Production and Testing of Calcium Magnesium Acetate in Maine

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ABSTRACT

The search for an effective substitute for the deicing agent sodium chloride has led to the development of calcium magnesium acetate (CMA). However, CMA is not commercially available. A project for the production of CMA using resources in Maine was carried out at the Maine Department of Transportation. After the product was made, other physical and chemical tests were also performed. The results indicated that CMA can be made in Maine from an apparent abundant source of high magnesium limestone and acetic acid (cider vinegar). A 10 percent solution of acetic acid with 10 min of agitation with the magnesium limestone coarse aggregate provides the best production of CMA for this grade. A commercial production of CMA should consider the constant reflux method with constant monitoring of the pH. Evaporation of the solution by solar energy is not effective because of the large amount of rainfall in Maine. Bituminous concrete batch plants have waste heat, which might be able to aid in this evaporation need. The field trial of CMA as a deicing agent demonstrated both advantages and disadvantages. A major concern is its dustiness. Outdoor uncovered storage of CMA is not practical. The corrosion effect of CMA solution toward metal or concrete needs further study.

The use of sodium chloride (NaCl) as a deicing agent on highways has been under scrutiny for some time. The chief concern is environmental compatibility. Sodium chloride is corrosive in nature and it affects the water-absorbing capability of soil (1,2). Many research agencies have been searching for an effective substitute for sodium chloride. In March 1980, Dunn and Schenk (3) of Bjorkste Research Lab, Inc., published their findings on their study for a salt substitute. Their project was sponsored by FHWA. The results indicated that calcium magnesium acetate (CMA) was a promising alternative for NaCl. This new deicing agent would react at about the same melting rate as NaCl in the temperature range of common activity, but CMA also had the advantage of being a corrosion inhibitor. The run-off from melting action would be beneficial to most soils, and there is an insignificant effect to water supplies. Realizing the potential of CMA use and the knowledge that CMA is not produced commercially, FHWA initiated a pooled fund project for CMA in May 1981 to find an efficient manufacturing process and to establish an evaluation procedure for the product. Ultimately, a production contract was awarded to SRI International, and an environmental study contract was awarded to the California Department of Transportation. Both research programs began in October 1981, and many interim reports have been published since then. The work undertaken at SRI International has been to produce acetic acid by using Clostridium thermaceteticum to ferment biomass-derived sugars. The acetic acid was then combined with dolomitic lime to produce CMA.
In the winter of 1981-1982 the Iowa Department of Transportation also undertook studies for the manufacture of CMA (4,5). The application of CMA was tested in the field in April 1982, as well as in the winter of 1982-1983. Their production method was to mix glacial acetic acid with a mixture of hydrated lime and dry concrete sand. This resulted in a product of CMA coated sand in a ratio of 3:1 (sand/CMA).

There are three major processes to produce CMA: (a) high magnesium quick lime (CaO) reacting with acetic acid, (b) high magnesium hydrated lime (Ca(OH)₂ + Mg(OH)₂) reacting with acetic acid, and (c) dolomitic limestone (or dolomite, CaCO₃ + MgCO₃) reacting with acetic acid. Because there is an abundant resource of dolomitic limestone in Maine, as well as possible waste of acetic acid (vinegar) in the apple orchard industry, a research effort was proposed to study the possible reaction process, the available raw materials, the by-products, and the ability to produce CMA from these waste products. The present study is the result of such an undertaking supported by the FHWA, U.S. Department of Transportation, as part of the Maine Department of Transportation Work Plan 1981 TOX HPR-PL-1(19).

**Experimental Procedures**

Dolomitic limestone, calcium carbonate (CaCO₃) and magnesium carbonate (MgCO₃), was chosen instead of quick lime or hydrated lime because it is a natural resource in Maine. The chemical reactions are as follows:

\[
\text{CaCO}_3 + 2\text{HAc} \rightarrow \text{CaAc}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{MgCO}_3 + 2\text{HAc} \rightarrow \text{MgAc}_2 + \text{H}_2\text{O} + \text{CO}_2
\]

where

\[
\text{HAc} = \text{CH}_3\text{COOH}, \text{acetic acid}
\]

\[
\text{MgAc}_2 = \text{Mg(OAc)}_2
\]

The dolomitic limestone was supplied by Lime Products Corp., Union, Maine, and was produced in two sizes: coarse and fine. The acetic acid was supplied by W.H. Shurtleff Chemical Company. Both products were provided to the Maine Department of Transportation (MeDOT) at no cost.

