DEVELOPMENT OF NONPOLLUTING DEICERS

In 1976 the Federal EPA published a report that attempted for the first time to assess the damage to the environment nationwide, due to the use of salt (sodium chloride) deicer (1). The increasing use of salt since the 1940s was shown to have a serious negative impact upon roads and highways, bridges, motor vehicles, groundwaters, vegetation and soils. Although the study did not pretend to be a highly detailed cost/benefit analysis, enough quantitative information was generated to call for research and development into novel, nonpolluting deicers to replace salt.

Accordingly, the Federal Highway Administration (FHWA) undertook the challenge by contracting to Bjorksten Research Laboratories, a research institute located in Madison, Wisconsin. The culmination of that work appeared as an FHWA report in 1980 (2). After having explored the entire chemical periodic table of the elements, and based upon both technical and economic guidelines, Bjorksten emerged with a chemical known as calcium magnesium acetate, or CMA. Preliminary laboratory and field data were developed to show that CMA was relatively non-corrosive, and an effective deicer.

The choice of CMA out of the several candidates examined was based partly upon the assumption that the acetic acid raw material to be used in its manufacture would be economically derived from wood and paper components of solid waste. This is the so-called biomass or bacteriological route.

The FHWA proceeded to examine the biomass approach by contracting to Stamford Research International (SRI). SRI examined the capital and operating costs of a selected bacterial route, based upon certain assumptions concerning the operability of a particular bacterial system (3). The projected operating costs at that time were only slightly lower than those associated with the
subject of the present paper. However, the capital costs were at least an order of magnitude greater than those which will be discussed in connection with the present address. Currently, as a result of inflationary pressures, even operating costs of the bacterial route offer no incentives over the scheme to be presented herein.

It is our opinion that the bacterial approach, although conceptually attractive, falls down on two accounts:

1. The process itself is complex, requiring many steps and extensive process control; and

2. A relatively dilute solution of CMA is the final product of the scheme, and this must be converted to solid CMA through a costly evaporation step.

Although researchers continue to explore bacterial approaches to acetic acid, to date a technically successful and economically attractive route to CMA does not exist.

THE SOLUTION ROUTE TO CMA

With the recognition that the bacterial route to CMA, even if it were successful, would take large amounts of capital and a long period for development, the FHWA sponsored the production of CMA from merchant acetic acid and dolomitic lime (4). The purpose of this program was to produce 200 tons of material to be used by selected state highway departments for expanded wintertime field testing. In this approach, a concentrated liquor was produced through batchwise reaction of dolomitic lime and acetic acid. The system was settled with the aid of surfactants, and then filtered. The solution was then superfiltered so as not to clog the spray nozzles used in the subsequent fluidized bed drying operation.

Production of the 200 tons was successful. However, product characteristics were unsuitable for effective deicer end use. In the course of the higher temperature evaporation process, substantial hydrolysis occurred:

\[ \text{CMA} + \text{water} \rightarrow \text{Basic Acetates} + (\text{volatile}) \text{Acetic Acid} \]

The consequences of hydrolysis were two:

1. CMA product pH was around 10 instead of the desired range of 7-9. This was due to volatilization of costly acetic acid in the process.

2. Product insolubles were undesirably high at approximately 5%, due to precipitation of basic acetates (or other basic products) formed during hydrolysis.

   Additionally, CMA product was too fine and dusty.

It was also undesirably friable. However, even if undesirable physical attributes were correctable, the consequences of hydrolysis would remain.
It is even conceptually possible to inhibit the hydrolysis phenomenon but not without costly acid losses. But one of the major drawbacks to the 200-ton CMA production program was the fact that it was a five-step process. Process complexity was reflected in the capital and operating costs. For example, the cost of a 1000-TPD plant was $74 million, with operating costs at 32¢/lb for CMA in 1984 dollars. By contrast, rock salt sells for about 1¢/lb.

The largest cost factor is raw material acetic acid, which accounts for 16-20¢/lb of CMA product. This factor is conceivably reduced through large-volume discounts, and/or use of lower grade, lower cost acid. In processing, however, the largest single cost is that associated with evaporation of water in converting CMA solution to solid product; this amounts to about 5¢/lb of CMA. It was at once evident that a new process was required which:

1. was simple in conception so as to reduce capital costs significantly below any conceived heretofore, and
2. required little or no water evaporation.

