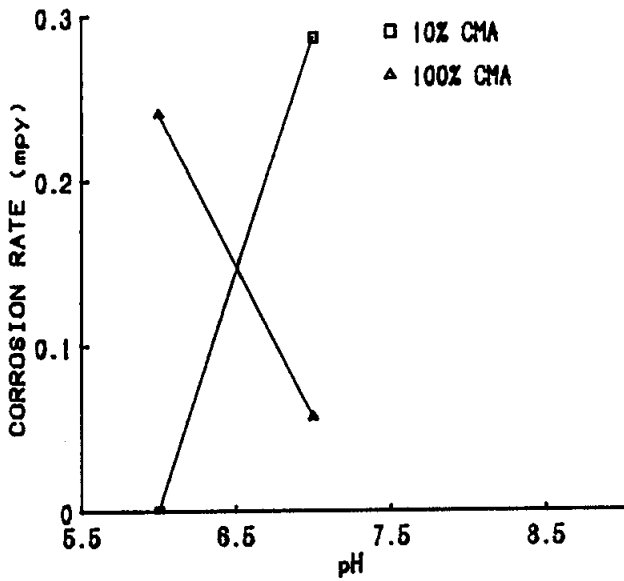


FIGURE 11: Corrosion Rate vs pH  
30 Day Test at 70°F for  
Steel 1 (30 day test)

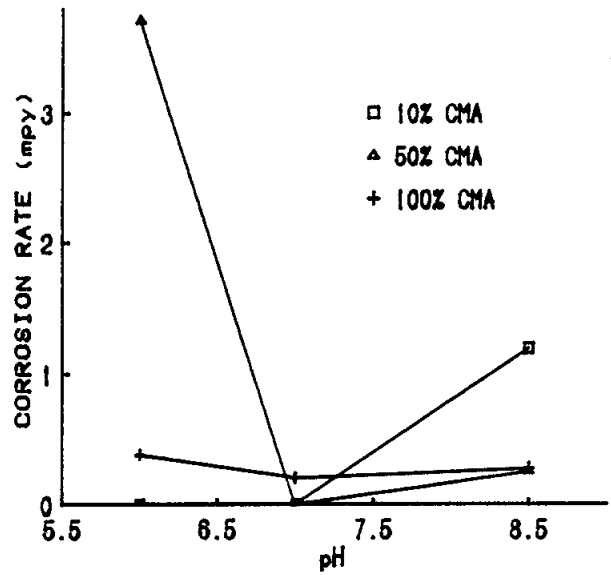


FIGURE 12: Corrosion Rate vs pH  
at 70°F for Steel 2  
(30 day test)

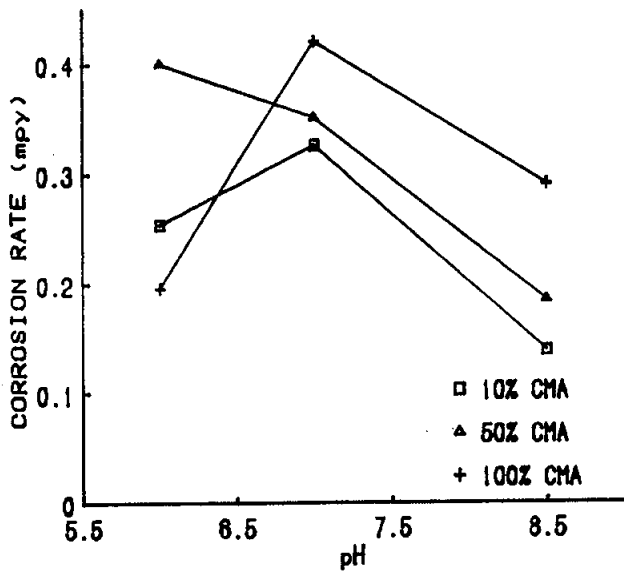


FIGURE 13: Corrosion Rate vs pH  
at 70°F for Steel 1  
(100 day test)

