

<i>Cryst. Res. Technol.</i>	35	2000	9	1035–1049
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Investigation of the Conditions for the Production of Calcium Magnesium Acetate (CMA) Road Deicer in an Extractive Crystallization Process

Calcium magnesium acetate (CMA) is considered as the best road deicer to replace the environmentally unacceptable NaCl and CaCl₂. However, the high cost of CMA prohibits its widespread use. The present study is dealing with the investigation of a crystallization method for the production of deicing CMA crystals of desired physical properties and the elucidation of the conditions under which such a product can be formed. Extractive crystallization is promising for the low cost production of CMA crystals considering that acetic acid is produced by a biochemical method and removed from the fermentation broth *in situ* by organic extractant systems. In this method, this organic phase, which contains the acetate ions is contacted with an aqueous phase which is the source of calcium and magnesium ions. The extractive crystallization process resulted in the production of well-formed, large, and non-spherical crystals of calcium acetate (CA), magnesium acetate (MA), and calcium magnesium acetate double salt (CMADS). The crystal size was affected by the concentration of acetic acid in both the organic and aqueous phases, whereas the crystal type and hydration level were determined primarily by the acetic acid concentration in the aqueous phase. The molar ratio of the precursor salts (CaCO₃/MgCO₃) in the reaction mixture was found to be the major factor for determining the habit and Ca/Mg content of crystals. Crystallization of CMADS was favored at high concentrations of acetic acid in the aqueous phase and at higher temperatures as shown from supplementary evaporation-to-dryness experiments.

Keywords: calcium acetate, magnesium acetate, calcium magnesium acetate, CMA, extractive crystallization, deicing, acetic acid extraction

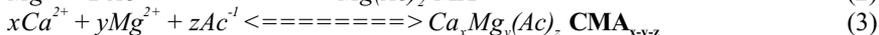
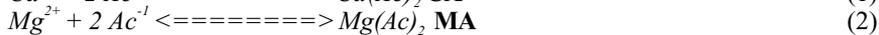
(Received February 28, 2000; Accepted July 26, 2000)

1. Introduction

CMA, a relatively new product in the world market, is a chemical with two major large scale potential applications for solving environmental problems [WISE et al. 1991]: (a) as the best road deicing salt candidate to replace the corrosive and environmentally unacceptable sodium chloride (NaCl) and calcium chloride (CaCl₂) currently in use for road and highway deicing [GIDLEY 1991; HORNER et al. 1991; SCHENK 1991-2] and (b) as a control agent for the toxic particulate, SO_x and NO_x emissions [LEVENTIS et al. 1993; SHUCKEROW et al. 1996; STECIAC et al. 1995], as well as an effective catalyst for the facilitation of coal combustion [LEVENTIS 1991].

Currently there is some uncertainty in literature and in practice about the definition of CMA. Calcium and magnesium are forming calcium acetate (CA) and magnesium acetate (MA) crystals, respectively, with various hydration levels depending upon the manufacturing conditions. When combined, they can also form crystals of a double salt, calcium magnesium acetate, Ca_xMg_y(C₂H₃O₂)_{2(x+y)}, i.e., a crystal of a compound that has both metals in its lattice. The term CMADS will be used in this study to designate crystals of the double salt. More

specifically, the term CMA_{1-2-6} will be used to denote crystals of $\text{CaMg}_2(\text{C}_2\text{H}_3\text{O}_2)_6$. In an aqueous environment, depending on the different conditions, the following reactions can occur [SU 1990]:



where Ac^{-1} stands for CH_3COO^- and z is equal to $2(x+y)$. Cryotech CMA Deicer, the current commercial product, has the following empirical formula: $\text{Ca}_x\text{Mg}_y(\text{C}_2\text{H}_3\text{O}_2)_{2(x+y)}$ where x can vary between 3 and 4 and y can vary between 6 and 7. Chemically the product is composed of 91% wt./wt. CMADS, 5% wt./wt. water (free and hydration), and 4% wt./wt. water-insoluble material. Physically, the product has the appearance of hard spherical pellets with specific gravity of 1.2 and generally uniform size. The product has a eutectic point of about -27°C which is lower than that of sodium chloride (-22°C) and urea (-13°C) [CRYOTECH 1994; SCHENK 1985, 1991-1; TODD 1990].

CMA is commercially produced by reacting a mixture of calcium and magnesium carbonates, mainly dolomitic lime, with acetic acid to produce a solution of calcium and magnesium acetate. The solution is then evaporated to dryness, usually in spray dryers, to obtain a crystalline powder of CMA, a result of massive crystal nucleation during the process. This powder is subsequently pelletized to provide a final product of large, spherical and porous particles [CRYOTECH 1994; TODD 1990]. The acetic acid used in the process is very expensive comprising about 70% of the total cost of CMA. Moreover, the spray dryers are very expensive equipment contributing to the high cost of CMA. The current price of commercial CMA ranges from about \$926 to \$2450 per metric ton [CRYOTECH 2000]. This high cost has been the major barrier for the large-scale application of CMA and many attempts have been made to develop alternative methods for acetic acid production.

The great importance of CMA has resulted to the study and development of a number of methods for its manufacturing, which can be divided in two groups. The methods in the first group utilize acetic acid obtained from natural gas or oil [GANCY 1984; TODD 1990], while those in the second group are based on the use of acetic acid produced biochemically by the fermentation of agricultural, municipal and industrial wastes, and forestry residues [BUNGAY and HUDSON 1987; PALASANTZAS and WISE 1994; REISINGER and KING 1995; WISE and AUGENSTEIN, 1988]. The most effective methods are those involving production of acetic acid by biochemical processes [MARYNOWSKI 1983; PALASANTZAS and WISE 1994].