**Preliminary Laboratory Screening of Reaction Process**

There were two types (coarse and fine) of dolomitic limestone used in this study. The fineness modulus (FM) values of the coarse and fine grade material were 3.2 and 0.78, respectively. The mole ratio of calcium and magnesium was 0.7.

Preliminary experiments indicated that concentrated (glacial) acetic acid does not react with the dolomite. Moreover, acetic acid has an extremely pungent odor. Therefore, concentrations of acetic acid of 20, 10, and 5 percent (by volume) were chosen for screening. Ultimately, a 10 percent solution was used. It was also apparent that the best yield of the reaction between coarse limestone and 10 percent acetic acid was around 20 percent. However, the unreacted limestone could be used as an abrasive agent or recycled for further reaction.

**Laboratory Pilot Study**

On June 24, 1982, 10 lb of the coarse limestone were mixed with 10 gal of 10 percent acetic acid in a concrete mixer for about 10 min. This batch was repeated five times, and all the mixtures were poured into a 3×11-in. × 4×ft 2-in. container that was lined with a heavy plastic sheet. The depth of the original solution was 5 in. The entire operation was situated adjacent to the Materials and Research building in Bangor.

The evaporation of this solution was constantly monitored. By July 16, 22 days after the mixing date, the CMA was dry. The product was analyzed and showed a mole ratio of Ca/Mg = 2.5.

**Batch Trial Production Using Coarse Grade Limestone**

The first large-scale production was carried out on July 30, 1982, in Warren, Maine. The Lime Products Corp. had constructed an evaporation site under a dome structure that was covered with heavy plastic sheets.

The mixing process used a commercial ready-mix concrete mixer. This truck was filled with, in sequence, water, glacial acetic acid, and coarse dolomite. The mixture was then agitated for 10 min and was poured into a 4×10.5-ft reservoir that was lined with a heavy plastic sheet. This operation was repeated several times. Because of a defective water meter, the concentration of the acetic acid solution was 2 percent instead of the intended 10 percent. The entire process used 100 gal of glacial acetic acid and 1,440 lb of dolomitic limestone. The latter was increased to a total of 4,000 lb to ensure excess limestone and alkalinity.

The summer of 1982 was cooler than normal. The plastic covering, while minimizing rainwater from entering the solution, greatly reduced the evaporation process. To hasten the evaporation, additional heating lamps and aeration devices were installed. By the end of November most of the surface was dry, with the exception of a few puddles of liquid. The pH of the liquid was 6.5. The liquid was transferred into another container. The remaining wet sludge was neutralized further to a pH of 9 with high magnesium quick lime. The final product was then transferred to five 55-gal drums for storage. The total weight of the wet material was 3,320 lb.

**Batch Trial Production Using Fine Grade Limestone**

On August 11, 1982, a second batch production was carried out by using the fine grade dolomite as the starting material instead of the coarse grade. The acetic acid was 10 percent by volume. The entire production consisted of 200 gal of glacial acetic acid, 1,800 gal of water, and 8,000 lb of fine dolomitic limestone. The dimension of the second evaporating basin was 10× 20 ft, half of the previous structure, and it was also enclosed in plastic sheeting. Heating lamps and aeration equipment were later installed as before to speed up evaporation.

By the end of October the solution began to congeal. The liquid showed a pH of 5.5. A small amount of semisolid material was dried and analyzed. It resulted in a product containing calcium acetate and magnesium acetate of a 4:1 mole ratio.