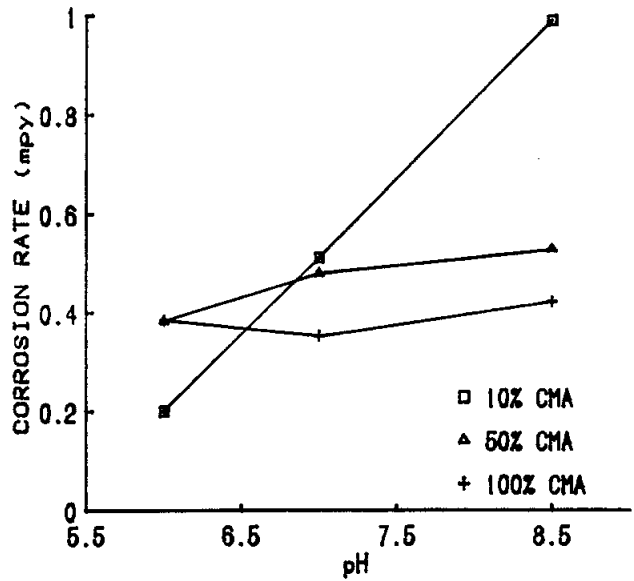


FIGURE 14: Corrosion Rate vs pH  
at 70°F for Steel 2  
(100 day test)

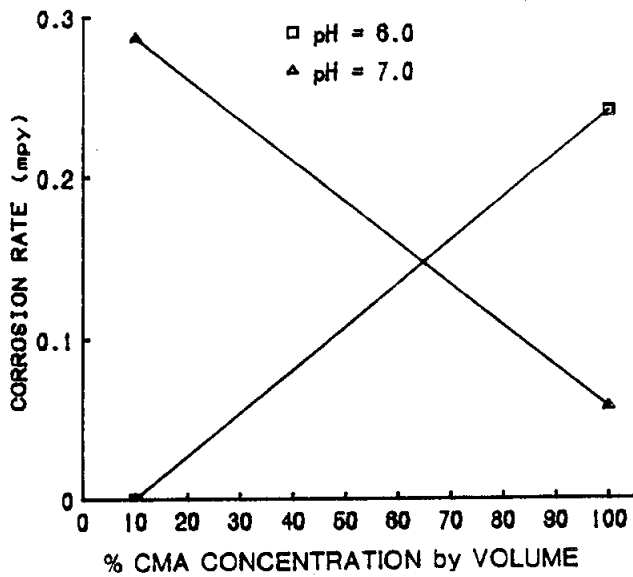


FIGURE 15: Corrosion Rate vs Percent CMA at 70°F for Steel 1 (30 day test)

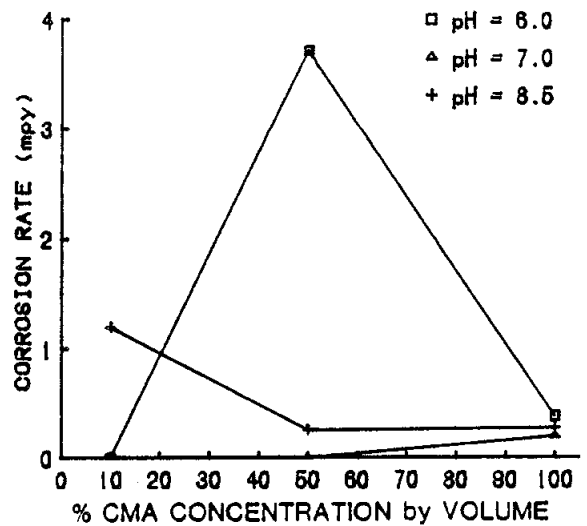


FIGURE 16: Corrosion Rate vs Percent CMA at 70°F for Steel 2 (30 day test)

