

PREFERRED DRYING METHODS OF CALCIUM MAGNESIUM ACETATE SOLUTIONS

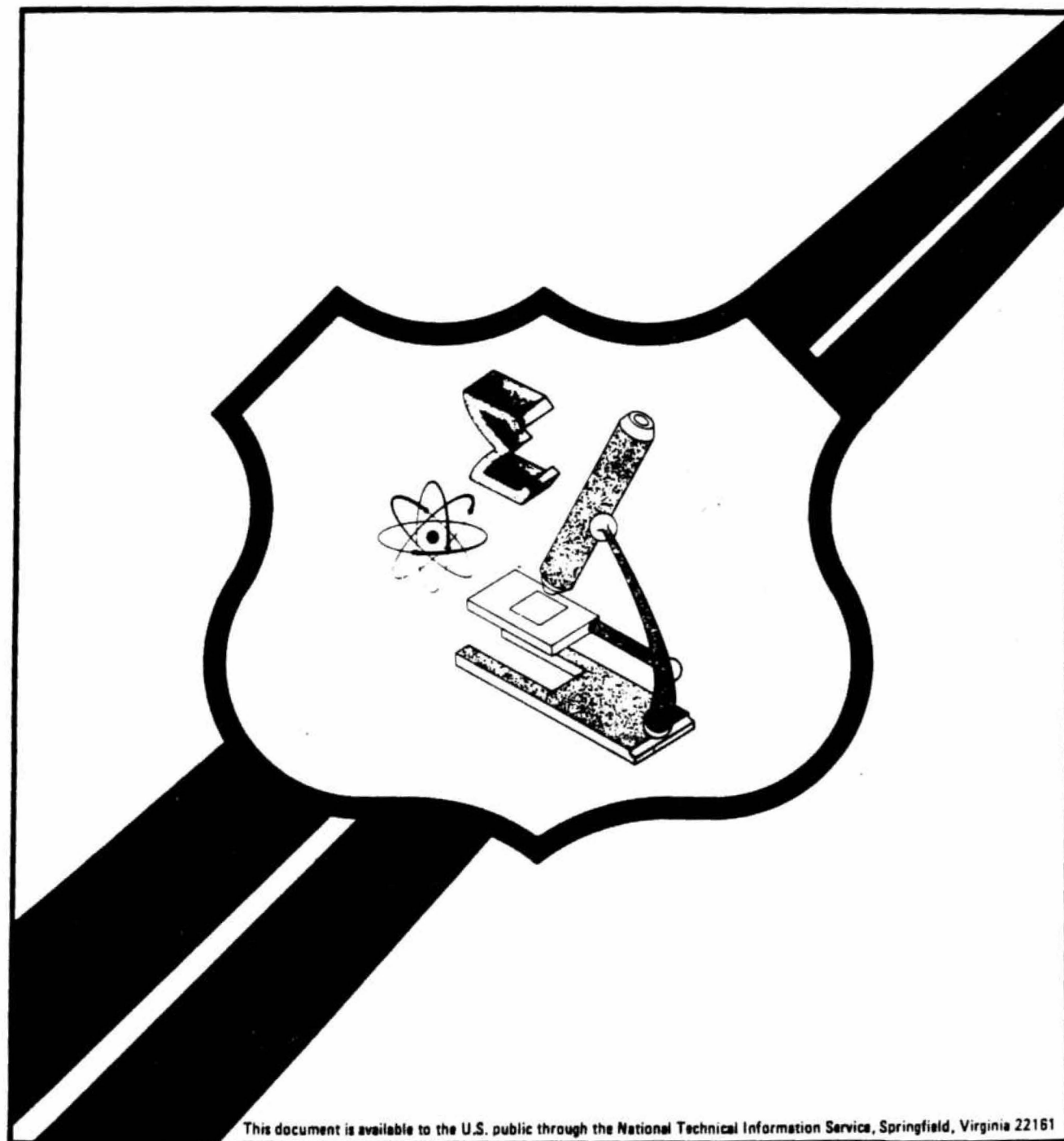
Research, Development,
and Technology
Turner-Fairbank Highway
Research Center
6300 Georgetown Pike
McLean, Virginia 22101-2296



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16. Abstract <p>Sodium chloride is currently used to remove ice from roads. While cheap, sodium chloride is corrosive and contaminates ground water and streams. The Department of Transportation under the aegis of the Federal Highway Administration (FHWA) began a search for a sodium chloride substitute. Calcium magnesium acetate (CMA) has been identified as an excellent candidate de-icing material.</p> <p>The objectives of this project were to examine the best way to prepare dry CMA from CMA solutions and to determine the ice melting ability of CMA. We would then recommend an optimum process for producing solid CMA. Energy & Minerals Research Company (EMR) examined approximately 19 different drying methods for CMA solutions. In addition, we attempted to recrystallize CMA using organic liquids. Several drying methods were finally selected for initial evaluation. Small quantities of CMA were produced, and the product properties were evaluated. Two methods were then selected for further evaluation. Larger quantities were produced and further evaluated. This report contains the data generated during the course of this study and our conclusions based on the data.</p>			
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I. INTRODUCTION

Sodium chloride is currently used to remove ice from roads. While cheap, sodium chloride is corrosive and contaminates ground water and streams. The Department of Transportation under the aegis of the Federal Highway Administration (FHWA) began a search for a sodium chloride substitute. Calcium magnesium acetate (CMA) has been identified as an excellent candidate de-icing material [1].

The objectives of this project were to examine the best way to prepare dry CMA and to determine the ice melting ability of CMA. We would then recommend an optimum process for producing solid CMA. Energy & Minerals Research Company (EMR) examined approximately 19 different drying methods for CMA solutions. In addition, we attempted to recrystallize CMA using organic liquids. Several drying methods were finally selected for initial evaluation. Small quantities of CMA were produced, and the product properties were evaluated. Two methods were then selected for further evaluation. Larger quantities were produced and further evaluated. This report contains the data generated during the course of this study and our conclusions based on the data. We also recommend an optimum process to dry CMA in quantity from solution. The specific contract tasks are briefly:

Task A

- Literature review of drying processes
- Attempt to crystallize; non-aqueous methods
- Recommend a list of possible drying processes

Task B

- Prepare small, pilot scale quantities of CMA by several processes (listed in Task A)
- Laboratory Testing of products

Task C

- Produce an optimum/or additional CMA based on Task B results
- Laboratory testing of products

Task D

- Final report

II. BACKGROUND

The search for a less corrosive and damaging de-icer than sodium chloride was initiated by the FHWA [2]. CMA was identified as an environmentally safe de-icer. Field testing of CMA noted that at high concentrations, CMA did affect more algae than NaCl and CMA replaces aluminum ions from the soil. Long-term effects of CMA at anticipated road application rates are not known. CMA also appears to be significantly less corrosive to bridge deck and car body alloys than sodium chloride [2].

FHWA identified the most promising method to produce CMA in solution. A fermentation process [3] using a wild strain of *C. Thermoaceticum* has been shown to produce acetic acid in very high yield. The bacteria have been found to grow using a variety of cheap carbon sources. Acetic acid is the only bacterial solution product. Dolomitic lime added to the fermentation broth results in producing CMA solutions. Cell free solutions must then be dried to produce solid CMA.

Workers at Bjoksten Research Laboratories [4] have studied the ice-melting characteristics of various CMA eutectics. The Ca:Mg (atomic) of 3:7 was found to give the most rapid initial rate of ice melting. Thus, cell free CMA solutions must be efficiently dried to produce solid CMA (3:7 Ca:Mg).

In prior work conducted under a FHWA contract, SRI International prepared 200 tons of CMA for laboratory and field testing [5]. SRI International used a fluid bed drying process; RAD Chemicals Division, RAD Services, Inc., Bowling Green, KY, performed the drying under subcontract. The product made had a Ca:Mg ratio of approximately 1:1. The SRI product was also light, porous and dusty. These properties render the SRI product unattractive for commercial use. Ideally, solid de-icers should be similar to sodium chloride in both physical characteristics and ice-melting ability. The fluid bed drying conducted for SRI suffered from loosely controlled bed temperatures and drying times. In this work, CMA solutions prepared by fermentation were not used. Rather, commercially available (synthetic) acetic acid was allowed to react with dolomitic lime; the resulting solution was dried. Cost analysis indicates that for this fluid bed drying process, using the fermented CMA solution results in a lower cost solid CMA product than using synthetic acetic acid [6].

The objective of this project was to examine alternative means for producing CMA solids from solution. Crystallization, precipitation from water solution, and alternative drying methods were all evaluated. Several drying processes were selected for further evaluation. The product CMA solids were subjected to extensive laboratory testing for chemical, physical and ice-melting properties. The results of these tests were analyzed and recommendations for further production are made.

III. PRELIMINARY PROCESS EVALUATION

A. Crystallization

A dense anhydrous or partially hydrated (poly)crystalline CMA could offer significant advantages over amorphous (dried from solution) CMA. If such crystalline material could be made, we would expect a dense, hard, non-porous product. Further, evaporation from ponds could be quite cost-effective if proper crystal habit could be assured. Preliminary laboratory exploratory experiments were conducted to grow CMA crystals [7].

Aqueous solutions containing Ca:Mg mole ratios of 1:0, 4:1, 2:1, 1:1, 3:7, and 0:1 were prepared. The solution concentrations were adjusted to be saturated at about 20°C above room temperature. Attempts at crystallizing the solutions were made at and below room temperature. Cooling was effected by placing CMA solution in a refrigerator maintained at 32°F and allowing the temperature to equilibrate over an eight hour period. Additional attempts to crystallize were made at the solution boiling points. Hence, supersaturation was induced by cooling and evaporation. Solutions were allowed to stand for periods ranging from 8 hours to 3 days to encourage crystal growth. Rapid nucleation was observed for all solutions upon supersaturation. The solutions also formed thixotropic gels. Only fine, needle shaped crystals were produced even after long growth periods. The ratio of nucleation to growth rate appears to be much higher for this system than for other viscous solutions (e.g., sucrose, urea, citric acid). We attribute poor crystal growth rates to the following factors: formation of thixotropically gelled solution; the surface reaction rate on the growing crystal face is low; the specific form and size of initial stable crystal is not proper for good growth. Gelled solutions can also lead to lower ionic diffusion rates to the crystal face.

These preliminary crystal growth studies indicated that crystallizing from aqueous solution would not easily give a good, solid CMA product. This was true for all temperature and concentration ranges studied. None of the solid products were further analyzed. We examined other methods.

B. Crystallization from/or Assisted by Non-Aqueous Solvents

Admixture of organic solvents to CMA aqueous solutions could result in nucleation, crystallization and growth of solid CMA. The inverse process (e.g., water-methanol recrystallization) has been practiced by organic chemists for well over 100 years. For CMA an organic solvent must be found that exhibits the following properties:

- ° Soluble in water at convenient temperatures.
- ° Very low solubility for CMA.
- ° Will not complex or solvate CMA.
- ° Can be easily recovered from mother liquors.
- ° Inexpensive (or completely and easily) recoverable.

There are several organic solvents that are soluble in water at a given temperature but separate at higher or lower temperatures. For instance, triethylamine is completely miscible below 18.7°C but immiscible above this temperature. Similar water solubility behavior is observed with other low molecular weight amines. Other solvents such as n-butanol, furfuryl, alcohol, methyl acetate, cyclohexane, n-hexane, and phenol are miscible with water above a critical temperature but immiscible below that temperature. In principal, if CMA could be separated from aqueous solution by adding an organic solvent, a very low-cost way to "dry" CMA would be obtained.