THE PATENTED GANCY CHEMICAL ROUTE TO CMA

A novel route to CMA was conceived that involved reacting dolomitic lime directly with acetic acid solution containing a minimum amount of water. The function of the water was to aid in reaction heat dissipation, and to distribute the acid. Using this approach meant that the CMA would contain all of the insoluble impurities present in the lime. The impurity dilution factor, on an anhydrous basis, would be 0.32 due to the large difference in molecular weight between raw material and product. Thus a lime containing 1% insolubles would result in a CMA product containing 0.32% insolubles. This was considered an acceptable compromise for a product which, after all, required no high degree of purity both for functional and even environmental reasons.

The first attempt to reduce this approach to practice in the laboratory resulted in disappointment. It was a batch process in which acetic acid solution was slowly fed to a stirred batch of dolomitic lime. The calcium oxide component of the lime reacted preferentially to the magnesium oxide component, with the evolution of considerable heat. During the early stage of the reaction, the batch was free flowing. However, as more of the MgO began to be converted to the acetate during the latter stage of reaction, the batch became sticky, and the stirrer would tend to seize up. This reflects the well-known highly viscous nature of concentrated (aqueous) magnesium acetate solutions. The sticking problem was not solved by varying the level of water input.

It was evident that a scheme was required which reacted each dolomite component completely with acetic acid during the entire course of the process. A laboratory scheme was therefore developed in which stoichiometric equivalents of lime and acid were simultaneously introduced to the reactor, in a semibatch mode. Initial streams were directed into a small stirred heel of product deriving from previous unsatisfactory attempts.

The continuous approach was successful. Water input was adjusted such that there was no stickiness throughout the course of the process. At the same time, sufficient water was used to:
1. minimize encapsulation of lime by product CMA;

2. minimize heat buildup, which would tend to volatilize unreacted acetic acid; and

3. eliminate dustiness.

The product emerged as pea-size imperfect pellets, or chunks.

Raw material and product were carefully weighed to determine water lost through evaporation. Product was then optionally equilibrated with air at room temperature to determine the degree of hydration of product.

The successful reaction formula was found to be $\text{CaO}_\text{MgO} + (4\text{HAc} + 3\text{H}_2\text{O}) \rightarrow \text{Product}$. In other words, an 81.6% acetic acid solution was reacted with dry dolomite. Incidentally, this approach allowed one to use unslaked dolomite, a minor cost saving over all previous approaches to the problem.

A 5% stoichiometric excess of acid was generally used in order to counteract any hydrolysis, and to ensure as complete a utilization of lime as possible, considering the potentials of acetic acid volatilization. Using this approach, the product CMA always had an odor of acetic acid. This odor was easily removed by oven-drying product CMA to constant weight at 100°C. The resulting product empirical formula was:

$$\text{Ca(Ac)}_2 \, 1.05 \, \text{Mg (Ac)}_2 \, 0.4\text{H}_2\text{O}$$

The water content was determined by carbon-hydrogen analysis. The residual water level was independently confirmed as the stubborn affinity of magnesium acetate for water. In fact, without excess acid present, damp magnesium acetate was shown to hydrolyze significantly during drying.

Yet CMA appeared to be not a simple mixture of the known compounds calcium acetate and magnesium acetate (tetrahydrate). In fact, careful laboratory scale experiments were performed in which sufficient input water was introduced to allow the tetrahydrate to form. When such preparations were air-dried to constant weight, the resultant empirical formula was:

$$\text{Ca(Ac)}_2 \, \text{Mg(Ac)}_2 \, 2\text{H}_2\text{O}, \text{ and not:}$$

$$\text{Ca(Ac)}_2 \, \text{Mg(Ac)}_2 \, 4\text{H}_2\text{O}$$

as may have been expected. Without x-ray diffraction or other analytical data as evidence, this leads to the tentative conclusion that the product formed through lime-acid neutralization is a chemical compounding of calcium and magnesium acetates. This was to prove important in subsequent programs in which the mol ratio of magnesium to calcium in the products was deliberately varied over the whole range possible.