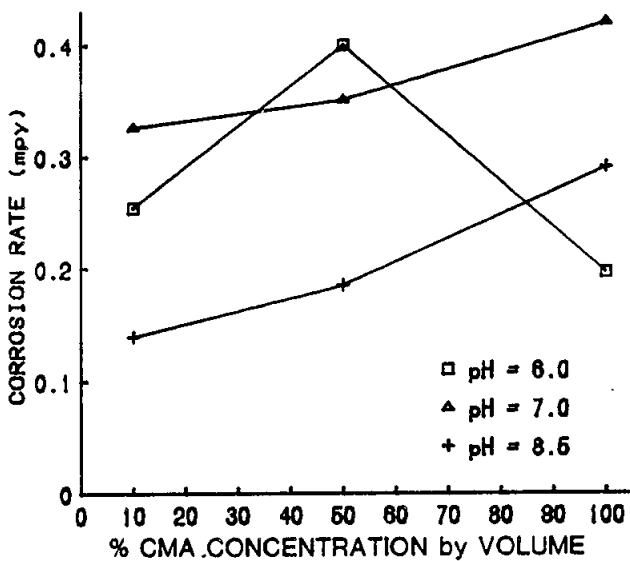


FIGURE 17: Corrosion Rate vs Percent CMA at 70°F for Steel 1 (100 day test)

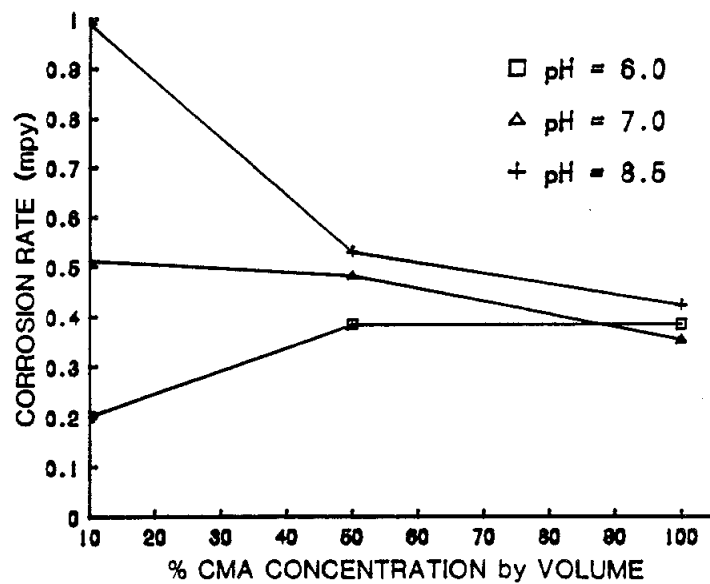


FIGURE 18: Corrosion Rate vs Percent CMA at 70°F for Steel 2 (100 day test)

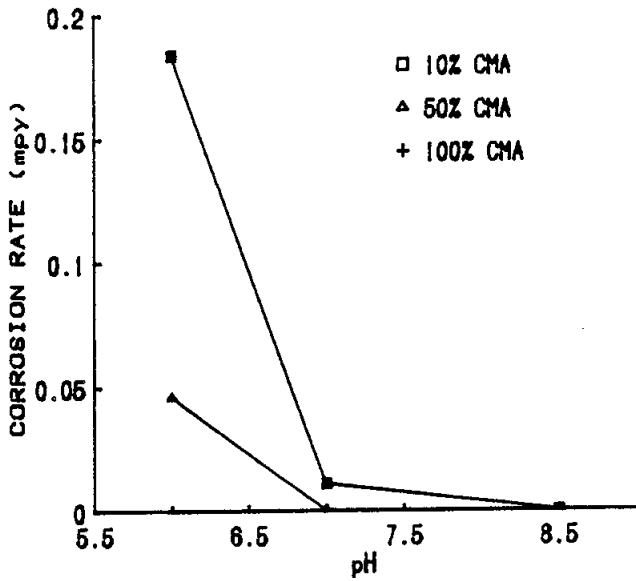


FIGURE 19: Corrosion Rate vs pH at 20°F for Steel 1 (30 day test)