We attempted to crystallize CMA from aqueous solution by adjusting admixture of acetone, n-butanol, and triethylamine at room temperature. Good granular crystals could not be obtained. Thixotropic gels were also formed in these mixed solvent systems with the

same resulting poor rates of crystal growth described above. Triethylamine addition resulted in a pH change that caused the gelatinous precipitation of Ca, Mg-hydroxides. We did not attempt to crystallize CMA using non-aqueous solvents at other temperatures. This approach was abandoned.

C. Drying Processes

It is clear from the above results that non-evaporative or natural crystallization fails to produce a suitable solid CMA. Evaporation to dryness is therefore the best way to produce solid CMA.

We conducted an extensive literature survey of drying methods. Nineteen different drying techniques were initially evaluated (table 1). Further evaluation was made by personal contact with 8 of the drying processors. Based upon initial literature and telephone information, we selected six drying processes for detailed analysis.

Product and Process Criteria

A commodity product like CMA is quite cost sensitive. Minimizing production costs while making a solid compatible with existing salt spreading equipment are of primary importance. Drying processes which produce a granular product directly in one step would tend to be more economical than a two-step process in which granulation has to be carried out after drying. Extra equipment, labor and maintenance costs are avoided. The criteria for process selection are: 1) a "good" granular product, 2) low capital and operating costs and 3) "good" process operability.

A "good" granular CMA product is one which has:

- 1) High density (i.e. low porosity, therefore low friability).

- 2) High hardness (i.e. good strength, therefore less dusting).
- 3) Particles between 6-30 mesh.

"Good" process operability would be:

- 1) Not labor intensive.
- 2) Easy to start-up, control and shut-down.
- 3) Has minimum maintenance.

Process Selection

Selection procedures for drying equipment are covered in chemical engineering text books on unit operations and in Perry's Chemical Engineer's Handbook (Fifth Edition, McGraw Hill, N.Y., 1973). The first step is to select classes of dryers which can handle the material we use as feed. The second step is to reject those classes which will not produce a suitable final product. The third step is to eliminate those classes which experience shows might be inappropriate economically for the product. The fourth step is to reject those processes which experience shows have performance incompatibilities with the product. For drying liquids (solutions, slurries and pastes) and solids powders, (granules, sheets or large objects) commercially there are 19 classes of drying equipment (table 1). Only 7 of the 19 dryer types are suitable for evaporating solutions to dryness on a large scale; the other 12 types of dryers are suited for drying solids (i.e. materials which are solid at the start) or for drying small batches of liquid (e.g. pharmaceuticals or fine chemicals). Of the 7 classes of dryers suitable for drying solutions continuously on a large scale, 3 can be rejected outright because of either high equipment cost, unsuitable final product or a combination of both.

The three rejected processes are: continuous tray or belt dryers, spray dryers, and heated screw conveyors. Continuous tray or belt dryers dry slowly. They require a long residence time, and they would therefore, be large and expensive. Drying any liquid solution in this type of equipment compounds the economic problem by requiring the recycling of a large portion of dried final product. The stickiness of CMA would also pose a potential operating problem. Spray drying is unsuitable for CMA because the product is always a porous, low density, friable material. Screw conveyor dryers are externally heated, therefore, the rate of heating is uniform but extremely slow. A large amount of expensive equipment makes this class of dryer highly unattractive for CMA. More importantly, the final product from screwdryers generally has a large amount of fines. The stickiness of CMA at the front end of the process also could give problems in this class of equipment.

The four classes of dryers which would be appropriate for drying CMA are:

1. Fluidized Beds.
2. Rotary or Tumbling Bed Dryers.
3. Drum Dryers.
4. Pneumatic or Flash Dryers.

Fluidized Bed Drying

Fluidized Bed Drying (FBD) stands out as being one of the more promising methods for producing a good granular de-icing product economically and with reasonable ease. SRI chose to employ FBD to produce the initial 200 ton batch of CMA. From a survey of recent literature it was found that fluidized beds are currently used over a wide range of products types (pharmaceuticals to fertilizers) and a wide range of production volumes (one ton batches to thousand ton per day continuous units) [8,9]. In addition to literature information on FBD, discussions with FBD equipment suppliers, users, and

consultants (e.g. Niro; Foster-Wheeler; James Smith, our company drying consultant) revealed additional advantages.

The principle advantages of fluidized bed drying are:

1. Dries and produces a granule in a single piece of equipment.
2. The solution being dried and granulated can be evaporated as dense layers on the granule. Layered drying would produce a non-porous less friable product.
3. There are many manufacturers of FBD equipment to select from and a lot of FBD equipment of varying capacity exists around the world. Considerable know-how also exists.
4. Equipment is relatively lightweight since it need not withstand high gas or hydrostatic pressures and has no moving parts. Therefore, equipment can be made from a variety of construction materials without high expense.
5. Start-up, operation and shut-down is highly automated requiring low labor.
6. Fuel efficiency is good ranging from 1500 to 1900 BTU/lb. of water evaporated, since the drying gas passes through and intimately contacts every particle in the bed.
7. Pilot facilities exist at several manufacturer's sites in the Northeast. Pilot testing at a reasonable scale is essential for obtaining a representative product and for establishing correct process conditions.
8. The potential exists eventually for conducting the entire CMA process from neutralization through granulation and drying, in a single fluidized bed unit once the granulation and drying steps have been developed.

9. Several salts similar to CMA are commercially made into granular beads using FBD. (e.g. calcium nitrate, calcium and magnesium chlorides; sulfates of sodium, ammonium, zinc, iron, magnesium and manganese).
10. There are no apparent disadvantages to fluid bed granulation and drying of CMA.

There are thirty-four (34) suppliers of fluid bed dryers. Two FBD suppliers, Niro Atomizer, Inc. and Foster-Wheeler/NSM Co. offer FBD systems which are specifically designed for high volume (low cost) production of granules. The principal difference between these two systems and other systems is in the method of introducing the solution to be dried. Niro introduces the solution high above the fluidized bed so that some evaporative concentration (similar to partial spray drying) occurs as the atomized solution falls through the drying gases rising from the fluidized bed. The concentrated solution spreads throughout the growing beadlets in the bed where complete drying occurs.

The Foster-Wheeler/NSM Co. FBD process introduces the solution directly into the bed where it coats the fluidized beadlets and subsequently dries in layers. A basic FBD system consists of a chamber having a gas distribution plate near its base on which the fluidized bed rests. A gas-solids disengaging space above the bed allows a direct return for solids sporadically propelled from the bed. A fine particle separator (e.g. cyclone, bag filter, etc.) is located after the fluidizing chamber. When solutions are to be dried, spray nozzles can be located anywhere in the drying chamber or they can be blended with the undersized solids being recirculated to the fluidized bed. Adjustment of the FBD chamber's L/D ratio and operating parameters such as drying gas temperature, fluidizing gas flow rate, bed volume and recycle ratio are necessary to accommodate differences in fluidizing bed behavior caused by the different feed methods.

Tumble Bed Drying

Rotary or Tumbling Bed Dryers granulate and dry solutions by successively coating layers of the liquid upon a core of fine particles as they are tumbled in a rotating cylinder, drum or pan. Hot drying gases are blown across the surface of the bed of material. Two sub-classes of tumbling bed dryers exist: large rotary shell units such as those used to pelletize fertilizers and industrial and sewage sludges (manufactured by Edw. Renneburg & Sons, Heil, Inc. and Environmental Services Products, Inc.), and drum or disc pelletizers (manufactured by Sprout-Waldron Div. Koppers Co., Edw. Renneburg & Sons, Allis Chalmers, Mars Mineral Co.).

The advantages of tumbling bed agglomerators are similar in a few instances to those of FBD. Being an older, less sophisticated drying/granulating technique with certain disadvantages, it has been undergoing replacement by FBD in many instances. Point-by-point comparison follows:

1. Dries and produces a granule in a single piece of equipment.
2. The solution being dried and granulated can be evaporated as dense layers on the granule.
3. While there are not as many manufacturers of tumbling bed granulators listed as for FBD equipment (fewer than half a dozen) there has been wide-spread use of tumbling beds to granulate ores, fertilizers and waste powders such as fly ash and bag-house dusts.
4. Equipment is simple and therefore relatively low in cost.
5. Start-up and shut-down are easy steps. However, operational upsets can occur rapidly if feed conditions fluctuate.

6. Fuel efficiency is poor (up to 2600 BTU/lb. of water evaporated) because of inefficient contacting of the hot gas stream and drying pellets.
7. Pilot facilities are available at most equipment suppliers.
8. The potential exists for conducting the entire CMA process from neutralization through granulation and drying within the tumbling bed.
9. Fertilizer salts similar in nature to CMA are commercially made into granular beads using tumbling beds.
10. Potential problems can be foreseen with CMA granulation in tumbling bed dryers - one is sticking. The nozzle atomized dispersed solution in a FBD is rapidly distributed within the highly agitated fluidized bed of solids. The solution fed to a tumbling bed is slowly distributed by the tumbling action. Sticking to the pan or clumping of particles can occur during this slow step. A second potential problem with tumbling beds is decomposition from hot spot formation combined with long residence times. In contrast to FBD where extremely uniform temperatures are maintained throughout the well agitated bed, particles in a tumbling bed are often overheated by the drying gas. Distribution of the heat is slow within the tumbling bed. The problem is compounded by the long residence times experienced in tumbling beds (15 to 20 minutes). Particle decomposition of CMA granules which are moisture free but trapped in the bed could occur.

Decomposition of CMA forms oxides of calcium and magnesium, plus acetone, acetic acid and water. The acetic acid would be of concern in the de-icing product. Even small traces of it could create corrosion problems. Removal of trace amounts of acetic acid should prove to be difficult since it is known to

form "bound" compounds with acetate salts [10]. Sodium acetate readily forms a "diacetate" with acetic acid which is commercially useful as a source of "Dry" acetic acid. CMA plus acetic acid could form "triacetates".

Drum Drying might form a granular CMA product, if large drums were used in conjunction with thinly spread layers of CMA solution (or slurry). Bulk drying in the laboratory formed soft friable (i.e. dusty) CMA product as a result of the co-precipitation of many nuclei of several different crystalline species. The softness of the "cake" was also due in part to micro capillaries formed by the escaping water from the bulk material.

A point-by-point comparison of drum drying with the previously described granulating techniques follows:

1. Dries and produces a granular product with a single piece of equipment.
2. The solution (or slurry) of CMA is dried as a bulk material with heat supply coming through one side only; escape of evaporated water also occurs through one side only. Fluid bed and tumble bed drying permit heat and mass evaporation at all surfaces of the drying material. In addition, fluid bed and tumble bed drying take place with incrementally thin (100-200 micron) layers. Drum dried layers would have to be on the order of 2-6 mm. in order to be economical.
3. Availability and experience with drum dryers is widespread in the food, pharmaceutical and chemical industry.
4. Equipment is generally considered expensive. Maintenance on the rotating seals, blades and scraped surface is also considered as "high" in the drying industry.

5. Start-up, operation and shut-down is very convenient.
6. Fuel efficiency is very good. Values of 1,200 BTU/lb/ of water evaporated are typical. There are no heat carry out losses by a gas stream. Steam is consumed for evaporation only as needed.
7. Pilot facilities exist at most equipment suppliers.
8. Drum drying is useful only for simultaneously drying and granulating. Eventually conducting a neutralization with acetic acid while simultaneously drying and granulating is not feasible.
9. Foods, pharmaceuticals and fine chemicals are typically drum dried. These are no high volume commodity items such as fertilizers, using drum drying.
10. The most apparent trouble spots with drum drying centers on product decomposition. Heat transfer through the drying layer of CMA will create a high thermal gradient from drum surface to air interface. High steam temperatures which would give high production rates and permit smaller equipment will have to be sacrificed in order to make sure decomposition is minimized.