It was evident that a low-cost process had now been developed in the laboratory that had potential for success using commercially available industrial-scale pelletizing hardware.
REACTION MECHANISM

It is worthwhile commenting on some of the subtleties of the complex series of reactions that make the entire process possible. It was mentioned earlier that lime encapsulation can be a serious problem. This was found to be true whether or not the lime was slaked prior to reaction. Incidentally, without resort to a pressure process, it is only the CaO component of dolomite that is slaked:

\[
\text{CaO} \quad \text{MgO} + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \quad \text{MgO} + \text{H}_2\text{O}
\]

Independent studies showed that the water input level was critical to avoid such encapsulation and consequent incomplete reaction of the lime. Even use of a stoichiometric excess of acid would not ensure complete lime utilization, if the water input level did not exceed a certain critical minimum.

On the other hand, too large an input level of water would obviously create a "wet" batch. This has undesirable consequences for pelletizing. But it also means a potential CMA product drying step which is to be avoided, if possible.

For the solution processes discussed earlier, about 50 mols of water must be evaporated for each mol of (anhydrous) CMA produced. In the present scheme, no more than 5 mols of water are associated with CMA. Of these, approximately two are volatized during the course of the exothermic reaction, leaving about 2-3 mols associated with the product.

These 2-3 mols of water can be largely eliminated by drying; this contrasts importantly with the 50 mols which must be removed in all solution processes.

It is extremely important to note that the product intermediate containing 2-3 mols of water is plastic at the temperature of a typical reaction batch. This indeed is what makes the pelletizing process possible at all. But when the product is cooled and allowed to stand, it becomes rock hard. Experiments in which product was stored in tightly sealed containers demonstrate that hardening is not due to a partial air drying. Pellets become rock hard even when forced to retain the 2-3 mols of water per mol of CMA. This, then, is a clear demonstration of a slow crystallization process, and is reminiscent of the behavior of magnesium acetate tetrahydrate.

The pure tetrahydrate melts at around 70 °C; when it is cooled, a glassy state is formed that is slow to recrystallize.

Thus CMA can be "cured" without a drying step after it emerges from the pelletizer. Curing to a rock-hard product requires one to two days. However, a separate curing operation is not necessary; product can go straight to the stockpile, or to a bagging operation where curing ultimately occurs automatically.

An oven-dried version of the new CMA product was found to be a superior deicer in tests conducted at the FHWA laboratories in Washington, D.C.
THE COMMERCIAL PELLETIZING OPERATION

Based upon the successful laboratory experience in producing and pelletizing CMA in a single-unit operation, a proposal for proving the concept on a pilot scale was made to the FHWA. A contract was awarded, and the following describes the successful piloting of CMA manufacture (5).

The process was not a straightforward pelletizing application, in that the pelletizer had to provide thorough mixing of the dolomitic lime and acetic acid to completely react and also to form irregular-shaped pellets. The pelletizer had to:

- thoroughly mix the ingredients to assure complete reaction;
- form shaped pellets with a similar size distribution as rock salt;
- be unaffected by the high heat of reaction during the mix/reaction stage;
- be able to perform during the "molten" stage of reaction to produce individual pellets instead of one large "pellet"; and
- provide cooling and shaping time.

With these parameters in mind, we set out to determine if agitation-type pelletizers could be utilized.

Four types of agitation-type pelletizers were considered; Deep Drum, Disc, Ampel Horizontal Pelletizer/Conditioner and Pin Mixer. The Pin Mixer was not chosen for testing due to its short retention time and inability to produce a larger particle size product of 5 mesh, to conform to rock salt sizing. The Pin Mixer would provide excellent mixing but the energy requirement and wear considerations made it the least preferred method of agglomeration.

The Disc Pelletizer was tested, and also proved to be inadequate for the reaction and formation of CMA pellets. The low retention time and the inability to establish normal growth patterns on the Disc led to control problems that could not be stabilized. The pellets produced were too small to be comparable to rock salt. The resulting -10 +16 mesh pellets could not be easily increased in size.

The Ampel Horizontal Pelletizer/Conditioner was also tested. The Ampel could be controlled, and definite zones were established within the unit; ie, mixing/reaction zone, pellet-formation zone and cooling/finishing zone. Pellet size, however, was difficult to control. Large pellets were formed, up to 1" diameter, that would require size reduction to meet product specifications. Continued operation of the Ampel resulted in excessive build-up of materials inside the unit, rendering the mixing paddles useless.