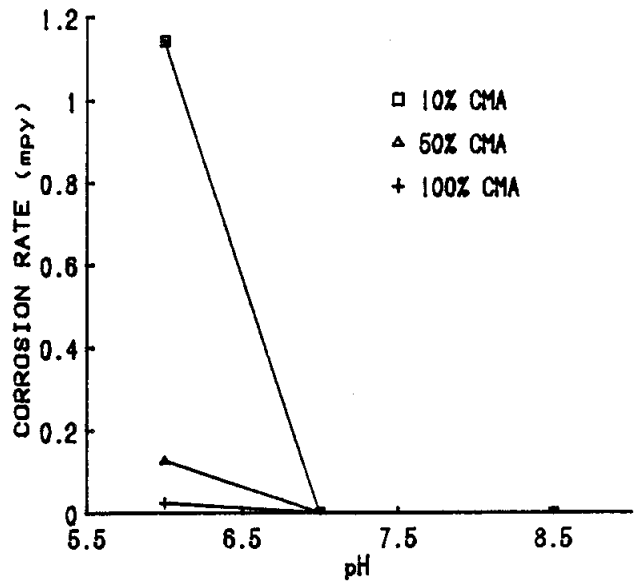


FIGURE 20: Corrosion Rate vs pH at 20°F for Steel 2 (30 day test)

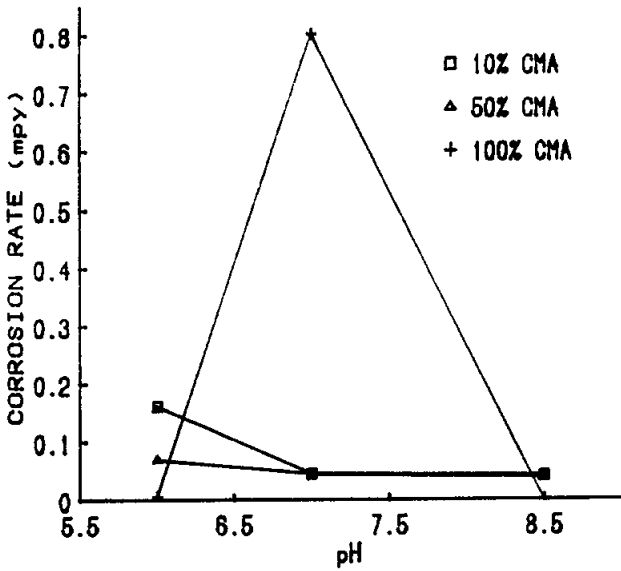


FIGURE 21: Corrosion Rate vs pH at 20°F for Steel 1 (100 day test)

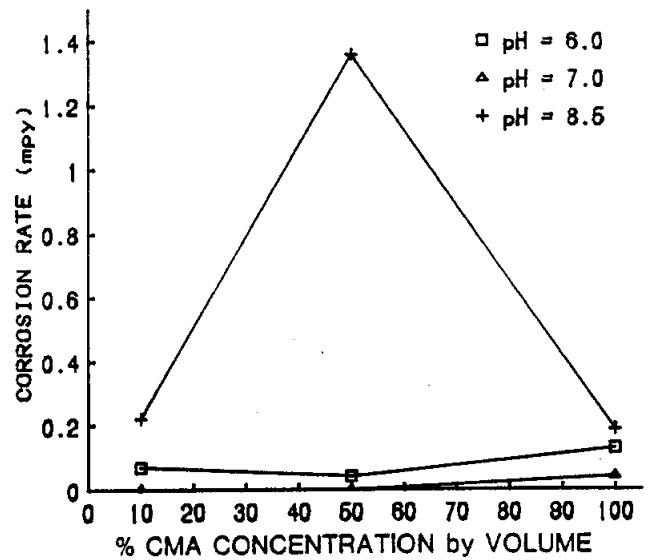


FIGURE 22: Corrosion Rate vs Percent CMA at 20°F for Steel 2 (100 day test)