Flash Drying (FD) has been included as a potentially appropriate method of producing CMA solids even though the fine powder produced would have to be agglomerated in a separate finishing step for the following reasons. Flash drying equipment is inexpensive and maintenance tends to be low. Start-up, operation and shut-down are convenient (automated with a minimal labor component). Fuel efficiency is excellent since the drying gas intimately mixes with the atomized spray of liquid. Typical fuel requirements are 1600 BTU/lb. of water evaporated. FD is used on heat sensitive materials because residence times within the equipment are extremely short (50-100

milliseconds) and the evaporating water maintains the particle at the wet bulb temperature. Therefore, decomposition is avoided. Bench scale pilot facilities are available at several suppliers which give valid scale-up data and representative samples of product.

The potential exists for conducting the neutralization step in sequence with the drying step in a flash dryer.

Numerous salts, pigments and clay (slurries) have been flash dried successfully on a large scale.

The only problem envisioned is potential sticking of CMA to the walls of the conduit. Agglomeration of the powder would be carried out in a tumbling bed unit of the disc or drum type. However, the disc (or drum) agglomerator would not be utilized for drying as previously described. Its function would be to evaporate the 5 to 10 percent moisture used to bring about agglomeration. therefore, the detrimental aspects of tumble drying/granulation will not prevail. With the use of appropriate binders such as, sugars, molasses or starches, a superior CMA granule might be developed.

Choice of Candidate Processes

Based on the above considerations, we chose to examine three different drying processes. Final choice of process and companies was arrived at with the concurrence of the FHWA COTR. The processes and companies chosen to produce small quantities of CMA for laboratory testing were:

- ° Fluidized Bed Drying by
Niro Atomizer Co., Columbia, MD
- ° Tumble Bed Drying by
Ferro-Tech, Inc., Wyandotte, MI
- ° Flash Drying followed by abbreviated
Tumble Bed Granulation by
Desicco, Inc., Lodi, OH followed by
Ferro-Tech, Inc., Wyandotte, MI

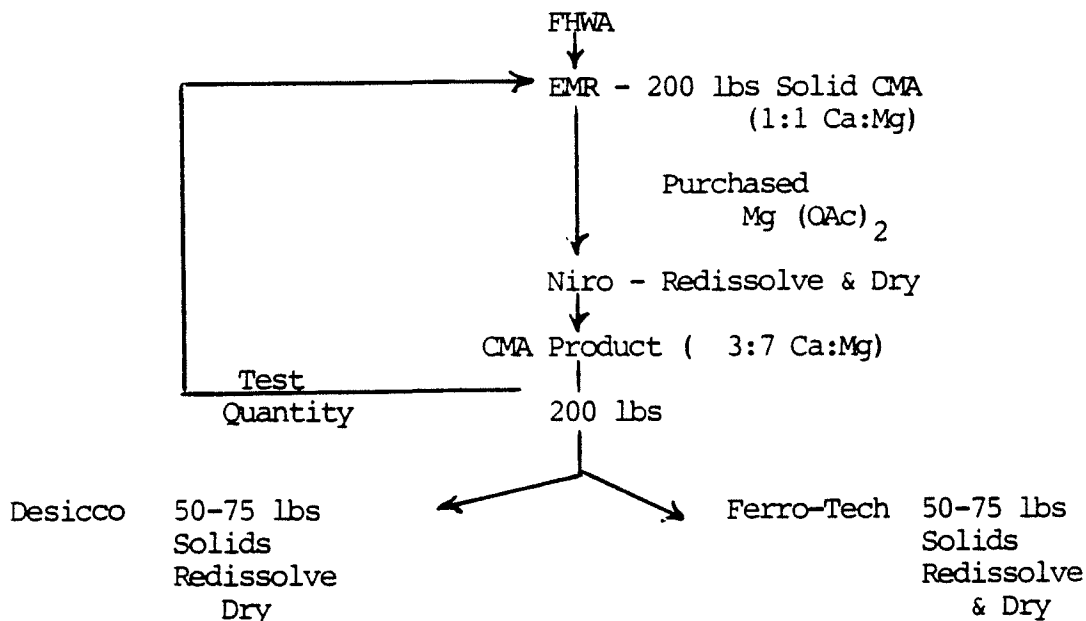
The processes chosen represent a range of drying processes in terms of energy efficiency. The processes all offer ease of start-up, operation and cost of equipment advantages over the remainder listed in table 1. In addition, contractor ability and willingness to process first small then possibly larger quantities of an experimental substance also played a role in the choice of subcontractor.

IV. PRODUCTION OF CMA
 A. Plan for Producing CMA

The three manufacturers listed above all desired enough CMA solution to produce about 500 pounds of solids. FHWA could provide us with only about 200 pounds of 1:1 Ca:Mg (atomic) CMA solids. This material was produced by SRI.

We decided to supply each manufacturer in a sequential fashion. Niro Atomizer was chosen to perform the initial work; very good control of the process dictated this choice. We supplied solid CMA to Niro along with enough purchased magnesium acetate to produce a 3:7 ratio of Ca:Mg (atomic). Niro redissolved the solids and dried the solution using fluidized bed methods. The product solids were then shipped to Desicco and Ferro-Tech. A small amount was to be saved for our laboratory testing. In turn, Desicco and Ferro-Tech would redissolve the Niro product and dry the solution in their flash and tumble bed dryers. An outline of the overall plan is shown below in Scheme I.

SCHEME I
Outline of Proposed CMA Production Plan



B. Production of CMA

1. NIRO Experience

Niro Atomizer Company's pilot plant facilities in Columbia, MD were used to produce the initial quantities of solid CMA. Niro received 1:1 Ca:Mg solid CMA produced by SRI. In addition, extra Mg $(OAc)_2 \cdot 4 H_2O$ was given to Niro to raise the Mg content of the product. White, gritty insoluble material was present in the first 30 gallon batch of solution prepared. We presume these insolubles are MgO which SRI used as seed material to core their CMA granules. Filtering of the solution through 100 mesh screen or cloth removed most of the large insoluble particles. White water insoluble material was observed by both Desicco and Ferro-Tech. Filtration was similarly employed to reduce nozzle clogging.

In the Niro fluid bed dryer, the solution to be dried is added from the top and begins to evaporate by encountering hot flowing gases. The partially dried droplets fall and distribute themselves throughout the bed. Niro used a small quantity of 1:1 Ca:Mg CMA to initiate the fluid bed spray granulation process (FBSG; residence time adjusted to produce granules). $Mg(OAc)_2 \cdot 4 H_2O$ was added to the solution to raise the Mg mole fraction. The 30-40 wt % CMA solution proved quite viscous. Niro used larger spray nozzles placed near the top of the fluid bed to help prevent nozzle clogging.

Niro produced 5 batches of about 12 pounds each of CMA; total CMA was 59 pounds. Niro used 30 wt % CMA solutions for runs 1, 2, 5 and 40 wt % solutions for runs 3,4. The finished granules all handle well. They were all hard, layered, dust-free and fairly dense. The time to produce these 3:7 Ca:Mg CMA products in the pilot was longer than initially thought. The complete set of operating conditions and problems encountered are detailed in a report prepared by Niro and appear as Appendix A at the end of this report. Samples of the Niro

products designated (Niro #1, 2, 3, 4, 5) were saved for analysis by EMR. The remaining material was shipped to Desicco for re-dissolution and flash drying.

2. Desicco Experience

Pilot runs in the Desicco flash dryer were attempted over a two week period. A 3 inch diameter loop flash dryer was used. The 3:7 solution was prepared at a concentration of 40 weight percent and filtered through cloth to achieve clarity. The solution was fed to the flash dryer by means of a stainless steel screw pump. High shear air atomization of the solutions was achieved in the dryer by means of a mixing nozzle. Air to the dryer was electrically heated to 200°C. A cyclone and cloth filter were located after the dryer for product collection. Solution feed rates of 5 to 40 pounds per hour (dry basis) were tried. Dryer exit temperatures from 110°C to 70°C were observed. Using a variety of drying conditions could not overcome the problem of product build-up on the dryer walls. All runs were unsuccessful. Material accumulated around the entire wall periphery during each run. Little product carry-over to the cyclone collector was achieved. This was somewhat surprising since the liquid feed with a 3:7 ratio did atomize well in tests outside the dryer. In addition, liquid with a 1:1 ratio was successfully flash dried last summer. The consistency of material on the dryer walls was like dry mud. It had an opaque appearance indicating that solids were still in solution. Sand was added to the dryer in an attempt to clear the walls. Unfortunately, the extreme stickiness of the material required a very large quantity of sand (6:1 weight sand to CMA solids). Extensive discussions were held with Desicco personnel. The probability of: 1) going to a flash dryer with a larger diameter (6" instead of 3") and 2) using a lower Mg content solution were fully discussed. It was felt that the use of a larger dryer might achieve greater turbulence and more rapid flash drying than the 3" unit. However, larger quantities of CMA would be required than were available. The second alternative proved to be inadvisable when it was learned that the results with the

1:1 solutions had been only marginally successful and that it had been hoped that by increasing the Mg content the properties would be improved.

3. Ferro-Tech Experience

The experience gained at Niro and Desicco was used to improve processing at Ferro-Tech. Ferro-Tech encountered no problems in handling and drying the CMA product. Ferro-Tech also had to filter the 30 wt % CMA solution; a filtered 3:7 Ca:Mg 30 wt % solution was used as feed. The solution was sprayed in small increments into a turbulator (pin mill mixer) that contained a small quantity of finely ground 1:1 CMA/Mg(OAc)₂ "seed" mixture. As wet granules formed, they were transferred to a Model 036 disc pelletizer. Sprayed solution was air dried in sequential layers on top of the seeded granules. Pellets formed and were transferred to a tray dryer. Initial water content of the pellets was about 30 wt %. The final pellets had moisture contents approach zero wt %.

V. PROPERTIES OF THE TEST BATCH

A. Test Batch Quantities and Types

Approximately 5 pounds of each of the initial run test samples were saved for laboratory testing and chemical analysis. Our strategy was to perform the tests requiring the most material first. In this way, material limitations would not preclude tests from being performed. All five Niro initial samples, a Ferro-Tech sample and a sample of rock salt (supplied by R. J. Collins and Pennsylvania Department of Transportation) were subjected to laboratory testing.

B. Preliminary Tests

The CMA products listed above were subjected to the following preliminary tests: particle size analysis; attrition loss; friability; chemical analyses (Ca, Mg, acetate, % H₂O); hygroscopicity; ice-melting (FHWA and S. Dakota); heats of solution; crystal habit; pH.

1. Outline of Test Procedures

a. Particle Size Analysis

Samples were sized by screening through standard U.S. mesh screens according to ASTM method D632-72 ("Standard Specification for Sodium Chloride"). This method applies to Grade 1 standard gradation for Type I sodium chloride. Type 1 NaCl is used primarily as road de-icer. We used the following screen sizes: 3/8 inch, No. 4, No. 8 and No. 30. A sample of Grade 1/Type 1 NaCl were used for comparison with CMA.

b. Attrition Loss

Particle strength by attrition was tested according to ASTM method D 4058-81. The test was conducted in the following way: a 10" diameter, 6" deep drum was constructed with a single radial (2" long X 6" high) baffle. A 100g sample of salt, all particles greater than 20 mesh was charged to the drum. The drum was sealed and then rotated at 60 rpm for 30 minutes (1800 revolutions). Gravimetric screen analysis of the recovered salt gave a quantitative measure of how much material was comminuted.