In another study for the preparation of deicing crystals from one-salt systems we reported that the extractive crystallization process proved to be effective and resulted in large single crystals of either calcium acetate acetic acid monohydrate or magnesium acetate tetrahydrate depending on the type of salt (CaCO_3 or MgCO_3 , respectively) used [DIONYSIOU et al. 2000]. In the present study, the acetate salts were crystallized from a solution containing both calcium and magnesium ions. The design of the extractive crystallization system was based on three premises. (a) The anticipated source of acetic acid is an organic phase containing the acetic acid extracted from a biomass fermentation broth; (b) The generation of supersaturation at room temperature by mass transfer from the organic phase to the aqueous phase containing the calcium and magnesium ions, is more economical than the evaporation technique currently used; and (c) The aim is the formation of relatively large, non-porous, and non-spherical crystals of CA or MA that can be applied directly as road deicer without prior pelletization. Other objectives of this study were to delineate the conditions under which CMADS or other CMA crystals (mixtures of CA and MA) can be formed, to investigate the effect of those conditions on the crystal habit and size, and to collect data that would facilitate the design of a scaled-up process.

2. Experimental Section

Reagents and Chemicals

Calcium carbonate, CaCO_3 , (>99.0%, Fisher Scientific), magnesium carbonate, MgCO_3 (reagent, assay: 40.0-43.5% as MgO , Fisher Scientific) and glacial acetic acid, CH_3COOH (99.7%, Fisher Scientific) were used as the starting material. CaCO_3 and MgCO_3 are in general insoluble in water (0.00153g/100 ml water and 0.04 g/100 ml water at 20 °C respectively). The extractant system comprised of 50/50 (v/v) mixture of Alamine 336 extractant (a mixture of tertiary amines consisting of trioctyl- and tridecylamines) (95-97%, Henkel Corporation) and 2-ethyl-1-hexanol (99.0%, Fluka Chemica-Biochemica Co). The selection of this extractant system for the extractive crystallization process has been discussed elsewhere [DIONYSIOU 1995; TSIANOU 1995]. Seeds of commercial CMA (Cryotech Deicing Technology) were used to study the effect of secondary nucleation in the process.

Equipment and Chemical Characterization

A Nikon MF-119 camera attached to a Nikon Microscope (Model N2000), a SZ-CTV Olympus Microscope connected with Sony Color Video Printer (GVP-G 700), and a Minolta XG-M with macro lenses (50 mm) and Vivitar Extension Tubes were used to examine and photograph the crystals, depending on their size. The need to use three different pieces of photographic equipment was due to the different sizes of the crystals obtained in the various experimental conditions investigated. RFP filters (Whatman and Marke Selecta, Germany) were used for the filtration of the saturated solutions. An isotherm oven was used for experiments conducted at elevated temperatures. Atomic Absorption (AA) Spectroscopy (Smith-Hieftje 1000 Automated AA/AE Spectrophotometer) was employed for measuring calcium and magnesium concentrations in the saturated solutions and for identifying the calcium to magnesium molar ratio in the obtained crystals. X-Ray Diffraction (XRD) (NICOLET, Model I 2/2000 and Rigaku with CuK_α radiation) was employed for the characterization of crystals.

Experimental Method

The extractive crystallization system comprised of two phases: an aqueous (bottom phase) as the source of calcium and magnesium ions and an organic (extractant system containing acetic acid; top phase) as the source of acetate ions. The aqueous phase comprised of a saturated solution of calcium or magnesium acetates while the organic phase comprised of a mixture of acetic acid in organic solvents simulating an organic mixture as extracted from a fermentation broth by solvent extraction.

The detailed experimental procedure was as follows: Saturated solutions containing both Ca^{2+} and Mg^{2+} were prepared by reacting mixtures of calcium carbonate and magnesium carbonate with acetic acid. Preparation of the saturated solutions as well as the formation of the two-phase system was carried out at 20°C ($\pm 1^\circ\text{C}$). The molar ratio (Ca/Mg) of the two elements usually varied in the range from approximately 88/12 to 8/92 (or 10/90 to 90/10 wt./wt. of the precursor $\text{CaCO}_3/\text{MgCO}_3$ salts; variable B in Table 1). The content of acetic acid in the aqueous phase (variable A) varied from 30% to 100% (v/v) (or about 31% to 100% wt./wt. as presented in Table 2). Systems containing less than 30% (v/v) acetic acid in the aqueous phase were not studied, since in the preliminary experiments this low acetic acid content failed to produce any crystals. Before the formation of the two-phase system, samples of saturated solution containing Ca^{2+} and Mg^{2+} were analyzed by AA.

Symbol	Variable	Range of variation
A	Content of acetic acid in the aqueous phase	From 20% to 100% by volume with 10% increment
B	Ratio of the precursor salts $\text{CaCO}_3/\text{MgCO}_3$ for varying the molar ratio of $\text{Ca}^{2+}/\text{Mg}^{2+}$ in the saturated solution.	From 100% to 0% by weight with 5% and 10% increments.
C	Content of acetic acid in the organic phase.	From 10% to 70% by volume with 10% increment.
D	Addition of seeds of commercial CMA.	D=0 : no seeds D=1: seeds added

Table 1: Variables and range of variation investigated in the extractive crystallization process.

Acetic acid in organic phase		Acetic acid in aqueous phase*	
% v/v	% wt./wt.	% v/v	% wt./wt.
10	12.5	20	20.7
20	24.3	30	31.02
25	30.0	40	41.16
30	35.5	50	51.20
35	40.9	60	61.15
40	46.1	70	71.0
50	56.2	80	80.76
60	65.8	90	90.42
70	75.0	100.0	100.0

* Before the addition of CaCO_3 and MgCO_3

Table 2: Acetic acid variations in organic and aqueous phases.

Subsequently, 5 ml of saturated solution was added in each of two series (duplicates) of 40 ml beakers. To each 5 ml saturated solution, 20 ml of organic phase was added slowly along the glass surface of the beaker using a 20 ml pipette to avoid mixing the two phases. The direct addition of organic phase to aqueous phase was avoided to prevent the formation of small droplets of one phase in the other phase, which was observed when mixing was not gentle. The highest content of the acetic acid used in the organic phase (variable C) was 70% (v/v) (i.e., 75% wt./wt as presented in Table 2). At higher content of acetic acid (>70% v/v) the formation of the two-phase system was not visually distinct. After five days, the obtained crystals were collected, cleaned carefully to remove any attached amount of organic phase, and photographed. The crystal yield was also measured after they were dried at room temperature in a desiccator.