The Deep Drum Pelletizer was also tested and proved to be the preferred device for the agglomeration of CMA. Initial testing was performed on a laboratory-size Deep Drum Pelletizer with drum dimensions of 14" diameter by 9" deep.
As with all of the test work, the dolomitic lime was added continuously to the pelletizer while a spray of acetic acid solution was being applied. The Deep Drum Pelletizer allowed the materials to be mixed, provided a reaction zone and a pellet formation/cooling zone. The advantage of the Deep Drum Pelletizer over the other pelletizing devices tested was that pellets could be continually produced within the desired particle size range.

As a comparison of particle sizing of rock salt and pelletized CMA, a sizing test was performed on a Forney sieve shaker on commercially available rock salt and pelletized CMA from a Deep Drum Pelletizer.

The analysis was as follows:

<table>
<thead>
<tr>
<th></th>
<th>Rock Salt (% Retained)</th>
<th>Pelletized CMA (% Retained)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ 5 mesh</td>
<td>12.3</td>
<td>46.1</td>
</tr>
<tr>
<td>+ 7 mesh</td>
<td>22.5</td>
<td>43.9</td>
</tr>
<tr>
<td>+10 mesh</td>
<td>18.3</td>
<td>8.9</td>
</tr>
<tr>
<td>+20 mesh</td>
<td>29.9</td>
<td>1.0</td>
</tr>
<tr>
<td>+45 mesh</td>
<td>11.6</td>
<td>.1</td>
</tr>
<tr>
<td>+60 mesh</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>-60 mesh</td>
<td>4.1</td>
<td>0</td>
</tr>
</tbody>
</table>

The pelletized product had a tighter range of particle sizing than rock salt and virtually eliminated the minus 45 mesh fraction. The CMA centers on the largest of the rock salt particles in the sample and this was judged to be a satisfactory result. It is possible to regulate pellet size produced in the Drum Pelletizer by adjusting the operating angle of the drum and/or by increasing feed rates. The increase or decrease of retention time will affect agglomerate size. The next step in the evaluation of the Deep Drum Pelletizer was to upgrade the test work to a production-size unit. The Model D-20 unit was chosen, which has a drum dimension of 2'-0 diameter by 1'-4" deep or a depth-to-diameter ratio of 0.66.

The pelletizer is equipped with an integral feeder that introduces the feed material at the rear center of the drum, where the initial mixing/reaction with the acetic acid occurs. The rotating drum continually agitates the feed material for even acid distribution and to promote pellet formation and growth.

The critical concern at initial pellet formation stages is to avoid the encapsulation of unreacted dolomitic lime. This was controlled by varying the dilution ratio of the acetic acid within narrow limits to increase or decrease the reactivity with the dolomitic lime. Higher dilution rates slowed the reaction, allowing the dolomitic lime to be reacted before encapsulation occurred.

The acetic acid was introduced to the pelletizer through a spray system with three fan-type spraying nozzles. The location of the spray points inside the drum pelletizer was variable. One spray was directed to the rear of the pelleting drum where the feed enters to initially react with the lime and to form seed pellets. The second two were positioned to further coat the seed pellets to
promote pellet growth. The formed pellets were then rolled in the outer portions of the Deep Drum where they cooled and were continually discharged.

The operation of the Deep Drum Pelletizer resembled usual applications. The major difference was the violent reaction of the acid and lime, which caused heat and vapor, that at times made it nearly impossible to visually observe what was taking place inside the drum. Seed pellet formation and progressive growth were normal as long as the proper ratio of acid to lime was maintained. An inadvertent excess acid addition made the pellet bed inside the drum too molten and large agglomerates were formed. Maintaining of the proper stoichiometric ratios, however, eliminated this problem.

A pilot plant was constructed at the Mars Mineral (MMC) laboratory to demonstrate the capabilities of the Deep Drum Pelletizer during sustained production runs. The plant consisted of a small storage bin for the dolomitic lime that fed into the pelletizer feeder inlet, D-20 Deep Drum Pelletizer, discharge product cooling belt conveyor, rotary dryer, vibrating screen and bagging station. The acetic acid was pumped from containers through a diaphragm pump into the pelletizer spray system. In order to better maintain the ratio of acid to dolomitic lime, a volumetric screw feeder was later inserted between the lime storage and the pelletizer inlet to provide a more accurate feed flow.