Rotating drum attrition loss data are used to determine the tendency of a solid to dust. The samples were prepared in two different ways. One series of samples were pre-sieved to remove all material smaller than +20 mesh; attrition tests were conducted as indicated above. In a second series of tests, the "as received" samples were submitted to attrition testing without pre-screening. Any bias in choosing stronger particles by pre-screening would be avoided by this procedure. In two cases, the attrited samples were screened, the -20 mesh gravimetrically determined, and the +20 mesh material resubjected to the attrition test. These latter tests confirm the tendency of the samples to be comminuted.

c. Friability

Particle friability was determined according to ASTM method C142-78. This test is a qualitative test. The CMA products are rolled between the fingers and the ease of particle break-up estimated.

d. Chemical Analyses

Quantitative analysis for Ca and Mg were performed by complexometric titration with EDTA. The literature indicates that calcium can be quantitatively determined in the presence of magnesium. We

subcontracted these tests to Chem-Clear, Inc., Devon, PA. Chem-Clear found that the EDTA titration methods did not adequately discriminate between Ca and Mg at high magnesium levels. Hence, we subsequently relied on atomic absorption spectroscopy to determine the concentration of both Ca and Mg.

Acetate is determined by gas chromatography (performed by Chem-Clear, Inc., Devon, PA). The method involves dissolving a weighed quantity of CMA in formic acid. An aliquot of the formic acid solution is analyzed by gas chromatography using a 3% Carbowax 20M/0.5% H_3PO_4 column with flame ionization detection. Water was determined by standard Karl-Fischer titration.

e. Hygroscopicity Tests

Initial testing for water absorption characteristics of CMA productions was performed in three different ways. In the first method, samples of CMA were allowed to equilibrate with ambient air for seven days.

The second method involved allowing CMA samples to equilibrate with dry atmosphere for 24 hours (placed in dessicator over $CaCl_2$ Drierite). The last method involved allowing CMA samples to equilibrate with a wet atmosphere; dessicate over saturated $Na_2SO_4 \cdot 12 H_2O$ (93% relative humidity). In all cases, samples were weighed before and immediately after testing; weight gain (loss) was reported.

f. Ice-Melting by FHWA and S. Dakota Methods

There are currently no ASTM, AASHTO, or other standard methods to test the ice melting rate of chemical de-icers. Two different test methods were used. The first method, known as the FHWA method, involves placing a quantity of de-icer on a pre-frozen pan of ice. The de-icer is evenly spread over a known surface area of the ice.

The ice and the de-icing material are maintained at a controlled temperature in a thermostatically controlled freezer. After a period of time, the melt is collected and weighed. In the second test, preweighed quantities of ice and de-icing material are mixed and placed in a funnel. The funnel is placed in a thermostatically controlled freezer. Melt is collected at the bottom of the funnel and weighed at a regular time intervals. The latter test is know as the S. Dakota Department of Highways test ^[11] (modified by EMR). The details of each ice melting test follow:

Freezer type: Sears-Kenmore Model 198/18092; temperature was controlled by use of an I²R model thermowatch temperature controller. The temperature could be stabilized to $\pm 1^{\circ}\text{F}$ of the desired set point between $+32^{\circ}\text{F}$ and 0°F .

FHWA Test: A rectangular glass pan, 9 X 11 inches was filled with 1/8" (200 ml) water and placed in the thermostated freezer for at least 24 hours. The de-icer of interest was spread over the ice surface. The de-icer was applied at the following rate:

0.96g - 200 lb/mile	1.912g - 400 lb/mile
1.434g - 300 lb/mile	3.822g - 800 lb/mile

These application rates are approximate field usage. After 24 hours, the glass pan is tipped and the melt is collected and weighed.

Modified S. Dakota Test: These tests were conducted in the same thermostatted freezer that was used for the FHWA tests. In this test ice was crushed to approximately 1/4" top size. 30 grams of ice were place in a 100 ml capacity funnel and allowed to equilibrate at the test temperature. 10 grams of CMA product were evenly layered over the surface of the ice. A beaker was placed under the funnel spout and the melt yield at 30 minute intervals was determined gravimetrically.

g. Heats of Solution

Heats of solution of CMA products were determined by measuring the vapor pressure over CMA solutions at several concentrations and temperatures. These data were used to calculate heat of solution using the Clapeyron-Clausius equation [12].

Integral heats of solution were measured for FBSG #3, #5 and TBG #1 CMA products by measuring vapor pressures above the solutions at three temperatures and three weight percent concentrations. Vapor pressures were measured using a stoppered 250 ml Erlenmeyer flask in a water bath with a water filled manometer.

The log reference plot method of Othmer [12] was then utilized to calculate the heats of solution, where:

L = Total heat required to vaporize one mole of solvent from the solution at temperature T ;

L^1 = Heat required to vaporize one mole of solvent from pure water at temperature T ;

L^* = The heat of solution, $L^* = L - L^1$ expressed as Kcal/g moles of solvent;

L^{**} = The heat of solution expressed as Kcal/g moles of solution,

$L^{**} = L^* \left(\frac{\text{moles water}}{\text{moles CMA}} \right)$.

h. Crystal Habit

The physical and chemical composition of the CMA solid phase produced from each drying process predominately will depend on solution composition, concentration and temperature. The rate of "drying" will determine the size and shape of these particles.

It is not expected that single crystals of CMA nor distinct crystals of calcium acetate and magnesium acetate will be produced from these processes. Either polycrystalline or a mixed crystal blend could be expected from rapidly conducted drying processes particularly in processes where bulk solution is sub-divided into droplets or spread in thin layers, then rapidly dried. The sudden increase in supersaturation leaves little time for individual crystal development and growth. Polycrystalline solids should predominate from the solutions of 3:7 atomic ratio of Ca:Mg.

The crystal morphology (i.e. habit and macrostructure) of the solid CMA produced will be defined for each of the industrial processes evaluated, as well for all materials made in laboratory experiments. Where individual crystal particles develop, identification by classification within the six crystal systems should be readily possible (i.e. cubic tetragonal, orthorhombic, monoclinic, triclinic and hexagonal). Where polycrystalline phases are developed, descriptions will be made according to definitions and techniques described in ASTM E20-62T. "Analysis by Microscopical Methods for Particle Size Distribution of Particulate Substance of Subsieve Sizes". The smallest discrete units will be classified as needles, plates, agglomerates, etc. or as shapes conforming to the six crystal systems. A low power stereo (0.7-4X) zoom microscope will be used as well as a 2X hand magnifier to facilitate observation of the solids.

i. pH

The pH of 10 wt % CMA solutions was determined using a Beckman pH meter.

j. Solubility in Water

Solubility-temperature relationships were determined for ten, twenty, and thirty weight-percent solutions of each CMA sample. These relationships were determined by heating stirred CMA solutions at a 1°C per minute rate utilizing a water bath until the temperature was observed at which CMA dissolved. To check this temperature the water bath was then subcooled 1°C and an ultrasonic probe was introduced into these solutions to induce nucleation and verify the observed solubility points.

k. Eutectic Properties

Eutectic properties of selected samples were measured. Solutions were made at 5, 10, 15, and 20 weight percent concentrations using Niro #5 and Ferro-Tech CMA samples. Approximately 5 ml of each solution was then placed into a test tube (25 mmD X 200 mmH). Temperature was measured with a fine copper Constantine thermocouple ($\pm 1.0^\circ\text{C}$) and plotted as a function of time using a Rustrak Model No. 22637 recorder. The recorder has a response time of 1 second and chart speed of 30 inches per hour. The sample tube was lowered into an ethylene glycol bath and chilled sufficiently to freeze the sample. When the solution was frozen the tube was removed from the bath, and clamped inside a larger glass tube to slow the rate of heat absorption. The sample was then permitted to warm slowly. The Liquidus and Solidus temperatures were determined for each sample on the cooling cycle and again on the warming cycle. On the cooling cycle Liquidus (Li) was detected as a sharp decrease in the rate of descent of the recorder pen (heat was being liberated as solids formed). A level plateau was sometimes observed, followed by a return to the original

rate of descent of the pen. The return to the original rate of cooling was taken as the Solidus (E_1) point. This point was also checked by observation. A similar Solidus (E_2) and Liquidus (L_2) curve was traced in reverse on the warm-up cycle.

2. Laboratory Test Results

In this section the test results for the preliminary CMA samples (Task B) are detailed. The results of the testing procedures described above (Section V.B.1) are presented in tables 2-12.

The commercial use of CMA will depend in part on how easily it can be handled and how rapidly and efficiently it melts ice. The results shown below give an indication of how CMA might perform in field use. We used these results to fine tune the processing; three additional samples were prepared after fine tuning the process (Task C) and tested.

The particle size distribution of the 'as produced' Task B samples are shown in table 2. Also shown are the particle size distribution limits for Grade 1 sodium chloride. All five Niro samples and the Ferro-Tech samples are somewhat smaller than the desired size for sodium chloride. However, both Niro and Ferro-Tech can recycle the product until the desired size distribution is achieved. Samples of CMA produced by SRI, Gancy Chemical as well as a rock salt sample provided by the State of Pennsylvania DOT were analyzed. The average particle size of the Gancy sample appears to be larger than the other CMA samples.

Table 3 lists the results of our friability testing. These are qualitative tests. The results indicate that CMA is more easily comminuted than rock salt. The quantitative attrition loss tests are a better measure of how much dusting might be expected in practice.

In table 4 are shown the results of attrition testing on our Task B CMA samples. The data indicate that the SRI sample used and the Ferro-Tech sample suffer the worst attrition losses. Niro samples #3, 4, 5 all show low attrition losses.

ASTM E20-62T was used to determine the crystal structure and habit of CMA samples. This test is used for macrostructure (shape and form) determination. The smallest discrete units identifiable are classified as needles, plates, agglomerates, or as shapes conforming to the six crystal system. A low power Stereo (0.7-4X) zoom microscope was used with a 2X hand magnifier to facilitate observation of particles. The procedure applies best to particles between 0.2 and 0.4 microns. The lower limit is imposed by the resolving power of the microscope. A No. 325 (44 microns) standard sieve was used as a for removing the smallest discrete particles. The particles above the subsieve range in size were segregated and analyzed. Those of the subsieve (No. 325 mesh) range were optically separated. From observations that were made (see table 5) it was concluded that all of the smallest discrete units (-325 mesh) produced by either FBSG or TBG were polycrystalline particles. The +325 mesh CMA solids were polycrystalline particles which formed enmeshed masses by layering. FBSG #3 CMA has a much smoother layering and TBG #1 has greater porosity than any other CMA produced. SRI CMA solids are also polycrystalline in nature with layered material of relatively smaller individual sizes than either the FBSG or TBG CMA. Gancy CMA solids are also polycrystalline particles. They are of a greater size and have a smoother surface. No single crystals of CMA components were found in any samples.

The hygroscopic tendency of the CMA products was determined. This property could effect how CMA will be stored in the field or how rapidly it has to be used after being manufactured. In table 6 are shown the results of three separate tests of hygroscopicity. The test procedures were outlined above (Section V.B.1). The data in table 6 indicate that these samples gain only small quantities of water. In

the worst case, 93% relative humidity, the Ferro-Tech sample increased 1.2 wt % of water; all others were lower. The data also show that if present, water will not easily leave the CMA crystal ('dry' data, table 6).

The results of chemical analysis for Ca, Mg, acetate, and water are shown in table 7. Since excess acetic acid can be strongly chemisorbed onto CMA, the pH of 10 wt % solution was also determined. Excess acetic acid would promote rapid corrosion of bridge deck rebars. The initial Niro and Ferro-Tech products all had Ca/Mg (atomic) values very close to the desired ratio of 3/7. Gancy and SRI products were close to equimolar in Ca and Mg. The finished ('as received') Ferro-Tech product had more moisture than the Niro products; prolonged drying or drying at a higher temperature (less than 200°F used initially by Ferro-Tech) would reduce the moisture content.

