

SYNTHESIS AND DEICING PERFORMANCE OF CALCIUM MAGNESIUM ACETATE FROM DOLOMITIC LIMESTONE OF ABBOTABAD REGION, PAKISTAN

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ABSTRACT

Calcium Magnesium Acetate (CMA) has recently gained much popularity due to its emerging applications in road deicing, and as an industrial adsorbent for removal of Hydrogen Sulfide (H_2S) gas and other odorous acid gases from gaseous streams. CMA is a multi-purpose, low-corrosion and concrete-safe alternative to the conventionally used sodium chloride (NaCl) deicers. CMA prevents snow and ice from bonding to either surfaces or itself. In the present study, CMA was prepared from dolomitic limestone of Abbottabad region, Pakistan. The prepared samples were characterized through various instrumental techniques like Scanning Electron Microscopy combined with Energy Dispersive X-Ray (SEM-EDX), X-Ray Diffraction (XRD), and Fourier Transform Infra-Red Spectroscopy (FT-IR). The performance of CMA was compared with NaCl. It was found that after 24 hours, 15 %, of ice melted, when no deicing agent was used. Likewise, 49.4 %, and 66.4 % of ice melted, when CMA and NaCl were used as deicing agents, respectively. Thus, the rate of ice melting increased by 70 % and 77.4 %, with CMA and NaCl respectively. The analysis showed that CMA could successfully be produced from dolomitic limestone of Abbottabad, and the same may be applied for deicing applications.

Keywords: calcium magnesium acetate, rock salt, deicing agent.

INTRODUCTION

Calcium Magnesium Acetate is a green substitute to the conventional deicing agents such as sodium chloride, calcium chloride, magnesium chloride, and potassium chloride etc. [1 - 4]. CMA has the additional advantage of non-toxicity regarding the human and animal health. Other advantages include non-corrosiveness to the steel structure, bridges, roads, and vehicles, as well as elimination of the risk to vegetation and soil dilapidation [4, 5]. The lower mobility of CMA in soil mitigates the contamination of groundwater. CMA has a eutectic temperature of -27°C , which is lesser than sodium chloride. This property enables CMA to be used for deicing in much lower temperature regions [6]. Another benefit of CMA is that it does not stain the aluminum metal surface. A drawback of CMA is its higher cost

as compared to sodium chloride. But, despite this shortcoming, CMA is a potential candidate for de-icing due to its huge long run benefits [7, 8].

Although, the traditional ice-melting agents may have a low cost, yet their potential hazards towards human beings, plants and vegetation, vehicles, concrete, and metallic infrastructure used in roads, could lead to a long-term drastic negative impact on economy. As an example, the usage of sodium chloride as a deicing agent causes high levels of sodium in drinking water, which leads to hypertension. It has been estimated that the total annual damage, resulting from the use of sodium chloride as a road deicer is at least 15 times the cost of the purchase and application of the salt [9, 10].

As compared to conventional deicing agents, CMA is environmentally safe. The acetate part is biodegradable and calcium and magnesium ions are biocompatible,

since they are already present in large amounts in most natural soils. Oxidation of CMA by soil microorganisms would generate calcium magnesium carbonates which are non-toxic and could even improve soil quality in some cases. One minor concern is a possible increase in biological oxygen demand (BOD) when CMA is flushed into natural waters, but this is not likely to cause damage because the run-off occurs when temperatures are low and biological systems function slowly. Hence CMA successfully addresses a number of issues, which are being faced by conventional deicing agents [11].

Another promising application of CMA, other than deicing agent, is the coal desulfurization. It can be used as an additive to coal combustion, where it catalyzes the combustion and at the same time acts as a “sulfur grabber”, forming solid calcium sulfate and thus substantially reducing sulfur dioxide in the stack gases. The coal merely must be impregnated with a CMA solution before combustion. Used in this manner, CMA would help to prevent acid rain, and would also enhance the efficiency of coal-fired boilers [11, 12].

In Pakistan, huge deposits of dolomite ore occur at Abbottabad, Mardan, Khyber Agency, Kohat and Mianwali regions. The average content of MgO and CaO in these deposits ranges from 17 - 22 % and 27 - 31 %, respectively [13, 14]. In the present study, CMA was synthesized from the dolomite ore of Abbottabad region. To the best of our knowledge, it is the first attempt to synthesize CMA from the dolomite ore of Pakistan. The research will pave way for the indigenous utilization of dolomite ore for industrial manufacturing of CMA as a deicing and desulfurizing agent. The CMA prepared on laboratory scale was characterized through various instrumental techniques like Scanning Electron Microscopy combined with Energy Dispersive X - Ray (SEM - EDX), X-Ray Diffraction (XRD), and Fourier Transform Infra-Red Spectroscopy (FTIR). The prepared CMA was found to be suitable for deicing and other commercial applications.