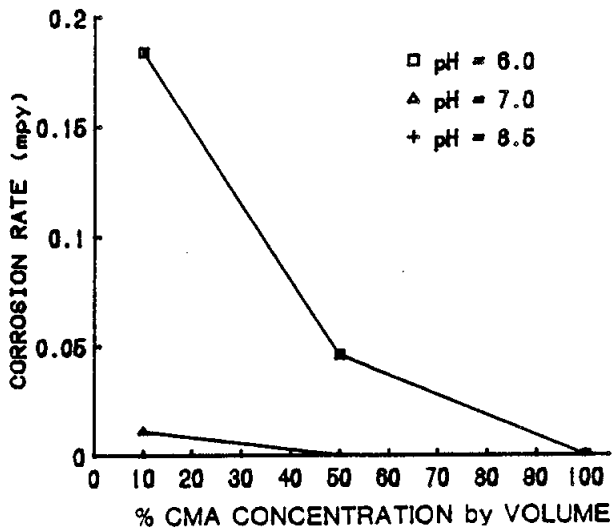


FIGURE 23: Corrosion Rate vs Percent CMA at 20°F for Steel 1 (30 day test)

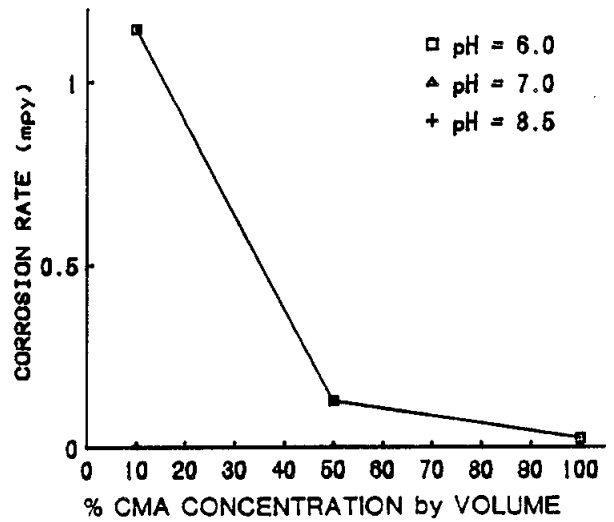


FIGURE 24: Corrosion Rate vs Percent CMA at 20°F for Steel 2 (30 day test)

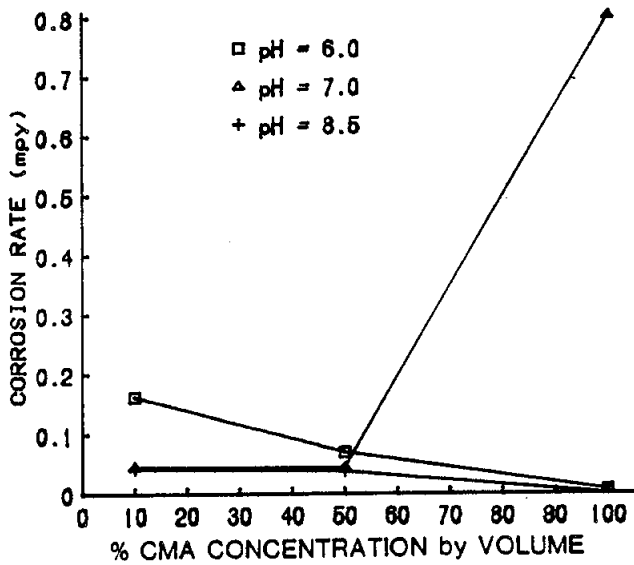


FIGURE 25: Corrosion Rate vs Percent CMA at 20°F for Steel 1 (100 day test)

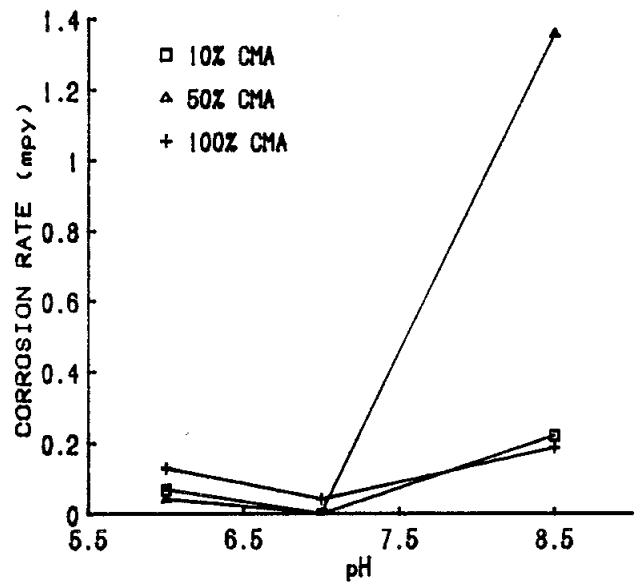


FIGURE 26: Corrosion Rate vs pH at 20°F for Steel 2 (100 day test)