Also shown in table 7 are the expected analyses for $0.6\text{Ca}.1.3\text{Mg} \cdot (\text{C}_2\text{H}_3\text{O}_2)_4 \cdot 0.5\text{H}_2\text{O}$. It should be noted that all the acetate analyses of the experimental CMA products are lower than expected. Clearly, excess acetic acid was not incorporated into any of the CMA products. The lower than expected values indicate that excess heating caused limited decomposition of the acetates; corresponding oxides result. The Niro #5 product was slightly worse in this regard than the other products. CaO.MgO in the product will lower the ice melting capability of the product. In addition, the oxides will slowly be converted to the hydroxides in water. More precise control of the drying temperature should eliminate this unwanted product.

The calculated heats of solution are tabulated in table 8. It is not clear why the Niro #3 sample has a distinctly lower heat of solution than the Niro #5 or Ferro-Tech samples. Heats of solution are usually determined for dilute solutions. It is possible that some

anomalous concentration effects are causing the observe results.

The loose bulk density of several CMA products was determined. The results are presented in table 9. CMA is about $\frac{1}{2}$ as dense as rock salt. The Niro # 1, 2, 3 samples had the highest loose bulk density.

The ability to melt ice is a critical property for de-icing solids. Initial ice-melting rate and total ice-melting capacity are important performance factors. In table 10 and 11 are shown the results of ice-melting tests using two different methods. Table 10 shows the results of the FHWA melting method for CMA products. In this test a small quantity of CMA is placed in the center of a pyrex dish that is partially filled with ice. The apparatus was contained in a thermostatically controlled freezer.

The FHWA test in our hands produced inconsistent results. For instance, results of Niro #5 sample are shown in table 10. While the quantity of CMA is approximately doubled, 1.912 g to 3.822 g, the quantity of melt collected increased by 8% (2.7 - 2.5/2.5). The results for the Ferro-Tech sample were even worse; no melt was collected at any quantity of CMA applied to the ice surface.

We also measured ice-melting ability of CMA using a modified South Dakota test. In this method, ice (30 gm) was placed in a funnel. CMA (10g) was layered on top of the ice. The temperature of the test is controlled by placing the apparatus in a thermostatically controlled freezer. The melt is collected over time and determined gravimetrically. The results of ice-melting capacity using this test are shown in table 11. Ice-melting capacity data for rock salt (Penn DOT sample) using this test are also shown. The ice-melting data were obtained at several temperatures. The data show the initial ice melting rate (0 time to +2 hr) for all Niro samples is faster than the Ferro-Tech material. However, all CMA samples were slower in melting ice than rock salt. The initial ice melting rate data are plotted in Figure 1 (for convenience). Again, there is a clear difference

between the CMA products; Niro CMA melts ice faster than Ferro-Tech CMA.

The data displayed in Figure 1 (and table 11) show that rock salt initially melts ice faster than the CMA products tested. However, the initial melting rates change with time and at longer times CMA melt rates approach that of rock salt. For instance, approximately 60 minutes after application, the observed melting rate for rock salt slows down and approaches that of CMA. After approximately 3 hours rock salt has produced the maximum quantity of melt. As shown below for production samples, quantities of melt similar to that of rock salt are produced by CMA at longer application times. Hence, ice melting capacity of CMA compares favorably with that of rock salt. The slower initial ice melting rate suggests that early warning and application of CMA in the field are important factors for maximum efficiency.

The individual CMA samples tested displayed some differences in ice melting rates (Figure 1). Niro #3 displayed a faster initial rate than the Ferro-Tech material. However, the melt capacity of the test CMA samples were all approximately equal at longer times. After 2.5 hours, the Niro #3 and Ferro-Tech samples gave 24.2g and 24.6g respectively. Under conditions of this experiment, there is no significant difference in the ice melting capacity between these samples. All CMA samples tested seemed to exhibit a decrease in ice melt rate around 2 hours after application. After 2 hours melting continues but at a slower rates.

The solubility temperatures of several CMA solutions were determined. The results are presented in table 12. The data show very similar solubility characteristics for the Ferro-Tech and Niro

samples. Also shown in table 12 are data for rock salt solubility. At every concentration tested, rock salt exhibits a lower solubility temperature than CMA; the solubility temperature difference between CMA and rock salt increases as the solution concentration increases. For instance, a 10% solution of NaCl in water gave a solubility temperature of 17°C; 10% CMA in water gave solubility temperatures 4-10°C higher. However, 30% NaCl dissolved at 30°C while 30% CMA in water dissolved at 63-72°C. This solubility behavior accounts for the faster initial ice melting rates of rock salt compared to CMA.

Eutectic properties were determined for the Ferro-Tech and Niro #5 samples. These properties were determined by measuring Liquidus and Solidus vs. temperature for varying CMA solution concentrations. The data are presented in Figures 2, 3. In theory, freezing point depression, a colligative property, is dependent only on the number of species in solution. In Figure 1, the Ferro-Tech sample, an increase in freezing point (Solidus) is noted as the CMA concentration increases. It is possible that an unexplained association is occurring. Alternatively, calcium may be precipitating (as $\text{Ca}(\text{OAc})_2$) from solution. We can offer not other explanations for this observation.

3. Conclusions

The sample quantities of CMA produced by Niro were excellent in all tests conducted. The Niro samples showed low attrition losses (table 4) did not absorb much atmospheric water (table 6) and melted ice (initially) faster than the Ferro-Tech sample. Both the Niro and Ferro-Tech samples were quite close to the desired 3:7 Ca:Mg (atomic) composition ratio. The Ferro-Tech sample seemed to have the least quantities of insolubles (visual examination of redissolved solutions). The presence of insolubles could be related to decomposition of the acetates during drying; Ferro-Tech CMA dried at a lower temperature than Niro product. However, the Ferro-Tech product had more moisture present (table 7).

Drying 40% CMA solutions at all three manufacturers proved difficult. The high viscosity and tendency of the solutions to form gel caused processing problems. Fine control over process variables must be achieved. After discussion of the data with the COTR we decided to proceed with Task C in the following way: a larger sample of 3:7 Ca:Mg would be prepared by Niro using their well controlled fluidized bed spray granulator; a sample of 1:1 Ca:Mg would be made by both Ferro-Tech using their tumble bed dryer and Niro using their fluid bed dryer. The latter experiment was included to observe the effect of lower Mg content on processing by both methods. Larger samples of CMA produced by two different methods allowed further comparison of drying methods. The larger sample sizes might allow the manufacturers to operate under conditions more like those used for commercial sized runs. The results of Task C follow.

C. Production Material Tests (Task C)

A larger quantity of CMA (3:7 Ca:Mg) was produced by Niro. Niro made two samples under conditions similar to Niro #2, #3 (above); Niro P #2 to have Ca:Mg of 1:1 while P #3 would have Ca:Mg 3:7. These will be designated Niro P #2 , P #3. Ferro-Tech produced another CMA sample of close to 1:1 Ca:Mg (designated TBG-P #1). We also examined the properties of two other production samples of CMA: 1:1 Ca:Mg produced by SRI International and Gancy Chemical.

An abbreviated series of laboratory tests were performed on these materials. The task B samples showed that most of the CMA test properties were similar. Therefore, the Task C testing was limited to those tests which would afford the best predictions of field use results. The tests performed were: attrition; particle size; hygroscopicity; bulk density; friability; ice-melting (FHWA and S. Dakota); chemical analysis (Ca, Mg, acetate, water). Due to limitations of sample size, all tests were not performed for all samples listed above.

1. Test Results for Production Samples

Test results for production samples (Task C) of CMA are listed in tables 13-20.

In table 13 are shown the results of the attrition losses of Task C samples. Attrition losses for the Niro samples were higher than in the pilot runs while losses for the Ferro-Tech (1:1 Ca:Mg) sample were lower than in the pilot runs (compare table 13 results to those shown in table 4).

Attrition losses will drive up the price of any de-icing product; dusts produced will be lost during shipping, transport and use in the field. CMA dust is not an efficient de-icer and can be easily blown off roadways or bridge decks. Large CMA de-icing particles melt through accumulated ice effectively. The presence of dust in the product decreases the amount of large particles used per truckload to efficiently melt the ice and snow.

The particle size of the production run samples is shown in table 14. The particle size distribution of these samples is somewhat different from the pilot run samples (table 14 vs. table 2). However, these differences probably do not account for the differences in the attrition rate observed.

As indicated above, these Task C CMA products have somewhat different particle size distribution from Task B samples. Both the Niro and Ferro-Tech processes can easily alter the particle size distribution of CMA. This is accomplished by recycling undersized material to the dryer. Oversized material can be crushed to the desired size and used directly. The wider size distribution of rock salt (table 14) is typical of a crushing operation rather than a controlled drying process.

The friability of the production samples was also determined (table 15). These results seem to indicate and confirm that the Niro P #2, and P #3 products are softer and more easily broken than the pilot run samples.

The hygroscopicity of the production samples were also measured. The results are shown in table 16. The Niro and Ferro-Tech Task C samples were all more hygroscopic than the pilot plant runs (compare data in table 16 with data in table 6). The increased affinity for water in these samples apparently affects the initial ice-melting rate (see below). We note that all products are more friable and more porous than the previous pilot plant products (table 15).

The bulk density (loose and packed) was determined for these production samples (table 17). The results are in the same range as the initial pilot run samples (table 9).

The chemical analysis of the production samples are shown in table 18. In these production runs the desired Ca:Mg was: Ferro-Tech TBG P1, 1.0; Niro P #2, 1.0; Niro P #3, 0.42. The Niro P #3 product was closest to the desired product. The water content of these products were also higher than in the previous pilot runs (table 7). The increased hygroscopicity, and water content could be important factors affecting ice melting ability (below).

Hygroscopicity of CMA products is probably controlled by porosity and pore size distribution. For instance, a non-porous or hard, film-like surface finish might lower the water absorption rate. We do not know if this property of CMA products can be controlled by any drying process.

The results of FHWA ice melting tests are shown in table 19. In general, good de-icers show reproducible quantities of melt in this test. The Ferro-Tech TBG P1 sample gave markedly lower melt yields than either Niro sample. In some cases, less melt was recovered

despite higher application rates of CMA product. For instance, applying 1.43g of Ferro-Tech TBG P1 CMA gave a melt yield of 0.33g; 1.91g of Niro TBG P1 gave a melt yield of 0.04g. These latter data illustrate the difficulties of the FHWA test with relatively poor de-icers. Hence, the Niro CMA products are better de-icers than the Ferro-Tech product according to this test.

The S. Dakota ice melting test results are shown in table 20. This test seems to be better suited to distinguish among relatively slow (compared to rock salt) de-icers. The data show that both Niro samples give significantly faster initial ice melting rates than the Ferro-Tech sample. Five hours after application, the melt yields from the Ferro-Tech and Niro samples are comparable. For instance, 30 minutes after application the S. Dakota melt yields average 6.46g compared to 1.8g melt from the Ferro-Tech sample. The 5 hour melt yields are: 25.02g for Ferro-Tech; 26.19g for Niro FBSG #2; 2318g for Niro FBSG #3. These data are also plotted in Figure 4. Figure 4 clearly shows the superior initial ice melting rate of the Niro samples.

Also shown in table 20 are S. Dakota ice melting test data for Gancy, SRI, and rock salt samples. These samples were run at a slightly lower temperature than the Niro and Ferro-Tech samples so that direct comparison between the two sets of samples is not possible. Rock salt, as expected, exhibits a very fast initial melt rate. We expect that at long times, these CMA products would produce about the same amount of melt as rock salt.