The rotary dryer was placed into the system to dissipate the excess acid from the pellets. The dryer was a smooth-bore rotary type, 22" diameter by 22'-0 long, gas-fired with counter current flow. The exiting pellet temperature was approximately 70 °C.

The pelletized CMA was discharged from the dryer to a vibrating screen that removed oversize and undersize pellets. The undersize was the product of attrition through the dryer and screen. A test was performed to determine the attrition losses of on-size product. ASTM D4058-81 was used to measure the attrition properties of dried CMA product and of dried rock salt. In this test, the dried material is gently sieved on a No. 20 mesh sieve to remove fines, then fed to a closed cylindrical vessel containing a single radial baffle extending the full length of the cylinder. After 30 minutes at 60 rpm rotation, the sample is removed and sieved again. The difference between the before and after weights is a measure of the attrition rate.

ATTRITION TEST
ASTM D4058-81

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sub-Sample</th>
<th>Attrition, %</th>
<th>Average, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock Salt</td>
<td>1</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>6.5</td>
<td>6.0</td>
</tr>
<tr>
<td>CMA</td>
<td>1</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.5</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.3</td>
<td></td>
</tr>
</tbody>
</table>

The attrition rate for pilot plant CMA is seen to be comparable to rock salt, if not better.
The screened product was then fed to a bin over a valve-type bagger and packaged in 25-pound poly bags for shipment. The product handled well through the bagger with little or no additional attrition losses.

The pilot plant was operated to produce approximately 3000 pounds of CMA that was sent to various locations for product evaluation. The results of the field test work have not been completely evaluated at the time of this presentation. Preliminary data indicate mixed reactions from the end users. The comments received ranged from product sizing to ice-melting capabilities at lower temperatures. These are both areas in which adjustments can be made to the process to make a product to meet individual customer specifications.

In conclusion, the above-described work has shown that the production of CMA pellets can be achieved on an agitation-type pelletizer:

Four industrial pelletizers were evaluated, which led to the selection of the Deep Drum Pelletizer as suitable for carrying out the synthesis and agglomeration of calcium magnesium acetate in one step.

Reaction chemistry, as performed in the laboratory, was found to be directly translatable to pilot operations.

The CMA product produced in the pilot plant was comparable to the laboratory-produced material in most aspects, excepting that it was less dusty and less friable. This may be due to a case-hardening phenomenon resulting from the tumbling of CMA agglomerates in the pelletizer.

Particle size distribution of CMA product was very narrow and centered on the largest of the particles in a commercial rock salt. Attrition resistance of this material is comparable to, or even better than, rock salt.

The agglomerates produced were irregular in shape, which is an advantage when applied to hard surfaces from moving vehicles, or to surfaces for pedestrian traffic. The irregular shape reduces the ability of the agglomerate to roll off the surface, and provides stable footing.

Solution tests on CMA product reflect a high degree of reaction completion, with a minimum of insolubles, and a desirable pH of 7.4. Chemical analysis of dried CMA product indicates that at least 0.2 mol of hydration water per mol of contained calcium acetate is retained.

Capital cost for an 80,000-tpy plant is estimated to be $3 million. Fixed and variable operating costs are approximately 5.5¢/lb over and above the cost of the acetic acid input. As in all processes employing merchant acetic acid, the acid input cost is the dominant operating factor. A significant feature in the pelletizing process is the fuel requirement of about 0.6¢/lb CMA. This is to be contrasted to the cost of evaporating a CMA solution to dryness, a figure approaching 5¢/lb CMA.
This paper has presented a pelletizing application that, in our estimation, was unique and not typical of mainstream agitation pelletizing. The results are from the evaluation of only four of the available agitation-type pelletizers and is not to say that other types or processes would not produce an acceptable product.

The goal of selecting a pelletizing device to produce CMA was indeed reached by using an "off-the-shelf" pelletizer, with little or no modifications required.

REFERENCES


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4. "Production of Calcium Magnesium Acetate (CMA) for Field Trials." FHWA-RD-83/062

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