In limited experiments, the effect of temperature on the formation of CMA_{1-2-6} was examined using an evaporation-to-dryness procedure instead of the method mentioned above. These experiments were performed to evaluate the importance of temperature on the crystallization of this material. In this method, 5 ml of saturated solutions containing mixtures of Ca^{2+} and Mg^{2+} were placed in an isotherm oven until all the liquid was completely removed leading to small dry particles. Saturated solutions were prepared from various systems of 30% to 50% v/v acetic acid in the aqueous phase and 50/50 to 20/80 $\text{CaCO}_3/\text{MgCO}_3$ mass ratio. The designed temperature range was from 40 to 120°C. For comparison, the same experiments were also conducted at room temperature.

The crystals produced were later ground to powder and analyzed by X-ray crystallography to identify their crystal structure. Solutions of the crystals in deionized water were analyzed by AA spectroscopy to identify their Ca and Mg content.

3. Results and Discussion

This investigation involved in general terms the study in the laboratory of a process producing CMA by extractive crystallization. This approach is anticipated to lead to a lower cost than the commercial process and in a product form having better applicability than the pellets of the commercial CMA currently used. The unique features of the process are as follows: (a) As a starting material, an organic liquid phase loaded with acetic acid is used. This stimulates the acetic acid-containing organic liquid extractant that is obtained from the extractive fermentation of biomass. (b) The organic phase is brought in contact with an aqueous phase containing calcium and magnesium ions. The acetic acid is re-extracted from the organic phase to the aqueous phase, where in combination with the high concentration of the calcium and magnesium ions generates supersaturation and thus crystals of calcium acetate and/or magnesium acetate or crystals of CMADS are formed. These crystals are recovered and constitute the final product. In this way the drying and pelletization stages are eliminated. (c) Crystals could be obtained that are well formed, relatively large (i.e., 2 to 10 mm), non-spherical, equidimensional (i.e., not needles or plates) and non-porous. Such crystals will behave more like the crystals of the sodium chloride deicer rather than the pellets of the commercial CMA. The latter have the disadvantage of bouncing of the pavement resulting to an uneven distribution during their application. Detailed results and discussion for the whole range investigation is presented elsewhere [DIONYSIOU 1995]. In this paper, only representative results and general trends will be discussed.

Saturated Solutions

As an example presented here, Figure 1 shows the concentration of Ca^{2+} and Mg^{2+} in the saturated solution as a function of MgCO_3 mass ratio (i.e., as a fraction of total $\text{MgCO}_3 + \text{CaCO}_3$) added in the aqueous phase containing 30% (v/v) acetic acid. As expected and shown in Figure 1, the concentration of Ca^{2+} decreases as the mass ratio $\text{CaCO}_3/\text{MgCO}_3$ of the precursor reacting salts decreases (i.e., increase in MgCO_3 content) [DIONYSIOU 1995]. The opposite occurs for Mg^{2+} . It was also observed that the concentrations of both Ca^{2+} and Mg^{2+} decreased as the content of acetic acid in the aqueous phase increased from 30% to 100% v/v. This trend was expected since both calcium acetate and magnesium acetate are soluble in water (25.8 g/100 g saturated solution and 38.8 g/100 g saturated solution, respectively at 20°C) but insoluble in acetic acid [SAURY et al. 1993; TSIANOU 1995]. As also shown in Figure 1, the total concentration of Ca^{2+} and Mg^{2+} increases as the MgCO_3 ratio in the reactant salts increases since the solubility of magnesium acetate is higher than that of calcium acetate at 20°C.

Nucleation and Growth

Nucleation occurred in about 24 to 30 hours for the non-seeded systems and in about 18 to 24 hours for the seeded systems. Crystal nucleation and growth at the early stages of crystal formation was taking place at the interface of the organic and aqueous phases where the supersaturation increased initially. When the crystals were large enough and the gravitational forces could overcome the interfacial surface tension forces, they submerged to the bottom of the beaker in the aqueous phase where they continued to grow.