VI. CONCLUSIONS

The production of pilot samples of CMA by tumble bed drying (Ferro-Tech), fluidized bed spray granulation (Niro), and flash drying (Desicco) encountered several problems. Solution viscosity of 40% CMA solutions was a significant problem. However, pumps exist to handle those solutions. Desicco encountered problems with partially dried material adhering to the dryer walls; a larger diameter flash dryer was recommended. Both Ferro-Tech and Niro pilot products were acceptable. The Niro products had higher initial ice melting rates than the Ferro-Tech product and were slightly more dense. In all other respects the pilot products were similar.

In Task C, three extra CMA products were made. Ferro-Tech produced a 1:1 Ca:Mg product. This product handled somewhat more easily than the 3:7 CMA product. However, the properties of 1:1 Ca:Mg tumble bed dried CMA were slightly inferior to the pilot run (3:7 Ca:Mg) product. For instance, ice melting rates of the Ferro-Tech 3:7 Ca:Mg pilot CMA product were significantly higher than the 1:1 Ca:Mg product.

The Niro production products, P #2 and P #3, were also slightly inferior to the pilot run products. The ice melting rates of the Niro production products were slower than the Niro pilot products. Interestingly, there was little difference in properties between the 1.2:1 Ca:Mg (Niro P #2) and 3:7 Ca:Mg (Niro P #3) CMA products. Both Niro production products exhibited slightly better physical properties than the Ferro-Tech samples.

The main purpose of this contract was to find efficient ways to dry CMA solutions. Presumably, fermentation methods will be used to produce CMA solutions. Efficient water removal will be an important part of commercializing CMA. However, the user of CMA is most concerned with whether CMA will melt ice. A second and very important user question will be whether the benefits of using CMA justify the increas-

ed cost compared to rock salt. Our data permit a partial answer to the first question.

There is no doubt that CMA melts ice. However, the rate of ice melting using CMA is slower than that of rock salt. These differences are especially pronounced at short times after application. Rock salt shows a much higher initial ice melting rate. One implication of these ice melting rate data is that early warning and action by road crews is probably more important for CMA than for rock salt. However, ice-melting capacity of CMA is comparable to rock salt. Hence, if de-icer is spread early enough, equivalent melt should be found from CMA and rock salt.

CMA is also a softer, less dense material than rock salt. Attrition losses and loss of dusty CMA from road beds will be greater than that of rock salt. Since the density of CMA is about 1/2 that of rock salt, a truck of about twice the capacity (volume) must be used. These properties of CMA are less desirable than rock salt. Hence, from handling and initial ice melt data, CMA is a less useful product. However, reduced corrosion and pollution using CMA render this product an attractive alternative to rock salt. Our data also indicate that fluidized bed drying of FMA solutions results in a better solid CMA product.

VII. RECOMMENDATIONS

We recommend that CMA solution be dried by fluidized bed spray granulation. We also recommend that further research be conducted into flash drying. Flash drying studies should concentrate on optimizing the dryer size and feed solution concentration and rate so that partially dried material will not adhere to dryer walls.

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Table 1
CLASSES OF DRYERS FOR LIQUIDS & SOLIDS
(Adapted From Perry's Chem. Eng. Handbook
5th Ed., Sect. 20, pp. 18 & 19)

Suited for Drying Liquids (Solutions, Slurries and Pastes)

1. Continuous Tray or Belt - suitable for pastes, sludges and filter cakes. Dried products are in cake or crumb form.
2. Rotary or Tumbling Bed Dryers - solutions and slurries can be dried, if they are preblended with a stream of previously dried product. Products range from fine powders to agglomerated granules.
3. Pneumatic or Flash - hot gases vigorously mix and dry injected solutions and slurries. Fine atomization of liquid causes rapid drying. Product is a fine powder.
4. Spray - similar to 3. However, a large chamber is used in which gas velocities are low. As a result, product is a mixture of coarse porous spheres plus powder.
5. Screw Conveyor - a heated screw or an externally heated rotating cylinder gently conveys pastes or a solution/slurry wetted recycle stream of dried product. The absence of a drying gas stream eliminates dust carry out. Products are in crumb form with some powder.
6. Fluidized Bed - a low velocity gas stream suspends and dries granules which are formed by injecting solution onto a pre-existing or recycle stream of fine particles. Hard layered granules can be made by controlling rate of liquid addition temperature and residence time.
7. Drum - solution is poured over an internally heated rotating cylinder. Dried material is scraped off. Product is granular upon process completion, however, the ultimate friability and strength of the product is dependant upon the material itself.

Suited for Drying Wet Solids (Powders, Granules, sheets, Large Objects)

8. Batch Compartment - Trays or shelves are used to hold drying pastes and sludges. High investment and operating costs. Long drying times; best for low capacities.
9. Batch Through Circulation - Similar to 8. Shorter drying times. Pastes and sludges must have stable shape to allow passage of drying gases.

Suited for Drying Wet Solids, Continued

10. Continuous Through Circulation - similar to rotary dryer. Tumbling flights are wide shelves which suppress tumbling action.
11. Continuous Sheeting - suitable for continuous fabric drying.
12. Vacuum Shelf - suitable for small batch production. Expensive, used on high value, heat sensitive materials.
13. Vacuum Freeze - suitable for high value, heat sensitive materials.
14. Pan - suitable for small batch evaporation to dryness, where recovery of solvent is necessary.
15. Vacuum Rotary - suitable for small batch drying of heat sensitive materials fr where solvent recovery is necessary.
16. Heated Rollers - useful for drying sheets of thin materials.
17. Vibrating Tray - useful for drying free flowing materials having low moisture content which need to be conveyed.
18. Infrared - useful for drying thin films (coatings); electricity is costly for of energy.
19. Dielectric - useful for removing small amounts of moisture from large objects. Electricity is a costly form of energy.

Table 2

PARTICLE SIZE ANALYSIS
(Percent by Weight Passing)

Sieve Size	<u>Fluid Bed Spray Granulation</u>				<u>Tumble Bed Granulation</u>			Penn Dot Rock Salt	ASTM Salt Limits
	Run 1	Run 2	Run 3	Run 5	Run 1	SRI	Gancy		
1/2"		100.0	100.0			100.0	100.0	100.0	100
3/8"	100.0	99.3	99.5	100.0	100.0	99.1	90.9	98.6	95-100
#4	99.3	96.8	98.8	96.2	95.0	98.9	23.0	85.2	20-90
#8	92.0	89.6	59.1	62.5	5.6	89.2	0.6	62.1	10-60
#30	1.3	5.3	0.2	0.2	0.1	0.12	0.2	11.9	0-10

Table 3

QUALITATIVE FRIABILITY TEST RESULTS FOR TASK B SAMPLES

Niro Samples:

All five samples were harder than the 1:1 SRI product and approximately as hard as the Ferro-Tech sample

Ferro-Tech Sample:

Harder than SRI sample; approximately as hard as Niro samples

SRI Sample:

Most friable CMA sample studied

Rock Salt:

Significantly less friable than any of the CMA samples

Table 4

ATTRITION LOSS (PERCENT)

<u>Sample</u>	<u>+20 Mesh Presieved Attrition loss (%)</u>	<u>Not Presieved^(a) Attrition Loss (%)</u>
Ferro Tech	8.74	7.5
Niro #1	2.00	9.8
Niro #2	4.72	2.4
Niro #3 ^(b)	1.96	3.4(1st) 2.6(2nd) 2.6(3rd) ^(c)
Niro #4	1.61	1.7
Niro #5	1.54	2.0
Rock Salt	5.47	15.0
SRI ^(a)	--	33.2(1st) 35.2(2nd) ^(c)

(a) Original % of -20 mesh subtracted from each -20 mesh after the run to obtain % loss.

(b) Three consecutive attrition tests were run using the same sample; the +20 mesh material was not removed from the drum.

(c) % addition loss from the succeeding sample.

Table 5

CMA MICROSCOPIC ANALYSIS OF CRYSTAL HABIT AND STRUCTURE

Sample	Observations	
	CMA (-325 Mesh)	CMA (+325 Mesh)
FBSG #1	Individual Polycrystalline Particles	Individual Polycrystalline Particles Forming an Emmeshed Mass
FBSG #2	" "	" "
FBSG #3	" "	Individual Polycrystalline Particles Formed into Very Smooth Layers of Meshed Mass
FBSG #4	" "	Individual Polycrystalline Particles Forming an Emmeshed Mass
FBSG #5	" "	" "
TBG #1	" "	" "
SRI	" "	Individual Polycrystalline Particles Forming Small Masses Relative to the Above
Gancy	" "	Individual Polycrystalline Particles Forming Larger Masses Relative to the Above
Rock Salt	Pure Crystal Particle	Relatively Large Pure Crystalline Individual Particles

Table 6

HYGROSCOPICITY TEST RESULTS FOR TASK B CMA SAMPLES

<u>Sample</u>	<u>H₂O Weight Gain⁽¹⁾, % of Starting CMA</u>		
	<u>Ambient⁽²⁾</u>	<u>93% Rel Hum</u>	<u>Dry</u>
Ferro-Tech	0	1.2	-0.034
Niro #1	0.08	0.99	-0.013
Niro #2	--	1.07	+0.25
Niro #3	0.25	0.97	-0.04
Niro #4	0.21	1.07	-0.01
Niro #5	0.25	1.01	-0.03
Rock Salt	0.04	0.51	-0.01
Gancy	--	58.5	--
SRI	--	62.1	--

(1) See Section V.B.1 for outline of test method.

(2) These tests were performed by allowing the samples to equilibrate ambient moisture over a seven-day period. The ambient humidity was determined using a wet bulb technique:
Rel. Humidity

Day 1, 53%
Day 2, 52%
Day 3, 59%
Day 4, 58%
Day 5, 69%
Day 6, 80%
Day 7, 85%

Table 7

RESULTS OF CHEMICAL ANALYSIS OF TASK B CMA SAMPLES

Sample	Analysis of CMA, wt %					
	Ca ⁽¹⁾	Mg ⁽¹⁾	Acetate	H ₂ O	pH	[Ca/Mg] ⁽³⁾
Ferro-Tech	9.66	13.13	71.0	11.7(4.8) ⁽²⁾	9.4	0.44
Niro #3	13.4	18.15	72.0	3.59(3.0)	9.3	0.44
Niro #5	8.7	14.12	69.0	3.19(1.4)	9.6	0.37
SRI	11.5	8.19	76.6	5.50	--	0.84
Gancy	13.7	9.7	72.2	4.00	--	0.85
Ca _{0.6} Mg _{1.3} (C ₂ H ₃ O ₂) ₄ · 0.5H ₂ O	8.00	10.51	78.5	2.99	--	0.46

- (1) Determined by atomic absorption spectroscopy.
- (2) Water values (in parentheses) determined by weight loss after drying at 110° for 24 hours.
- (3) Mol ratio of Ca/Mg.

Table 8

HEATS OF SOLUTION OF SOME TASK B CMA PRODUCTS

<u>Sample</u> (Kcal/gmw)	<u>CMA</u> (wt %)	<u>Temp.</u> (°C)	<u>L' (H₂O)</u> (Btu/lb)	<u>L^M</u> (L/L')	<u>L (CMA)</u> Btu/lb)	<u>L (CMA)</u>
Niro#3	5	21	1054		4343	3539
		23	1052	4.12	4334	3531
		27	1048		4318	3519
	10	21	1054		3267	2662
		23	1052	3.10	3261	2658
		26	1049		3252	2650
Niro#5	5	21	1054		5175	4218
		23	1052	4.91	5165	4209
		27	1048		5146	4194
	10	21	1054		4364	3556
		23	1052	2.73	4355	3549
		25	1049		4343	3540
Ferro-Tech	5	21	1051		5249	4278
		23	1052	4.99	5248	4278
		26	1049		5235	4266
	10	21	1054		3815	3109
		23	1052	3.62	3808	3104
		26	1049		3797	3095

Table 9

LOOSE BULK DENSITY OF TASK B CMA PRODUCTS

<u>Sample</u>	<u>Density (lb/ft³)</u>
Ferro-Tech	24.8
Niro #1	34.2
Niro #2	35.7
Niro #3	34.2
Niro #5	31.3
Rock Salt	73.4
Gancy	29.
SRI	37.