At the same time the bottom of the basin became impermeable and claylike. Therefore, the liquid-sealed portion of the product was then transferred to four 55-gal drums. Quick lime was added to bring the pH to 12, and finally the pH was adjusted to 9 or 10 with acetic acid. The drums of this semisolid were brought to the Materials and Research Laboratory in Bangor for further drying. The resultant CMA powder material contained unreacted limestone and quick lime. The total weight was 1,180 lb.
Analysis of a few hatches of this CMA product revealed the CMA content to be around 75 percent. Test data also indicated that nearly all of the product was calcium acetate.

Field Trial on Delicing Power of CMA

On January 6, 1983, a snowy day with the temperatures around 30°F, a field trial was conducted on the driveway of the Materials and Research parking lot. Forty-five pounds of sodium chloride (NaCl) were applied on one part of the driveway (50 ft long) and an equal amount of CMA powder was applied on another area (also 50 ft long). A 30-ft untreated area was left in the middle. The general impression was that CMA reacted slower than NaCl, but it remained on the road for a longer period, the evidence of unreacted limestone and lime, tracking around 30°F, a field trial was conducted on the same lot. Forty-five pounds of sodium chloride (NaCl) were applied on one part of the driveway (50 ft long) and an equal amount of CMA powder was applied on another area (also 50 ft long). A 30-ft untreated area was left in the middle. The general impression was that CMA reacted slower than NaCl, but it remained on the road for a longer period; the evidence was its apparent effectiveness the next day when fresh snow fell on the pavement again. However, because of the unreacted limestone and lime, tracking into the building by laboratory personnel was considered an annoyance.

Runoff and Leaching of CMA-Sand Stockpile

A CMA-sand stockpile was prepared by mixing 3 yd³ of sand with 500 lb of CMA powder on December 29, 1982. The CMA was noted to be extremely light and there was a considerable amount of dust as it was being mixed. A trench was dug around the pile, which allowed the water to run off the stockpile into a container recessed in the trench. The concentration of CMA in the runoff was monitored weekly. At the same time, samples of the CMA-sand mixture were obtained weekly to be analyzed for calcium acetate and magnesium acetate content. The same type of leaching test was conducted also for a NaCl-sand pile for comparison.

Corrosion Test of CMA Solutions

Calcium magnesium acetate solutions of various concentrations were prepared in which steel test strips (1 x 6 x 0.015 in.) were immersed for 2 weeks. All strips were prepared with the same types of cutting edges. The test strip was suspended in a 400-ml beaker filled with 300 mL of the desired solution. The solution was then covered with a plastic bag and sealed with a rubber band around the beaker. By using a magnetic stirrer, the solution was agitated at a slow, uniform rate for the entire duration.

The MeDOT CMA solutions used in the testing were prepared by first making a saturated solution of this material. Later testing of this solution on the atomic absorption spectrophotometer indicated this saturated solution to be a 13.2 weight percent CMA solution. Solutions of other concentrations were prepared by simple dilution of this saturated solution.

A corrosion test was also performed with solutions of CMA that was produced under the SRI contract with FHWA (6). The concentrations were expressed in weight percent also. Two more corrosion tests were carried out, one on deionized water for control and one on 10 percent NaCl for comparison. In addition to the experiments previously mentioned, 7 percent solutions of pure calcium acetate and magnesium acetate were also tested for their corrosion property.

Ponding Test—Corrosion of Rebars in Concrete

A ponding test was performed on concrete blocks according to AASHTO Designation T259-80. Steel rebars were placed within the slabs at a depth of 2.5 in. from the surface. The dimension of the blocks was 21 x 12 x 3.25 in. A confinement of the dimension of 18 x 9.5 x 1 in. was made on top of each block with the use of wooden frames and wax seals. The solutions tested were 3 percent CMA produced by MeDOT, 3 percent CMA supplied by SRI, 3 percent NaCl, and water.

The solutions were maintained at a depth of at least 0.5 in. during the test. At the end of 90 days, the solutions were removed from the slabs. The slabs were allowed to dry, and subsequently sawed near a rebar so as to expose the rebar for examination.