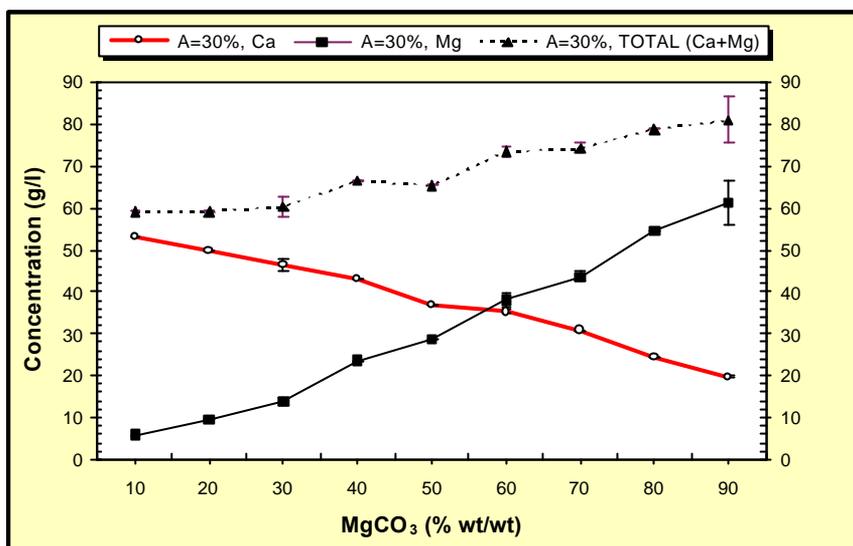


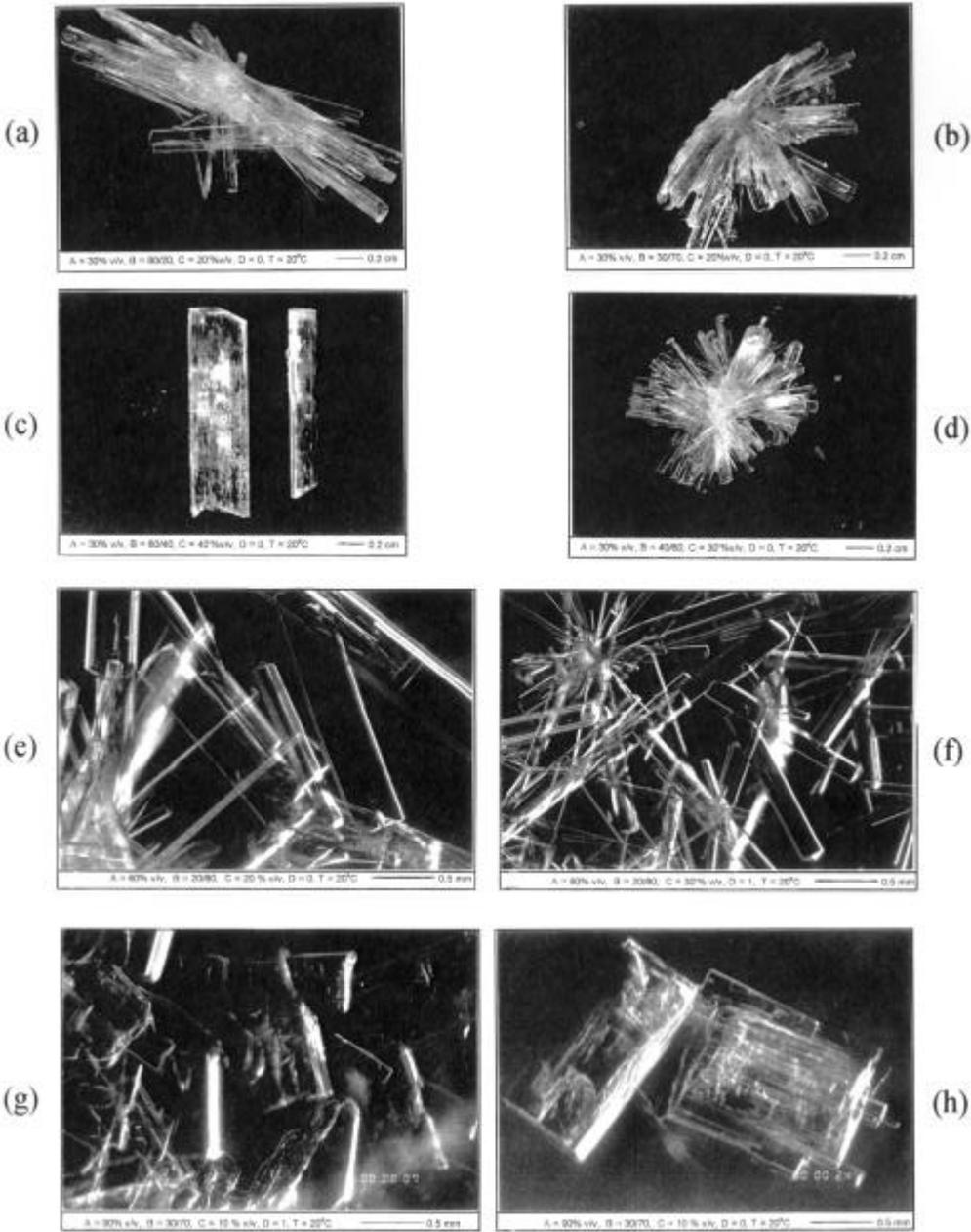
Fig. 1: Concentration of Ca^{2+} and Mg^{2+} in the saturated solution in the system with $A=30\%$ v/v acetic acid in the aqueous phase and at various $\text{MgCO}_3/\text{CaCO}_3$ mass ratios of the reacting precursor salts. The "error bars" in the figure represent the maximum and minimum values for the two points and not the statistical error bars [DIONYSIOU 1995].

At low content of acetic acid in the aqueous phase ($A=30$ and 40% v/v) and high to intermediate $\text{CaCO}_3/\text{MgCO}_3$ mass ratio ($B>30/70$ wt./wt.), large size crystals and clusters with length up to 3 cm and diameter up to 0.4 cm were usually obtained for the systems containing 20% to 50% v/v acetic acid in the organic phase. In systems containing 10% acetic acid (v/v) in the organic phase, needle-like crystals were obtained on the glass surface of the beaker in the organic region. This is probably due to migration of Ca^{2+} and Mg^{2+} ions from the aqueous to the organic phase along the glass surface and formation of crystals (on the glass surface) in the organic phase. Preliminary findings of this phenomenon are reported elsewhere [DIONYSIOU 1995; TSIANOOU 1995]. Figure 2-a, b shows large clusters obtained at low content of acetic acid in the aqueous phase ($A=30\%$ v/v), high and intermediate $\text{CaCO}_3/\text{MgCO}_3$ mass ratio, ($B=80/20$ and $30/70$ wt./wt.), and low content of acetic acid in the organic phase ($C=20\%$ v/v).

Figure 2-c, d also shows the formation of single crystals and starlike clusters (spherulites) obtained under similar conditions. Formation of crystal clusters, aggregates or conglomerates with no symmetrical properties is a phenomenon that is not fully understood, but it is very common especially in large-scale crystallization systems. Factors that may favor the formation of such crystals include poor agitation, presence of certain impurities in the crystallization solution, seeding at high degrees of supersaturation, and the presence of too many seed crystals [MULLIN 1972]. The most important reason for the formation of crystal clusters with no symmetrical properties observed in our study is mainly believed to be the absence of agitation.

When the content of acetic acid in the aqueous phase was increased to 50% and 60% v/v the size of the obtained crystals also decreased as shown in Figure 2-e, f (note change in scale). At higher ($A\geq 70\%$ v/v) content of acetic acid in the aqueous phase, the obtained crystals were even smaller and were seen through the microscope. Crystals obtained at such conditions are shown in Figure 2-g, h.

At higher content of acetic acid in the organic phase the size of crystals decreased and in some cases no crystals were obtained. Figure 2-i, j, k, l shows the morphology of crystals obtained as a function of two parameters: volume concentration of acetic acid in the organic phase and $\text{CaCO}_3/\text{MgCO}_3$ mass ratio. The concentration of acetic acid in water was kept constant at 30% v/v.