EXPERIMENTAL

Dolomite ore of Abbottabad region was used as a source of calcium and magnesium, while commercial grade acetic acid (99.5 %) of JLP Corporation, Seoul, Korea was used as acetate source, for the synthesis of CMA.

For the synthesis of CMA, glacial acetic acid can

be reacted with any one of dolomitic limestone ($\text{CaCO}_3 \cdot \text{MgCO}_3$), dolomitic quick lime ($\text{CaO} \cdot \text{MgO}$), or dolomitic double hydrated lime ($\text{Ca}(\text{OH})_2 \cdot \text{Mg}(\text{OH})_2$). In order to make the process most economical, in the present study, dolomitic limestone was directly reacted with glacial acetic acid. The process is claimed to be economical because dolomite ore is used in its raw form and no heat or pressure is required to produce dolomitic quick lime or double hydrated lime.

The dolomitic limestone lumps having an average size of 15 - 20 cm were crushed in a Jaw Crusher, down to a size of 1.25 - 2.50 cm. The crushed dolomite ore was then fed to a rod mill, where the size was further reduced to 0.0094 - 0.0102 cm. The dolomitic limestone powder was stored in plastic bags for further usage.

For the preparation of CMA, dolomite powder was reacted with glacial acetic acid in a ratio of 1 : 1.3. Dolomite powder was slowly added to glacial acetic acid with continuous stirring, until the effervescence stopped. The reactants were stirred for at least 2 hours to ensure completion of the reaction. The chemical reaction between dolomite powder and glacial acetic acid proceeds as following.



After the completion of reaction, the supernatant liquid was decanted and then filtered to remove any solid residue. The filtrate was heated up to 80°C and the evaporation process was continued until crystallization of CMA started. Heating was then stopped, and the solution was left overnight to complete the settling of CMA crystals. The obtained orthorhombic CMA crystals were dried in an oven and then stored in sealed polyethylene bag for further analysis. The stepwise synthesis process of CMA is shown in Fig. 1.

Characterization Studies

The CMA crystals were crushed to fine powder for gravimetric and titration analysis. Deicing performance of CMA was evaluated in comparison with NaCl. The efficiency of both deicing agents was tested on a laboratory scale.

The main functional groups of CMA crystals were identified through FTIR (Fourier transform infrared Spectrophotometer), model PerkinElmer Spectrum 2/

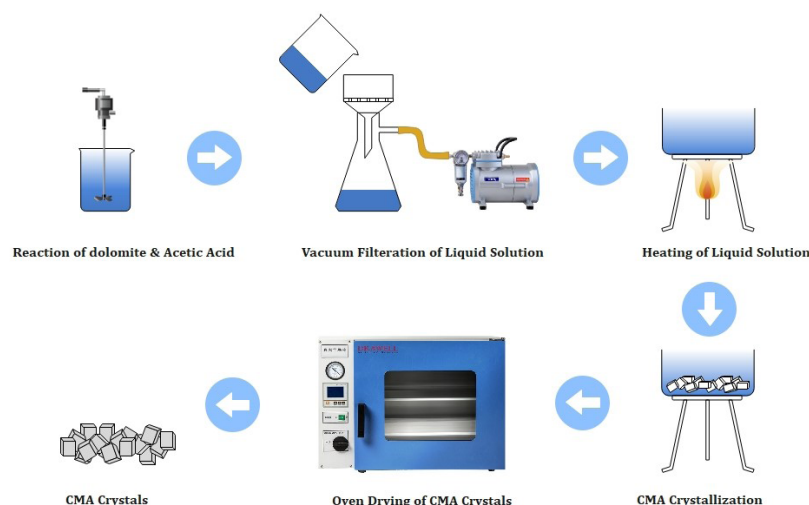


Fig. 1. Synthesis process of CMA.

UATR, 103385. The mineral phases in CMA crystals were determined through XRD, model JDX-3532, JEOL, Tokyo, Japan. The elemental composition and the surface morphology of CMA crystals were studied through an Energy Dispersive X-ray (EDX) coupled with Scanning Electron Microscope (SEM), model JSM5910, JEOL, Japan.

Deicing Performance of CMA

For evaluating the deicing performance of CMA, 250 mL of deionized water was frozen at a temperature of $-18 \pm 2^\circ\text{C}$ in 3 separate Pyrex beakers in a freezer (Dawlance, Pakistan). 5 g each of CMA and NaCl in the size range of -0.063 to $+0.0315$ cm were weighed separately on a precision balance. After 48 h, the frozen water in Pyrex beakers were taken out and labelled as Blank, CMA, and NaCl, respectively. The beakers labelled as CMA and NaCl were sprinkled evenly with 5 g of CMA and NaCl, respectively. The beaker labelled as Blank, was left as such to allow comparison with the use of no deicing agent. All the three beakers were kept in fridge portion at $4 \pm 1^\circ\text{C}$. After every 1 h, each beaker was taken out in turn, and the melted liquid was collected in another beaker. The weight of solid ice was noted down. The melted liquid was then repoured in the respective beaker, and then put back in the fridge. Based on obtained data, a comparison was made between the deicing performance of CMA and NaCl.