Table 10

FHWA ICE MELT TEST RESULTS FOR CMA PRODUCTS

<u>Sample</u>	<u>CMA wt. gms</u>	<u>Temp. (°F)</u>	<u>Melted H₂O gms.</u>
Niro#5	(1) 0.956	15	0
	(2) 1.434	15	0.97
	(3) 1.912	15	2.5
	(4) 3.822	15	2.7
Ferro-Tech	(1) 0.956	15	0
	(2) 1.434	15	0
	(3) 1.912	15	0
	(4) 3.822	15	0

Table 11

ICE MELTING RATE AND CAPACITY TESTS FOR TASK B CMA PRODUCTS

Sample	Temperature		Initial Bottle Wt	Melted H ₂ O Weight (Grams)											Time/(hr)	
	°C	°F		.30	1:00	1:30	2:00	2:30	3:00	3:30	4:00	4:30	5:00	78:00		85:00
Ferro-Tech	-20	-4.0	76.64	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	4.47	6.37
	-10	14.0		NC	NC	X	X	5.17	6.80							
	-5	23.0		8.13	12.74	16.85	20.96	22.12	24.40	26.55						
	-2	28.4		12.24	17.24	19.75	23.03	24.62	26.39							
Niro #1	-20	-4.0	75.15	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
	-10	14.0		1.41	3.41	X	X	6.15	7.06							
	-5	23.0		12.4	16.68	20.01	24.02	25.05	26.93	29.21						
	-2	28.4		13.01	17.41	19.90	23.35	24.6	25.12							
Niro #2	-20	-4.0	76.58	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1.02	2.33
	-10	14.0		1.02	3.49	X	X	4.92	5.72							
	-5	23.0		11.24	15.34	17.95	20.76	21.57	23.37	26.37						
	-2	28.4		13.49	16.36	18.01	19.49	20.33	21.69							
Niro #3	-20	-4.0	76.45	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	4.89	5.66
	-10	14.0		4.01	7.48	X	X	11.82	12.96							
	-5	23.0		11.51	15.95	19.95	23.41	24.22	25.93	27.76						
	-2	28.4		13.48	16.68	19.08	23.00	24.46	25.78							
Niro #4	-20	-4.0	75.28	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	0.96	1.78
	-10	14.0		NC	2.17	X	X	5.74	7.08							
	-5	23.0		11.93	16.18	22.1	22.19	22.37	23.54	25.51						
	-2	28.4		15.41	19.28	21.03	22.94	24.07	24.80							
Niro #5	-20	-4.0	75.33	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	1.93	2.85
	-10	14.0		4.66	6.87	X	X	9.44	10.66							
	-5	23.0		11.91	16.23	19.43	22.31	22.57	23.88	25.70						
	-2	28.4		13.95	17.53	19.7	21.89	22.81	24.62							
Rock Salt	-20	-4.0	76.95	4.4	5.6	7.87	11.69	13.45	14.86	17.02	17.76	19.06	19.92	25.34	31.20	
	-10	14.0		9.44	17.7	X	X	31.35	33.46							
	-5	23.0		18.68	24.64	29.55	31.99	32.10	32.62	34.37						
	-2	28.4		20.56	27.22	30.34	31.86	31.82	31.87							

Table 12

SOLUBILITY CHARACTERISTICS OF 10, 20, 30 WT % TASK B CMA SAMPLES

<u>Sample</u>	<u>Wt % CMA Solution</u>	<u>Solubility Point, °C</u>
Ferro-Tech	10	27
	20	37
	30	63
Niro #1	10	21
	20	32
	30	68
Niro #2	10	24
	20	36
	30	64
Niro #3	10	23
	20	36
	30	65
Niro #4	10	27
	20	37
	30	73
Niro #5	10	23
	20	34
	30	72
Rock Salt	10	17
	20	22
	30	30

Table 13

ATTRITION TEST RESULTS FOR FERRO-TECH AND NIRO
TASK C CMA PRODUCTS

<u>Sample</u>	<u>Before Attrition</u>	<u>After Attrition, 30 min</u>		<u>% Losses</u>
	<u>+20 Mesh, gm</u>	<u>+20 Mesh, gm</u>	<u>-20 Mesh, gm</u>	
Niro, P#2	46.22	42.65	3.57	7.72
Niro, P#3	81.60	73.20	8.40	10.29
Ferro-Tech, TBG P1	45.43	42.67	2.76	6.08
Rock Salt ⁽¹⁾	--	--	--	5.47
SRI ⁽¹⁾	--	--	--	33.2

(1) Data from table 4; for comparison.

Table 14

PARTICLE SIZE DISTRIBUTION OF TASK C CMA PRODUCTS

Sieve Size	Ferro-Tech TBG P1		Niro, P#2		Niro, P#3		Rock Salt [1,2]	
	wt, gm	wt%	wt, gm	wt%	wt, gm	wt%	wt, gm	wt%
+3/8	0.00	0	0.00	0	0.00	0	1.41	1.42
-3/8 +4	21.6	21.5	0.04	0.037	0.00	0	13.26	13.34
-4 +8	74.4	73.9	8.40	7.81	0.40	0.4	22.99	23.12
-8 +30	4.3	4.3	97.80	90.98	93.70	94.46	49.90	50.19
-30 (pan)	0.3	0.3	1.26	1.17	5.10	5.14	11.87	11.94
	100.6	100.0	107.50	99.99	99.20	100.00	99.43	100.01

¹ Penn Dot sample of rock salt; analyzed by sieving at EMR.

² The following limits are described by ASTM D632 for Grade 1 sodium chloride (to pass): -1/2", 100%; -3/8", 95-100%; #4 U.S. Mesh, 20-90; #8 U.S. Mesh, 10-60%; #30 U.S. Mesh, 0-10%.

Table 15

RESULTS OF FRIABILITY TESTING ON TASK C CMA PRODUCTS

<u>Sample</u>	<u>Friability</u>
Ferro-Tech, TBGP1	Slightly more friable than Ferro-Tech (pilot run sample); larger size than TBG#1; TBGP2 more porous than Ferro-Tech (pilot run; see table 3)
Niro, P#2	Small, dense hard; more friable than Niro (Niro pilot samples 1-5; see table 3); very little porosity
Niro, P#3	Small particle; more friable than Niro (Niro pilot samples 1-5; see table 3); very little porosity

Table 16

RESULTS OF HYGROSCOPICITY⁽¹⁾ TESTS FOR TASK C CMA SAMPLES

<u>Sample</u>	<u>Initial Weight (gm)</u>	<u>Final Weight (gm)</u>	<u>H₂O Weight Gained (gm)</u>
Ferro-Tech, TBGP1 (TBG #2)	3.94	5.89	1.95
Niro P#2	3.98	6.26	2.28
Niro P#3	3.97	7.55	3.58
Gancy	4.15	6.58	2.43
SRI	4.04	6.55	2.51

(1) Samples were pre-weighed and placed in a dessicator over saturated $\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ (93% relative humidity) for 7 days. The samples were then rapidly removed, weighed and gain in water weight determined.

Table 17

BULK DENSITY OF TASK C CMA PRODUCTS

<u>Sample</u>	Density				
	<u>Sample wt., gm.</u>	<u>Volume, ml.</u>		<u>Density g/ml</u>	
		<u>Loose</u>	<u>Packed</u>	<u>g/ml</u>	<u>lb/ft³</u>
Ferro-Tech, TBG#2	30.00	6.50	--	0.46	29
	30.00	--	6.30	0.48	30
Niro, FBSG#2	30.20	51.5	--	0.59	37
	30.20	--	51.5	0.59	37
Niro, FBSG#3	30.00	57.0	--	0.53	33
	30.00	--	56.8	0.53	33
Gancy	30.00	63		0.47	29
SRI	30.00	50		0.60	37

Table 18

CHEMICAL ANALYSIS OF CMA PRODUCTS⁽¹⁾

<u>Sample</u>	<u>Analysis</u>		<u>Ca, wt%</u>	<u>Mg, wt%</u>	<u>Ca/Mg Atomic</u>
	<u>% Acetic Acid</u>	<u>% H₂O</u>			
Ferro Tech, TBG P1	61.1	15.7	9.05	6.90	0.78
Niro, P#2	66.4	9.2	15.35	7.16	1.29
Niro, P#3	61.0	5.8	8.74	14.01	0.37

¹¹⁾ All analyses were performed by Chem-Clear, Inc., Wayne, PA 19087.

Table 19

FHWA ICE MELTING CAPACITY TESTS AT 25°F FOR TASK C CMA SAMPLES

<u>Sample</u>	<u>Pan No.</u>	<u>Wt. CMA, gm.</u>	<u>Wt. Melted H₂O, gm.</u>
Ferro-Tech			
TBG P#1	3	0.96	0.17
	9	1.43	0.33
	2	1.91	0.04
	11	3.82	0.21
<hr/>			
Niro, P#2	5	0.96	6.14
	11	1.43	7.33
	2	1.91	9.17
	3	3.82	22.80
<hr/>			
Niro, P#3	4	0.96	3.49
	8	1.43	5.97
	0	1.91	4.51
	9	3.82	26.64

Table 20

SOUTH DAKOTA ICE MELTING CAPACITY TESTS AT 25°F (10g CMA/30g ICE
VIAL WEIGHT WITH MELT, gm (gm MELT)

Sample	Initial														
	Vial	0.5 hr	1.0 hr	1.5 hr	2 hr	2.5 hr	3 hr	3.5 hr	4 hr	4.5 hr	5 hr	5.5 hr	6 hr	6.5 hr	24 hr
	wt. gm.														
Ferro-Tech TBG#2	70.21 (1.8)	72.01 (1.8)	75.02 (4.81)	80.51 (10.3)	83.84 (13.63)	85.06 (14.85)	85.69 (15.48)	86.02 (15.81)	88.73 (18.52)	91.47 (21.26)	95.23 (25.02)	98.00 (27.79)	98.53 (28.32)	98.66 (28.45)	100.35 (30.14)
Niro FBSG#2	71.26	78.02 (6.76)	80.10 (8.84)	84.71 (13.45)	88.56 (17.30)	90.10 (18.84)	90.87 (19.61)	91.08 (19.82)	92.50 (21.24)	95.33 (24.07)	97.45 (26.19)	99.08 (27.83)	99.28 (28.02)	99.30 (28.04)	99.49 (28.23)
Niro FBSG#3	69.90	76.00 (6.10)	78.84 (8.94)	83.59 (13.69)	86.45 (16.65)	86.67 (16.77)	87.87 (17.97)	87.90 (18.00)	88.36 (18.40)	90.26 (20.36)	93.07 (23.18)	95.28 (25.38)	95.90 (26.00)	95.99 (26.09)	98.00 (28.10)

SOUTH DAKOTA ICE MELTING RATE AND CAPACITY TESTS

Sample	Temperature		Initial Bottle Weight (gm)	Melted H ₂ O Weight (gm)							
	°C	°F		Time (hr):	0.5	1.00	1.5	2.00	2.5	3.00	22.5
Gancy	-5	23	75.10	NC	2.69	9.86	--	--	--	--	--
SRI	-5	23	75.42	3.2	10.43	18.81	--	--	--	--	--
Rock Salt	-5	23	75.19	8.45	19.26	28.26	--	--	--	--	--