FIGURE 27: Photograph showing some pitting in steel due to corrosion in CMA at 150°F

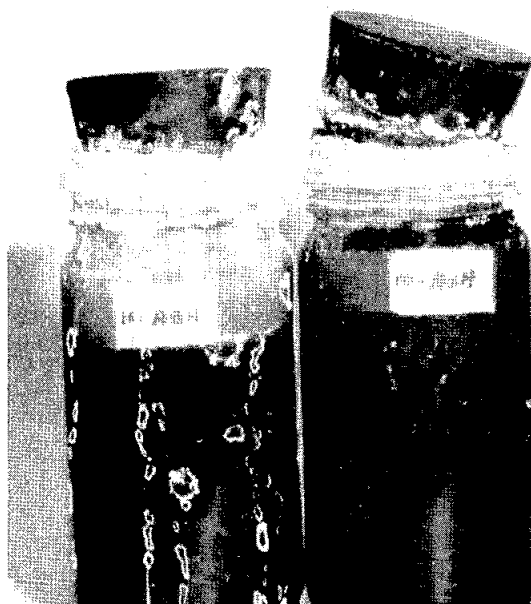


FIGURE 28: CMA crystallization due to dehydration  
at high temperature

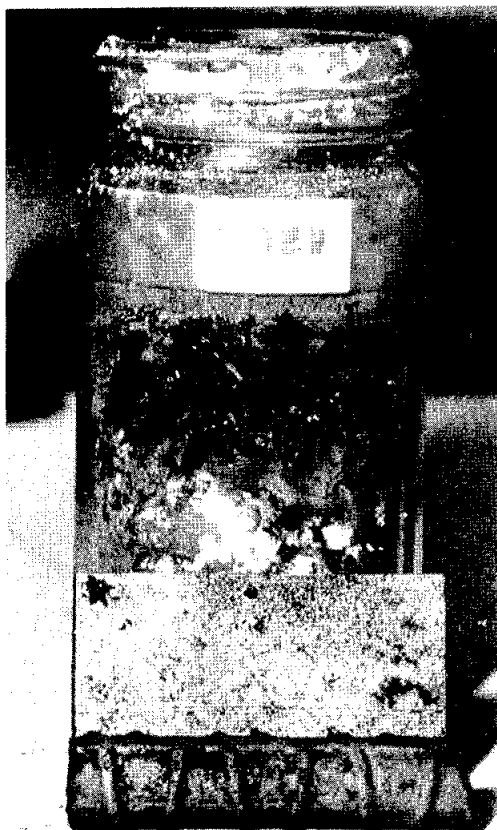


FIGURE 29: Deposits of CMA as samples that persisted even after thorough cleaning

## V. CONCLUSIONS

The current research efforts indicate that CMA is generally less corrosive than salt. Corrosion rates of less than 2 mpy for steels are indicated for CMA as opposed to greater than 25 mpy for salt solutions.

High pH and high CMA concentrations have been shown to have the lowest corrosion rates.

Even though CMA is indicated to be a much less corrosive medium than normally used road salts, the problems of crystallization, cleaning, and disposal should be addressed before CMA is used in large quantities as a road deicer.

## **VI. RECOMMENDATIONS FOR FUTURE WORK**

Although CMA was found to be a non-corrosive solution, its application as a road deicer needs to be further confirmed. The optimum conditions of CMA to be used in terms of percent concentration, pH, sand and gravel content, and the carrying medium should all be determined. The long term effects of CMA deposition on surfaces needs to be determined. Further, the corrosion characteristics of CMA with respect to materials other than steel such as paints, plastics, and other metals used in vehicles should be determined. The mechanisms of corrosion or lack of corrosion involving CMA are not yet fully understood. Much work is needed in these areas of research.

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