Elucidation and Characterization of Commercially Produced CMA Road Deicer

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ABSTRACT

CMA (calcium magnesium acetate) road deicers have gained popularity in recent years as an environmentally friendly alternative to traditional rock salt,[1] and as an absorbent for removing H_2S, other odor causing compounds, and acidic gases from gas streams.[2] Despite its increasing commercial use, its exact composition and structure remain unknown,[3] with subsequent problems in evaluating properties of commercial CMA. The purpose of this project was to elucidate the composition and structure of CMA using single crystal x-ray diffraction, SC-XRD. Attempts to grow crystals suitable for SC-XRD from aqueous solution failed due to formation of various calcium acetate hydrates. Crystals of a mixed metal calcium-magnesium acetate were eventually obtained under mostly water-free conditions from hot glacial acetic acid by slow evaporation of solvent. SC-XRD revealed CMA to crystallize in the orthorhombic space group *Pnma* with a formula of $Mg_2Ca(OAc)_6$ (OAc = acetate anion), with no water included in the crystal lattice. Analysis of commercial CMA by powder XRD, x-ray fluorescence, and SEM-EDS did match the results from SC-XRD.

INTRODUCTION

In recent years, calcium magnesium acetate (CMA) has been gaining prominence as an environmentally friendly road deicer as an alternative to traditional rock salt (sodium chloride).[1]

<u>CMA</u>	<u>Sodium Chloride</u>
Environmentally friendly	Degrades roadside environment
Non-corrosive	Corrosive
Safe for animals	Toxic to animals if ingested

Although CMA is gaining popularity, its crystal structure and subsequent properties remain unknown.[3]

<u>This study sought to:</u>

- Elucidate the crystal structure and chemical composition of CMA using single crystal diffraction
- Analyze commercially sold CMA samples
- Compare the obtained structure to commercial CMA samples

EXPERIMENTAL

Procedural Outline:

1. Single crystals were grown from commercially produced CMA using the procedure outlined in Figure 1.

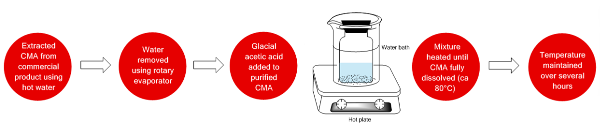
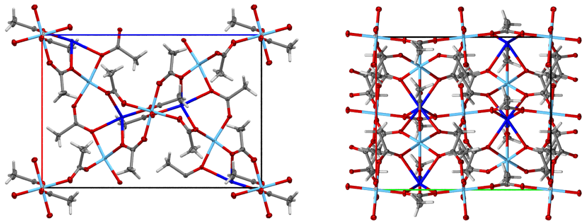


Figure 1: CMA was extracted and purified from the commercial product using hot water and rotary evaporation. Glacial acetic acid, CH_3COOH, was added to purified commercially produced CMA. The resulting mixture was placed in a water bath and heated until CMA fully dissolved. Part of the acetic acid was then slowly evaporated off at ca. 80°C over several hours upon which large crystals suitable for single crystal diffraction formed.

EXPERIMENTAL



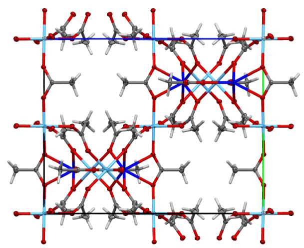


Figure 2: Unit cell of purified CMA crystal structure

Chemical formula, M_r	$CaMg_2(OAc)_6$, 442.96 g/mol
Crystal system, space group	Orthorhombic, *Pnma*
Temperature (K)	100
a, *b*, *c* (Å)	10.8706 (5), 12.4318 (6), 15.6141 (7)
V (Å^3), Z	2110.11 (17), 4
Crystal size (mm)	0.28 × 0.25 × 0.13
Diffractometer	Bruker AXS D8 Quest CMOS diffractometer, Mo $K\alpha$ radiation
Absorption correction	Multi-scan, Apex2 v2014.1-1 (Bruker, 2014)
No. of meas., indep. and obs. $[I > 2\sigma(I)]$ reflections	115110, 6877, 4979
θ values (°)	$\theta_{max} = 45.3$, $\theta_{min} = 2.6$
Range of *h*, *k*, *l*	$h = -17 \rightarrow 20$, $k = -19 \rightarrow 19$, $l = -31 \rightarrow 24$
R_{int}	0.043
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.104, 1.04
No. of refl., param., restr.	6877, 140, 0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.88, -0.91

Computer programs: Apex2 v2014.1-1 (Bruker, 2014), *SAINT* V8.34A (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2014*/7 (Sheldrick, 2014), SHELXLE Rev656 (Hübschle *et al.*, 2011).

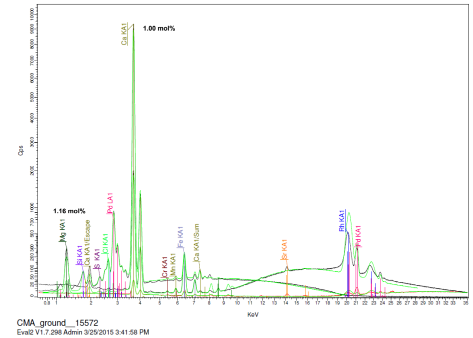
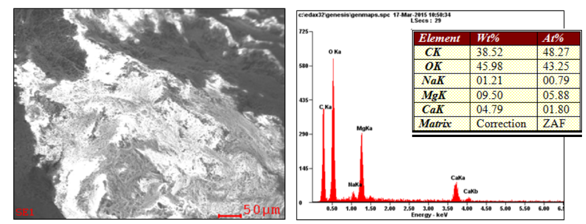


Figure 4: X-ray fluorescence spectrum of commercial CMA product



Element	Wt%	At%
CK	38.52	48.27
OK	45.98	43.25
NaK	01.21	00.79
MgK	09.50	05.88
CaK	04.79	01.80
Matrix	Correction	ZAF

Figure 5: Energy dispersive x-ray spectroscopy data of commercial CMA product

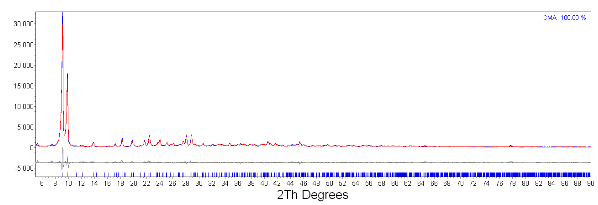


Figure 3: Powder x-ray diffraction spectrum of commercial CMA product versus purified CMA crystal structure

CONCLUSIONS

- Successful elucidation of CMA crystal structure
- CMA crystallizes with a Mg to Ca ratio of 2:1
- No water is included in the crystal lattice of CMA (in contrast to most Mg acetate and Ca acetate structures)
- Characterization of commercial product confirmed crystal structure
- Variations in composition ratio possibly due to commercial product impurities

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