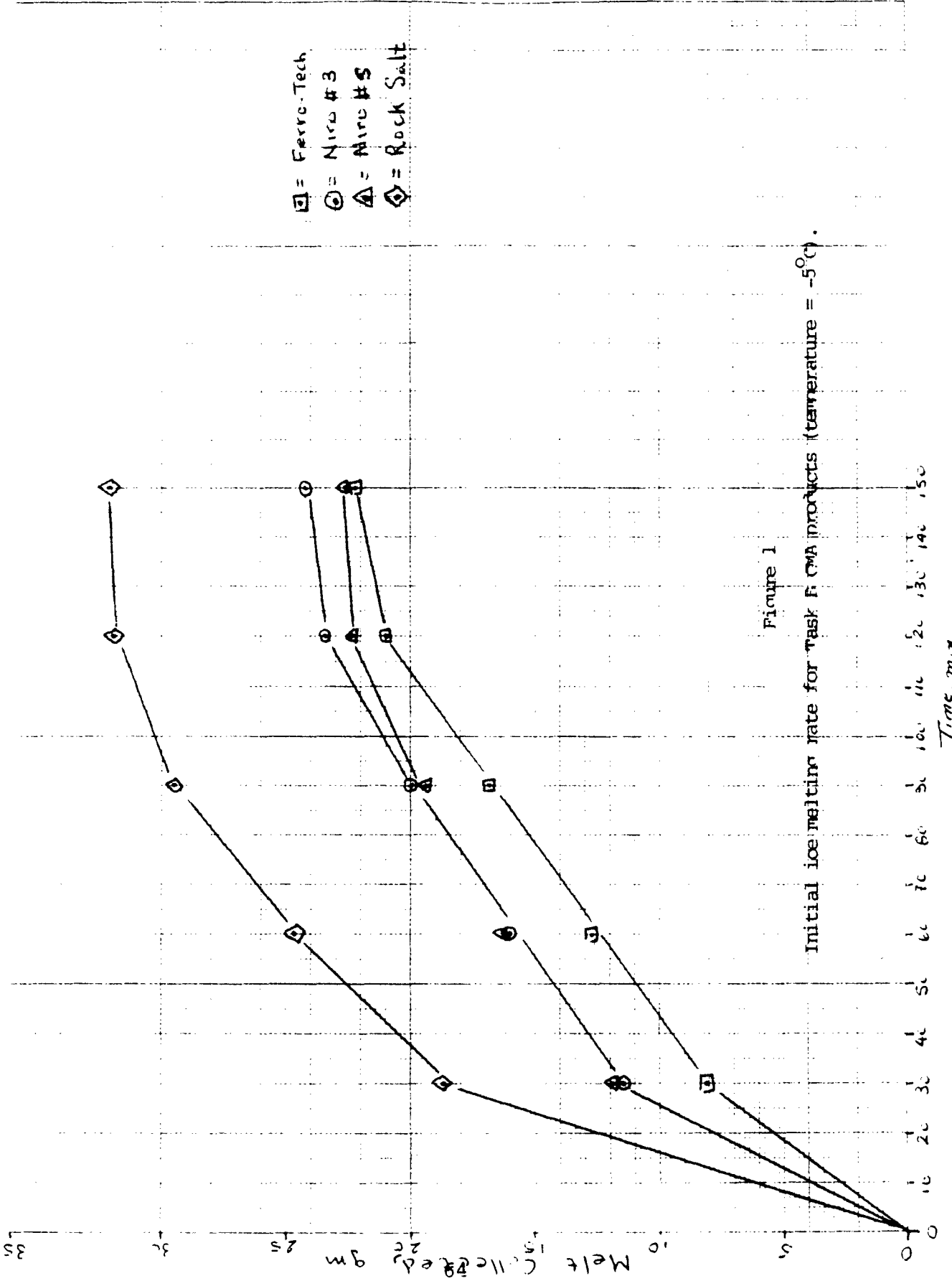


Figure 1

Initial ice melting rate for Task F CWA products (temperature = -5°C).

Time, min.

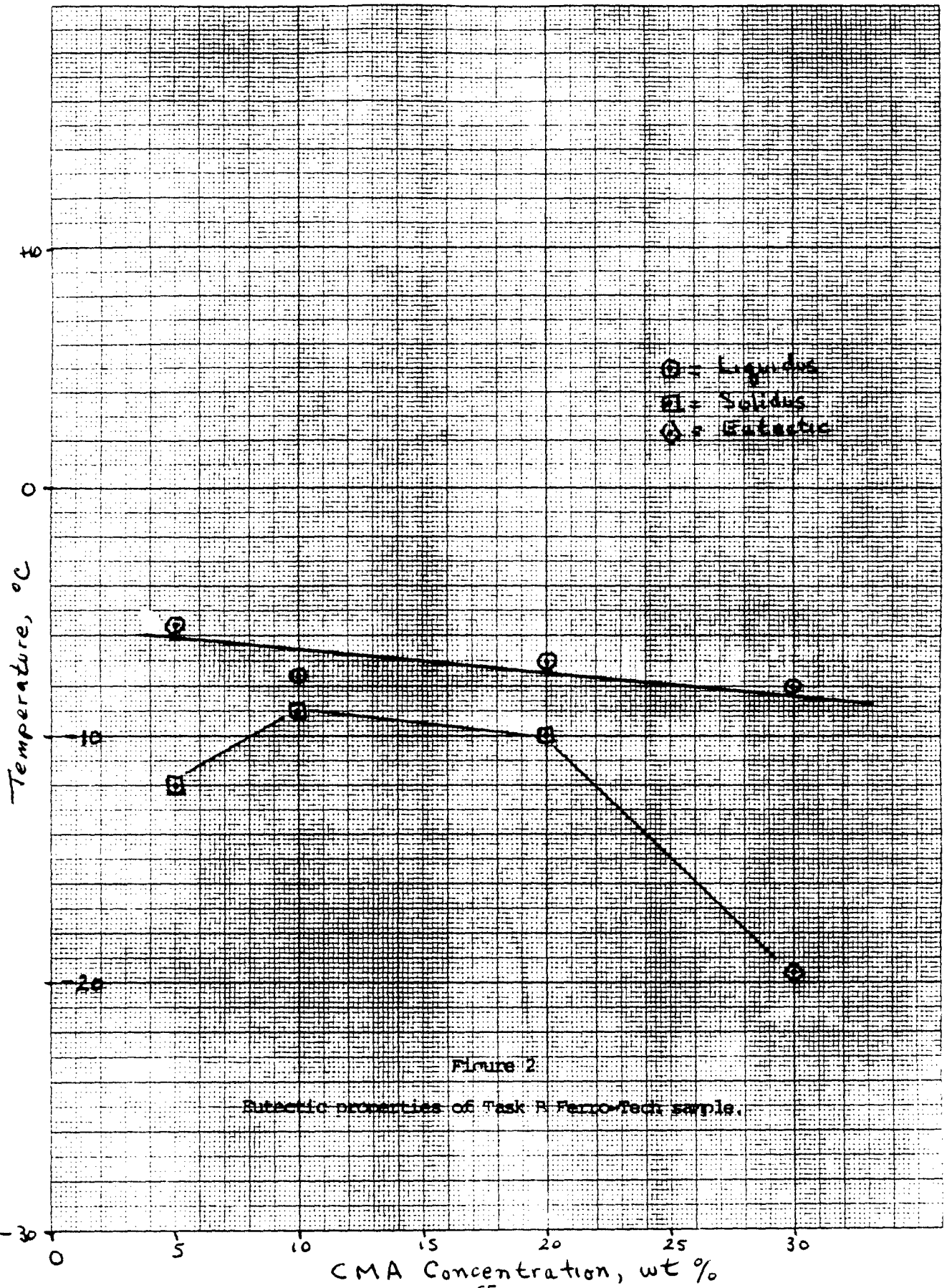


Figure 2

Eutectic properties of Task B Ferro Tech sample.

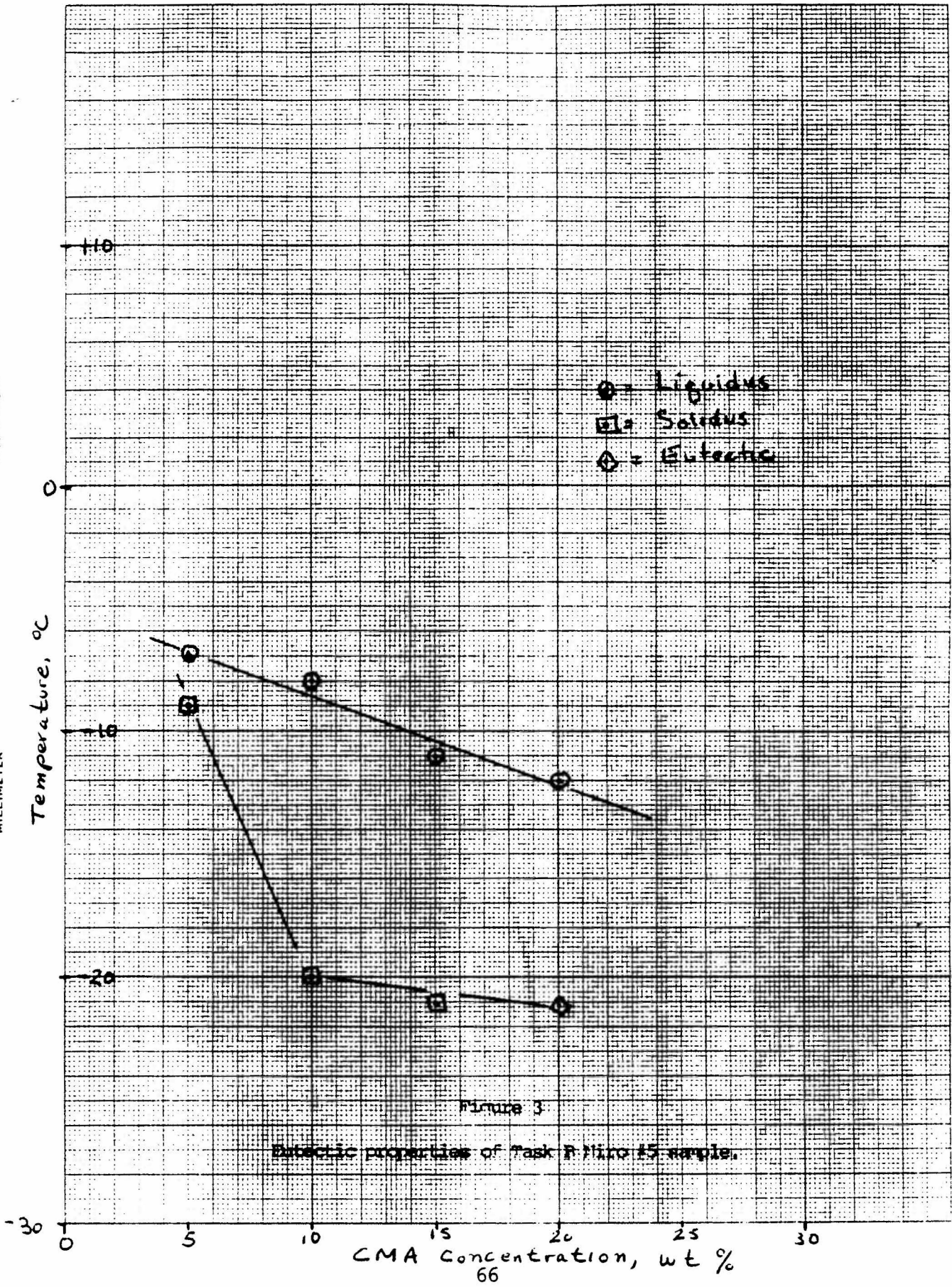


Figure 3

Eutectic properties of Task R Micro 15 sample.