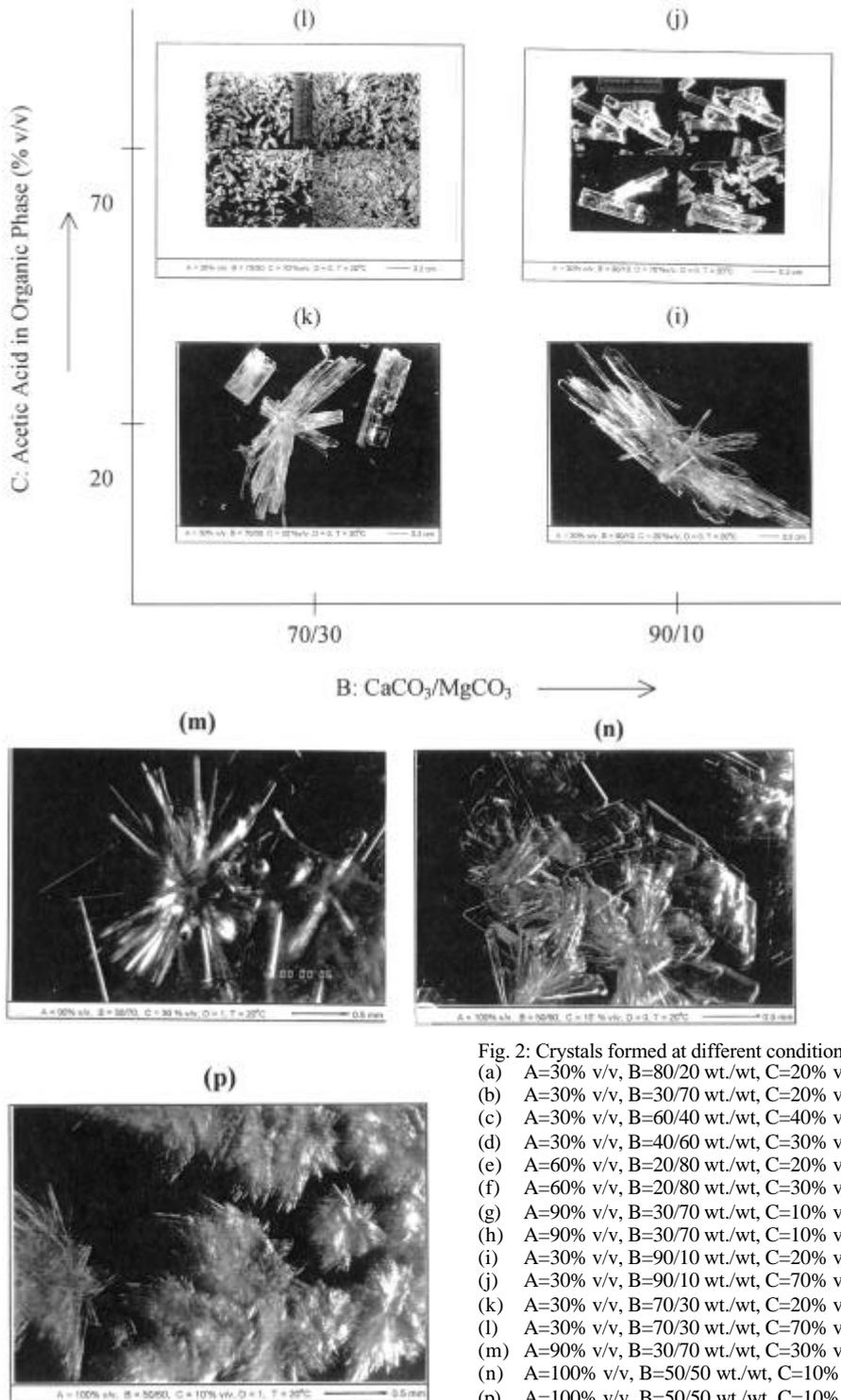


Fig. 2: Crystals formed at different conditions.
 (a) A=30% v/v, B=80/20 wt/wt, C=20% v/v, D=0.
 (b) A=30% v/v, B=30/70 wt/wt, C=20% v/v, D=0.
 (c) A=30% v/v, B=60/40 wt/wt, C=40% v/v, D=0.
 (d) A=30% v/v, B=40/60 wt/wt, C=30% v/v, D=0.
 (e) A=60% v/v, B=20/80 wt/wt, C=20% v/v, D=0.
 (f) A=60% v/v, B=20/80 wt/wt, C=30% v/v, D=1.
 (g) A=90% v/v, B=30/70 wt/wt, C=10% v/v, D=1.
 (h) A=90% v/v, B=30/70 wt/wt, C=10% v/v, D=0.
 (i) A=30% v/v, B=90/10 wt/wt, C=20% v/v, D=0.
 (j) A=30% v/v, B=90/10 wt/wt, C=70% v/v, D=0.
 (k) A=30% v/v, B=70/30 wt/wt, C=20% v/v, D=0.
 (l) A=30% v/v, B=70/30 wt/wt, C=70% v/v, D=0.
 (m) A=90% v/v, B=30/70 wt/wt, C=30% v/v, D=1.
 (n) A=100% v/v, B=50/50 wt/wt, C=10% v/v, D=0.
 (p) A=100% v/v, B=50/50 wt/wt, C=10% v/v, D=1.

The Figure shows a decrease in the crystal size (in terms of needle length) as the content of acetic acid in the organic phase was increased from 20 to 70% v/v at the high $\text{CaCO}_3/\text{MgCO}_3$ mass ratio (B=90/10 and 70/30 wt./wt.) used. From a comparison between Figure 2-i, j, k, l, it can be seen that the formation of small single crystals instead of crystal clusters was much more pronounced at high acetic acid concentrations in the organic phase. The results obtained by varying the acetic acid in the organic phase in this study were generally in agreement with those obtained previously in the one salt systems [DIONYSIOU 1995; DIONYSIOU et al. 2000].