Electrical half-cell potential measurements of the reinforcing steel were taken (7). In addition, a small portion of the slab was sawed off from each block. The small pieces were then polished and examined for penetration. A powdered sample of each slab was also prepared according to the depths of the slab, 0 to 1.75 in. and 1.75 to 3.5 in. These samples were then tested for either chloride content in the case of NaCl or for acetate in the case of CMA materials.

Relative Slipperiness of CMA Solution Compared with Other Deicing Chemicals

Testing was carried out on four deicing chemicals in terms of their relative slipperiness. Water was used as a standard for the comparison. Each of the four chemicals was mixed with water to produce a saturated solution. The chemicals used and the resultant specific gravities were as follows: sodium chloride (1.193), calcium chloride (1.420), calcium magnesium acetate (1.106), and urea (1.135).

The instrument used for determining the relative slipperiness was a British portable tester. Testing was performed in accordance with ASTM E-303. The results are in British pendulum numbers (BPN) and do not necessarily agree or correlate with other slipperiness measuring equipment.

The surfaces of bituminous concrete pavement and portland cement concrete were used for the comparison. The five lubricants (water plus the saturated solutions) were applied separately to each of the two surfaces. A total of 10 (BPN) values was obtained for each lubricant on each surface. The mean value was considered representative for each of the respective lubricants.

The testing surfaces were flushed with water and dried between the testing of each lubricant.

RESULTS AND DISCUSSION

Production of CMA Using Dolomite

The method used in this project possessed the following advantages:

1. The price per pound of limestone was about one-hundredth of that of lime,
2. Solar energy was used instead of electricity or fuel, and
3. The minimum amount of machinery and physical facilities were employed.

However, from the experience gained so far, it appears that many obstacles do exist. The following are among the important ones.

1. The reaction of limestone with acetic acid involves the formation of carbonic acid, and subsequently the evolution of the carbon dioxide (reac-
tions 1 and 2). Theoretically, these reactions could be driven to completion by constant reflux, but in reality this is difficult to achieve. However, the reaction between quick lime (calcium oxide and magnesium oxide) and acetic acid involves only combination of the two reactants; thus it would be more efficient:

\[
\begin{align*}
\text{CaO} + 2\text{HAc} & \rightarrow \text{CaAc}_2 + \text{H}_2\text{O} \\
\text{MgO} + 2\text{HAc} & \rightarrow \text{MgAc}_2 + \text{H}_2\text{O}
\end{align*}
\]

(3) (4)

2. Calcium carbonate and magnesium carbonate react with acetic acid at different rates, which also vary as the pH of the solution changes. This also holds true for calcium oxide and magnesium oxide. Thus the products from this project had a Ca/Mg mole ratio of 2.5 in the preliminary coarse material trial. The ratio was 4.0 for the product with the fine grade trial batch when the pH of the original solution was 5.2. However, when the pH was adjusted to 9 or 10, the final product was nearly devoid of magnesium acetate. Recognizing that magnesium acetate has a lower eutectic point than calcium acetate, the deicing effectiveness of the final product would be somewhat diminished.

3. The dependence on solar energy is not realistic for Maine’s climate. During summer months overcast or rain is a common occurrence (~40 in. of average precipitation per year). A method to evaporate the solution economically is needed. (The addition of more ventilation to the covered plastic evaporation pits would have greatly accelerated the evaporation rate).

Field Application of CMA

Although only one application was made in the use of CMA for deicing, it was apparent that the CMA produced from this project (mainly calcium acetate) initially reacted slower than NaCl, but persisted for a longer period of time. The easily detected tracking problem may be caused by the unreacted limestone and the lime that could be avoided if the reaction was carried to completion.

Storage of CMA Outdoors and Uncovered—Leaching Effect and Runoff

The results of the calcium acetate and magnesium acetate contents in the CMA-sand stockpile that was left uncovered outdoors were plotted in Figure 1. The data in this figure show that the content of calcium acetate and magnesium acetate diminished gradually with time. The fluctuation of these data is the result of uneven mixing and random sampling sites. Allowing for these imperfections, it is apparent that CMA was leached out by rain or snow when stored outdoors and uncovered.