As the $\text{CaCO}_3/\text{MgCO}_3$ ratio of the precursor salts decreased, the size of crystals also decreased. At such conditions, the obtained crystals were usually prismatic and they formed at low concentrations of acetic acid in the organic phase. At these conditions the obtained crystals were usually single crystals and cluster formation was not favored. At intermediate $\text{CaCO}_3/\text{MgCO}_3$ ratio the crystals had intermediate size and their habit resembled that of both type of crystals obtained at high and low $\text{CaCO}_3/\text{MgCO}_3$ ratio. This result is also in agreement with that obtained from the experiments with the one salt systems [DIONYSIOU 1995]. In the extreme case of CaCO_3 as the only precursor salt, the obtained crystals had a rodlike shape, whereas the crystals obtained in the opposite extreme case of MgCO_3 as the precursor salt the obtained crystals were prismatic and smaller [DIONYSIOU et al. 2000].

Experiments with seeded systems showed that seeds could result in either growth of the seeds or secondary nucleation of other crystals. A typical growth of a seed crystal is shown in Figure 2-m, compared to no crystal formation at the same conditions for non-seeded experiments. Results for the system of A=30% v/v acetic acid in the aqueous phase, B=10/90 wt./wt. of the precursor reactants $\text{CaCO}_3/\text{MgCO}_3$, and C=20% and 30% v/v acetic acid in the organic phase showed that crystals were only formed in the seeded systems. The habit of crystals obtained in the seeded systems was generally found to differ slightly from that of the crystals obtained from the non-seeded experiments shown in Figure 2-n, p. At the very high content of acetic acid in the aqueous phase (A=90% and 100% v/v), the obtained crystals had a prismatic habit compared to the rodlike habit obtained at the systems where this concentration was low (see Figure 2-c). Figure 2-n, p also shows that the crystals obtained from the seeded experiments had a habit similar to that of twin crystals. As in the case of parallel growth, twinning is generally observed in undisturbed crystallization solutions and is a phenomenon more frequently observed for crystals belonging to the orthorhombic or monoclinic systems [MULLIN 1972].

The number of crystals obtained in the seeded experiments was generally higher. On the other hand, the crystal size was smaller for the seeded systems mainly due to secondary nucleation. Secondary nucleation occurs only with the presence of a seed crystal in a saturated solution and in general leads to the formation of small and many crystals [MULLIN 1972].

Ca/Mg Content of the Obtained Crystals

In an attempt to investigate the conditions of complex crystal formation, samples of the obtained crystals from seeded and non-seeded experiments were analyzed with AA spectroscopy. Since one of our objectives was to determine the conditions under which CMA_{1-2-6} can be formed, crystals that were found to have a Ca/Mg mass ratio close to that of CMA_{1-2-6} were also analyzed with XRD for determining their type and hydration level. It is important to emphasize that the samples with different Ca/Mg mass ratio than that of

CMA_{1-2,6} that were not analyzed with XRD, could also contain CMADS. For the CMA_{1-2,6} the Ca/Mg mass ratio is 0.8245 and the weight fraction of Mg as part of the total weight of Mg and Ca is 54.81%. AA analysis of large rodlike single crystals obtained at low content of acetic acid in the aqueous phase (A=30% to 50% v/v) showed that these crystals contained only calcium. In one case (A=30% v/v, B=40/60 wt./wt., C=30% v/v, D=0) a large single prismatic crystal was found to contain only magnesium [DIONYSIOU 1995].

Except for the very large single crystals containing either Ca or Mg, mixtures of smaller crystals were found to contain both Ca²⁺ and Mg²⁺. The smaller size of crystals containing both calcium and magnesium may be due to the lower growth rate of the CMADS crystals. These crystals have a more complex lattice configuration and the surface attachment and rearrangement process becomes the slower and controlling step. It was also observed that at the high and low CaCO₃/MgCO₃ mass ratio, the obtained crystals contained high and low Ca/Mg mass ratio, respectively.

The concentration of acetic acid in the organic phase was also found to affect the Ca/Mg mass ratio of the obtained crystals. Generally the Mg content increased at the very low concentrations (12.5 % wt./wt.) of acetic acid investigated. This observation is probably connected with the migration phenomenon and the formation of small crystals on the glass surface of the beaker as previously explained. The tendency of Mg²⁺ to migrate and form crystals on a glass surface underneath the organic phase may be higher compared to that of Ca²⁺.

Crystals obtained from seeded experiments were also found to contain slightly higher amounts of magnesium compared to crystals obtained from non-seeded experiments. It is well known that crystals formed due to secondary nucleation are the same type as the seeds [MULLIN 1972].

Type and Hydration Level

XRD analysis has been employed for determining the type of *selected samples* of crystals with Ca/Mg ratio close to that of CMA_{1-2,6}. The XRD spectra obtained from these samples were compared to all documented XRD patterns for calcium acetate and magnesium acetate with various levels of hydration and acetic acid content, including the CMA_{1-2,6} spectrum obtained by Su for X₃ shown in figure 3 [JCPDS 1993; SU 1990].

The study showed that various crystals were produced under different conditions investigated and that all samples were consisted of at least two different type of crystals. Those include calcium acetate acetic acid hydrate (C₆H₁₀CaO₆.H₂O; X₁), magnesium acetate tetrahydrate (*monoclinic*: α-C₄H₆MgO₄.4H₂O; X₂), calcium magnesium acetate (C₁₂H₁₈CaMg₂O₁₂; X₃), calcium acetate pentahydrate (C₄H₆CaO₄.5H₂O), calcium acetate acetic acid (C₆H₁₀CaO₆), and magnesium acetate (*orthorhombic*: α-C₄H₆MgO₄). Most of the XRD lines could not be identified because they were not available in the JCPDS spectra examined. This may imply the formation of complex crystals having both calcium and magnesium in their molecular structure. This is also supported by the fact that calcium magnesium acetate CMA_{1-2,6} crystallized in many of the cases examined.

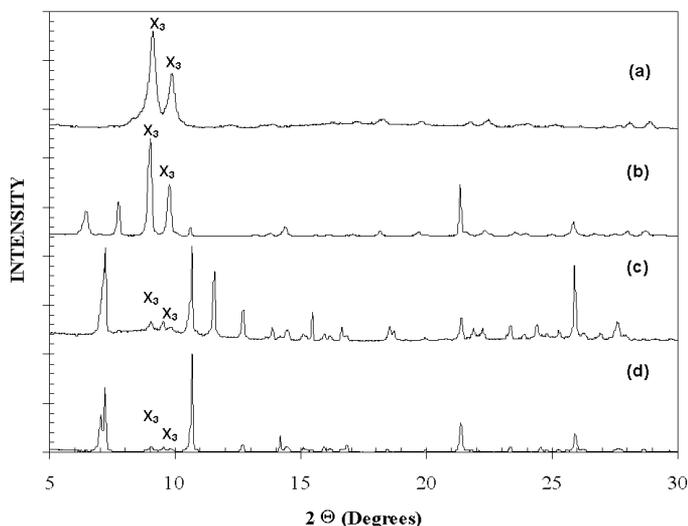
This result is also supported from previous investigations [SCHENK 1991-1]. In another study, Iwaki suggested the formation of either 2(CH₃COO)₂Mg.3CH₃COOH.3H₂O or 5(CH₃COO)₂Mg.10CH₃COOH.7H₂O when the concentration of acetic acid exceeds about 35.77 g/100g saturated solution in the system magnesium oxide - acetic acid - water at 25°C [LINKE 1958]. Unfortunately, crystal spectra for those compounds do not exist in the JCPDS library for identification.

Because of the large number of samples analyzed and the possible existence of complex crystals not listed in the JCPDS X-Ray Powder Diffraction File, only general observations and trends with emphasis on the conditions for CMA_{1-2,6} formation will be discussed here.

At low content of acetic acid in the aqueous phase, (i.e., 40% v/v), formation of CMA_{1-2,6} was not observed. Calcium acetate acetic acid hydrate (X₃) was the major compound formed from the system with CaCO₃/MgCO₃ of 80/20 (wt./wt.). Formation of magnesium containing crystals or other calcium containing crystals could not be verified, but it was not excluded. At higher content of acetic acid in the aqueous phase (A=60% v/v) small amounts of CMA_{1-2,6} were obtained for both seeded and non-seeded experiments. Samples obtained at even higher content of acetic acid in the aqueous phase (A=80-90% v/v) showed a considerable increase in CMA_{1-2,6} formation especially in the samples obtained in the conditions with CaCO₃/MgCO₃ of 50/50, 40/60 and 30/70 (wt./w.).

In general, formation of CMA_{1-2,6} was more pronounced in the systems with high (80-90% v/v) content of acetic acid in the aqueous phase. More specifically the systems containing 90% v/v acetic acid in the aqueous phase gave the best results for CMA_{1-2,6} formation. A comparison between various spectra of samples obtained from systems with 60%, 80% and 90% v/v acetic acid in the “aqueous phase” is shown in Figure 3. The systems containing 100% v/v acetic acid in the aqueous phase did not favor CMA_{1-2,6} formation due to the lower calcium content of the saturated solution compared to that of magnesium. Since the type of crystals obtained mostly depends on the aqueous phase environment, the effect of the concentration of acetic acid in the organic phase may appear insignificant for determining the type of crystals formed. Figure 4 is a schematic simply showing the trends of the effect of Ca/Mg molar ratio in solution and of the concentration of acetic acid in the aqueous phase on the type and hydration level of the crystals. In general, at low concentrations of acetic acid in the aqueous phase, hydrated Ca- and Mg-containing crystals are formed. At low Ca/Mg molar ratio, the crystals contained mostly Mg; the opposite occurs for high Ca/Mg molar ratio. Intermediate Ca/Mg molar ratio favors the formation of hydrated crystals containing Ca, Mg or mixture of Ca/Mg. In all cases the hydration level decreases as the content of acetic acid in the aqueous phase increases (up to 90% v/v). Formation of non-hydrated crystals of calcium magnesium compounds, including CMA_{1,2,6} is favored at high concentrations of acetic acid in the aqueous phase.

Fig. 3: X-ray spectra of commercial CMA (a) and crystals obtained in this work. Effect of concentration of acetic acid in the aqueous phase on the formation of CMA_{1-2,6}.
 (b) A=90% v/v, B=50/50 wt./wt., C=20% v/v, D=0.
 (c) A=80% v/v, B=50/50 wt./wt., C=20% v/v, D=0.
 (d) A=60% v/v, B=45/55 wt./wt., C=20% v/v, D=0.



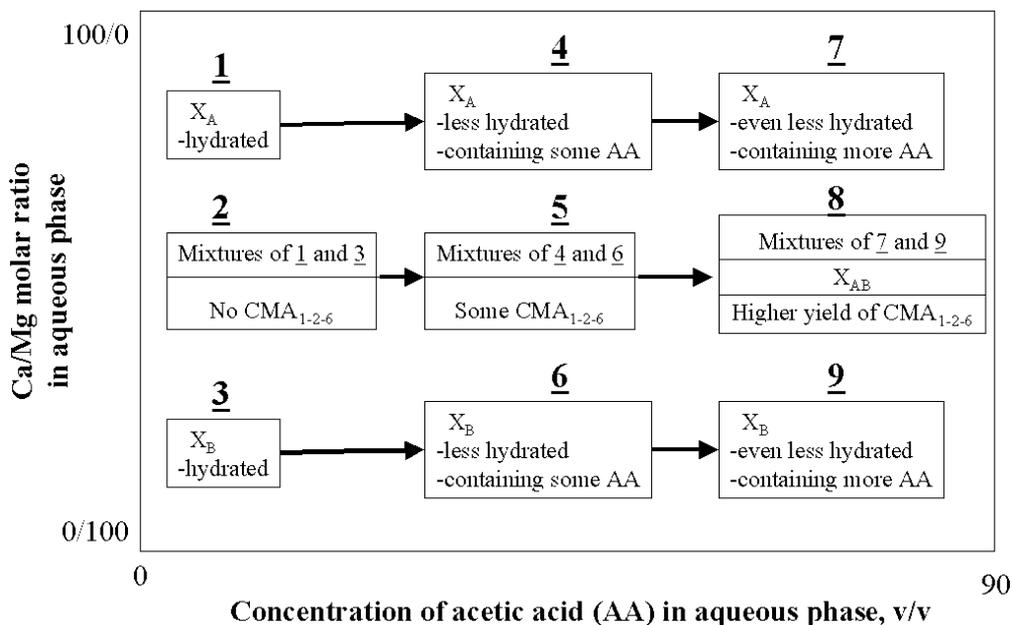


Fig. 4: Schematic for the trend of formation of CMA crystals as a function of Ca/Mg molar ratio in solution and the concentration of acetic acid in the aqueous phase.