The results of analysis for the runoff from the CMA-sand stockpile are shown in Figure 2. There were considerable fluctuations for the Ca++ and Mg++ content in the runoff. This is mainly the consequence of the weather change in the precipitation occurrence. A heavy rainfall or snowstorm followed by melting gave rise to high Ca++ and Mg++ content. The opposite was true for low precipitation. On one occasion (January 19, 1983) there was no runoff in the collection vessel because of freezing conditions.

Corrosion Test of CMA Solutions

The results of the corrosion test for CMA solutions, prepared from the material produced by MeDOT and by SRI, are given on Table 1. The results on water and 10 percent NaCl solution are also given as a comparison. In an attempt to compare the corrosion effect of the two individual ingredients in CMA, 7 percent solution of magnesium acetate (MgAc2·4H2O) and 7 percent solution of calcium acetate (CaAc2·H2O) were also tested. The results are also given in Table 1.
Cathode (reduction)or highly ionic medium would facilitate the transfer, solution. High pH (basic) means that the concentration of H is low; reactions 6 and 7 will have less tendency to move to the right, thus less corrosion.

The corrosion effect of an electrolyte has been well established (8). In a corrosion process the predominant reactions at the anode and cathode are as follows:

Anode (oxidation) \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 2e^- \] (5)

Cathode (reduction) \[ \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2 \] (6) or

\[ 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^- \rightarrow \text{H}_2 \text{O} \] (7)

These oxidation-reduction reactions could be viewed as an electron transfer process. Therefore, a highly ionic medium would facilitate the transfer, thus the corrosion.

Another important factor would be the pH of the solution. High pH (basic) means that the concentration of H is low; reactions 6 and 7 will have less tendency to move to the right, thus less corrosion.

Sodium chloride is considered a neutral salt; theoretically, the pH of a NaCl solution is 7. On the other hand, both calcium acetate and magnesium acetate are considered basic salt, which yields a solution of pH higher than 7 when dissolved. This is the predominant factor that contributed to the corrosion-inhibition character of CMA. This can be substantiated qualitatively from the results given in Table 1. (However, the high percent weight loss exhibited by the 6.8 percent MeDOT CMA is difficult to explain.) Realizing that the starting material for the production of CMA at MeDOT contained many other ingredients in the limestone while the production process for SRI CMA enabled the removal of all other impurities, further analysis is needed to explain this abnormality.

Ponding Test—Corrosion of Rebars in Concrete

Because of the limited time of testing (90 days), the rebars in the concrete did not appear to be corroded. Closer examination of the electrical half-cell potential measured against copper-copper sulfate half-cell indicated voltages as follows: 0.08 V and 0.09 V for H$_2$O ponding test slabs; 0.18 V and 0.18 V for NaCl; 0.11 V and 0.10 V for MeDOT CMA, and 0.07 V and 0.30 V for the two SRI CMA slabs. With the exception of the last value, it is apparent that CMA does have less corrosion effect than NaCl. A major reason is that Ca$^{2+}$ and Mg$^{2+}$ undergo hydrolysis in water:

\[ \text{Ca}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + 2\text{H}^+ \] (8)

and produce calcium hydroxide, Ca(OH)$_2$, and magnesium hydroxide, Mg(OH)$_2$. The solubilities of these hydroxides in water are extremely low, with Mg(OH)$_2$ being considered insoluble. A thin white film that formed on the MeDOT CMA slabs was evident. Therefore, it is not surprising that the CMA slabs showed little penetration, whereas analysis of the chloride in the NaCl slabs gave an average chloride content of 5.6 and 2.6 lb/yc for the 0 to 1.75-in. and 1.75- to 3.5-in. layers, respectively.

Relative Slipperiness of CMA Solution Compared with Other Deicing Chemicals

The friction results are given in Table 2. The data indicate that calcium chloride created a significant reduction in the frictional characteristics of both surface types. This is not unusual, because calcium chloride is a hygroscopic water absorber. It also poses a problem to the driver because it forms, particularly on the windshield, a thin film that is difficult to flush off.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>BPN (avg)</th>
<th>Reduction (%)</th>
<th>BPN (avg)</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>78.2</td>
<td>-</td>
<td>37.1</td>
<td>-</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>70.9</td>
<td>9</td>
<td>32.2</td>
<td>13</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>60.3</td>
<td>23</td>
<td>24.6</td>
<td>34</td>
</tr>
<tr>
<td>CMA</td>
<td>70.1</td>
<td>10</td>
<td>28.4</td>
<td>28</td>
</tr>
<tr>
<td>Urea</td>
<td>71.1</td>
<td>9</td>
<td>34.4</td>
<td>7</td>
</tr>
</tbody>
</table>

$^a$Based on water as a standard.

The CMA performed nearly the same as the other lubricants on the bituminous surface but indicated a significant reduction of BPN on the dense concrete. It should be noted that all deicing agents reduced the frictional resistance when compared to water.

CONCLUSIONS

1. CMA can be made in Maine from an apparent abundant source of high magnesium limestone and acetic acid (cider vinegar).

2. A 10 percent solution of acetic acid with 10 min of agitation with the magnesium limestone coarse aggregate provides the best production of CMA for this grade.

3. A commercial production of CMA should consider the constant reflux method with constant monitoring of the pH.

4. Evaporation of the solution by solar energy is not effective because of the large amount of rainfall (> 40 in.) in Maine. Bituminous concrete batch plants have waste heat that might be able to aid in this evaporation need.

5. The field trial of CMA as a deicing agent indicated both advantages and disadvantages. A major concern in its dustiness.

6. Outdoors uncovered storage of CMA is not practical.

7. The corrosion effect of CMA solution toward metal or concrete needs further study.
REFERENCES


The contents of this paper reflect the views of the author, who is responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration. This report does not constitute a standard, specification, or regulation.

Publication of this paper sponsored by Committee on Winter Maintenance.

Corrosion of Galvanized Steel Floor Slab Reinforcement

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ABSTRACT

A 17-year-old parking facility in metropolitan Detroit is experiencing floor slab deterioration. An investigation was performed to determine the nature and extent of deterioration and identify probable restoration alternatives. The investigation involved visual observation, materials testing, a chain drag delamination survey, and determination of concrete cover to slab reinforcement. The structural frame consists of a 12-in.-thick flat plate floor slab system spanning in two directions supported by columns approximately 30 ft on centers. Floor slab reinforcement in the top and bottom slab sections are galvanized reinforcing steel bars. The floor slab and ceiling deteriorated from corrosion-induced spalling. Chain drag and coring surveys indicate that approximately 26 percent of exposed floor surfaces and 5 percent of ceiling surfaces are delaminated or spalled to a depth of about 2 in. Clear concrete cover is generally good, with a low cover of about 1.25 in. and an average cover of about 2.25 in. The chloride content of the concrete, determined within the top 3 in. of the slab, ranged from 25.2 to 8.5 lb/yd³ of concrete. The average concrete compressive strength of the floor slab is about 5,670 psi. The average air content of the concrete was determined to be 2.3 percent. Slab concrete pH ranges from 9.93 at the deck surface to 10.82 at the 3-in. depth. Reinforcement section loss of upwards to 20 percent was noted at isolated areas.

The objective of this paper is to provide a report on the field performance of a 17-year-old parking structure with galvanized floor slab reinforcement.

The case study is for the Kennedy Square Parking Garage in Detroit. The parking facility, built in 1965, consists of a slab on grade and two supported levels of parking. The parking levels are located directly beneath a pedestrian plaza, complete with plantings and a wading pool. The structural system for the supported level consists of a conventionally reinforced flat slab with drop panels and circular columns. The slab has galvanized steel reinforcing bars in the top and bottom mat of slab reinforcement. Typical slab reinforcement is shown in Figure 1.

Concern with the structure developed because of observed concrete spalling and cracking. An engineering investigation into the physical condition of the parking facility was completed in June 1982. The investigation objective was to determine the physical condition of the structures and to recommend appropriate repair procedures. The scope of the work included evaluating the parking facility through