X_A denotes crystals of calcium-containing compounds.

X_B denotes crystals of magnesium-containing compounds.

X_{AB} denotes crystals of calcium magnesium acetate compound.

AA denotes acetic acid.

The amount of $CMA_{1-2,6}$ obtained from the seeded experiments was somewhat higher compared to that of the non-seeded experiment and formation of calcium acetate acetic acid hydrate (X_1), magnesium acetate hydrate (X_2), as well as unidentified magnesium containing crystals were also observed [DIONYSIOU 1995]. Seeding did not result in a considerable increase in $CMA_{1-2,6}$ formation because the most important factor that determines the type and hydration level of the obtained crystals is most probably the amount of water in the aqueous phase.

Experiments at Higher Temperatures

The obtained crystals in this experiment were very small since their formation occurred through evaporation. This process is rapid and leads to small crystals due to the high degree of supersaturation. Figure 5 shows the X-ray analysis of samples obtained from the evaporation to dryness method at various temperatures. The crystals obtained at room temperature (20°C) were mostly a mixture of calcium acetate acetic acid hydrate (X_1) and magnesium acetate hydrate (X_2) while those obtained at temperatures higher than 40°C were mainly $CMA_{1-2,6}$. This can be easily proven by comparing the spectra shown in Figure 5 with that of $CMA_{1-2,6}$ shown in Figure 3a. Formation of small amounts of other crystals was also observed. Similar results were obtained from the system with A=60% v/v and B=20/80 wt./wt at 85°C.

This experiment proved that a temperature higher than 40°C is an important factor for the formation of $CMA_{1-2,6}$ from aqueous solution. As stated in the previous section, the systems

containing both Ca^{2+} and Mg^{2+} and high concentration of acetic acid in the aqueous phase favored the formation of CMA_{1-2-6} crystals as opposed those in which such a concentration was low. Combining these two results, one can conclude that the deficiency in water in the crystallization process is an important factor for CMA_{1-2-6} formation. A double salt can be either stable or unstable in the presence of water [MULLIN 1972]. The results obtained from the extractive crystallization experiments at high concentrations of acetic acid in the aqueous phase and from the evaporation-to-dryness at elevated temperatures support the hypothesis that CMA_{1-2-6} is a double salt unstable in the presence of water. This hypothesis is further supported by the fact that CMA_{1-2-6} does not contain any water in its molecular structure.

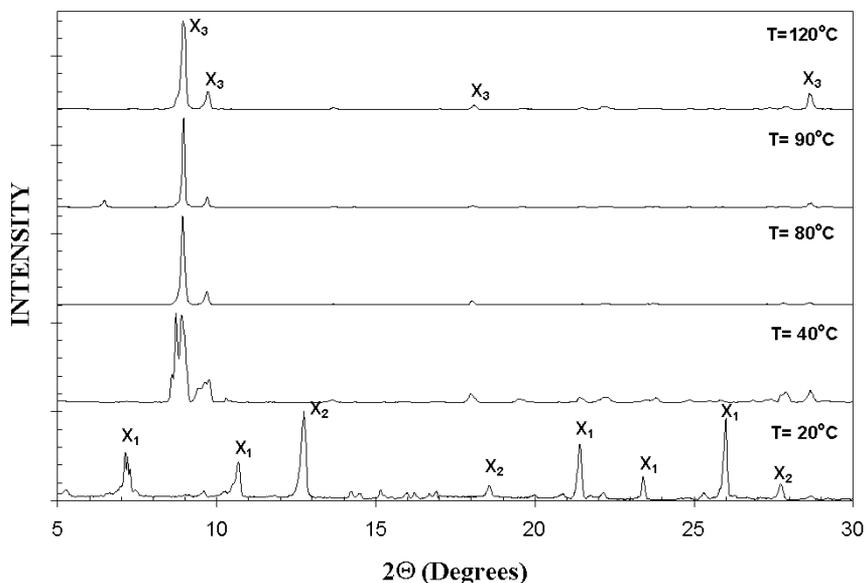


Fig. 5: Effect of temperature on the crystallization of CMA_{1-2-6} in the evaporation-to-dryness experiments.

4. Conclusions

In summary, extractive crystallization is capable of producing crystalline forms of the environmentally benign CMA road deicer. Large, well-formed and non-spherical crystals of mixtures of calcium acetate (CA), magnesium acetate (MA), and calcium magnesium acetate double salt (CMADS), collectively known as CMA, were produced under most of the conditions investigated. Due to their size and shape, these crystals do not bounce-off the pavement during their application and they can be used directly as deicers without the requirement of the high-cost drying and pelletization stages which are used in the current commercial processes for CMA manufacturing. The study also delineated the trends in the conditions for increasing the size of the crystals and for the production of the desired crystalline species. For instance, increasing the concentration of acetic acid in the oil phase leads to smaller sizes; the formation of hydrates is favored at low acetic acid concentration and lower temperatures; the formation of $\text{CMA}_{1, 2, 6}$ crystals is favored at high acetic acid concentration and higher temperatures.

These guidelines will be useful in the designing of a large-scale process, which of course will differ from the laboratory process, in terms of the way the two phases are contacted. This new way will hopefully increase the interfacial area of contact as well as the mass transfer coefficient, and reduce the residence time.

Acknowledgments

The authors are grateful to the Center of Environmental Management (CEM) at Tufts University for financial support thought grants from the US Environmental Protection Agency.

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