RESULTS AND DISCUSSIONS

Chemical and SEM-EDX Analysis

The chemical analysis of dolomite ore of Abbottabad region is shown in Table 1. The synthesized CMA was subjected to chemical analysis. The composition and surface morphology of CMA was further tested through SEM-EDX and the results were then compared with theoretical composition, as shown in Table 2. Fig. 2 shows, the SEM EDX images of CMA at three random spots.

The major constituents of prepared CMA were found to closely follow the theoretical composition. The purity of CMA was found to be 94.34 % by Chemical analysis, while 98.15 % by EDX analysis. The results depict that CMA was successfully prepared.

XRD Analysis

XRD analysis of the prepared CMA is shown in Fig. 3. Peaks at 2θ degrees of 5.03 and 7.25 most probably emerge from traces of $\text{Ca}(\text{CH}_3\text{COO})_2$ hemihydrate or $\text{Ca}(\text{CH}_3\text{COO})_2$ dihydrate. The prominent peaks at 2θ degrees of 8.84 and 9.59 represent the

Table 1. Chemical analysis of dolomite ore.

Contents	CaO	MgO	LOI
%	26.15	25.00	45.00

Table 2. Chemical composition of CMA.

Parameter	Actual Composition of CMA, %		Theoretical Composition of CMA, %
	EDX Analysis	Volumetric Analysis	
Calcium as Ca	16.30	10.44	13.33
Magnesium as Mg	7.80	7.10	8.00
Acetate as $(\text{CH}_3\text{COO})_4$	74.05	76.80	78.66

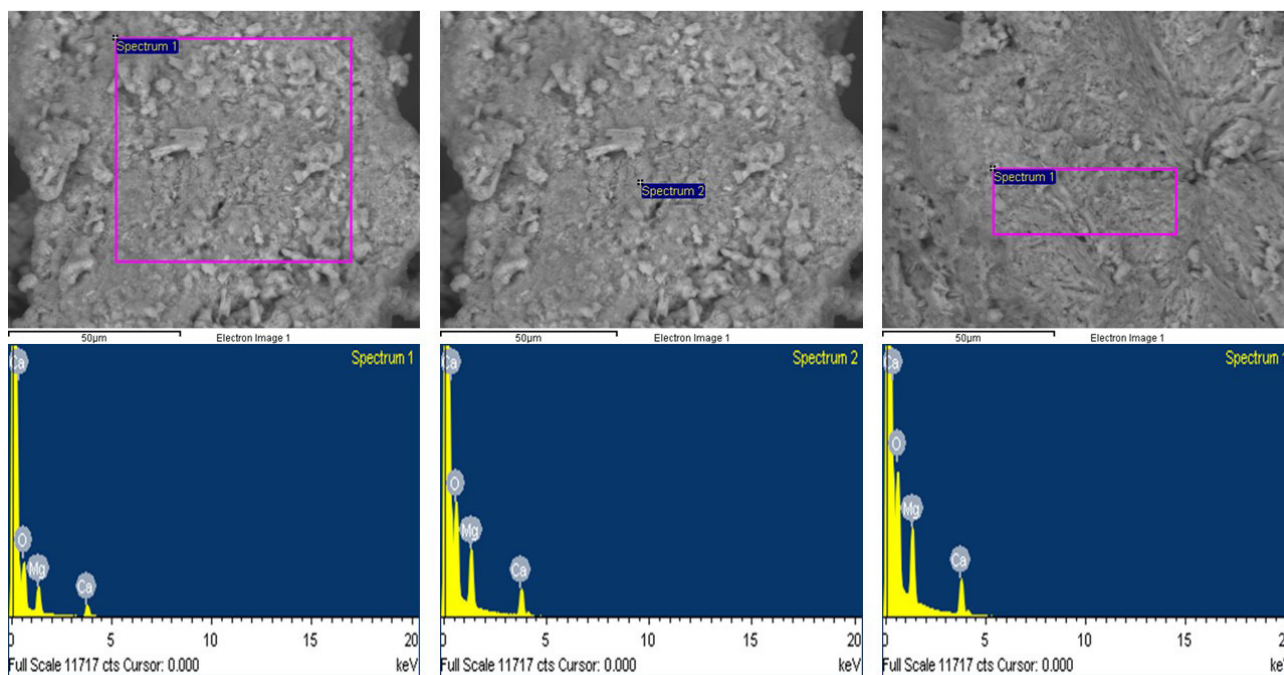


Fig. 2. SEM-EDX images of CMA.

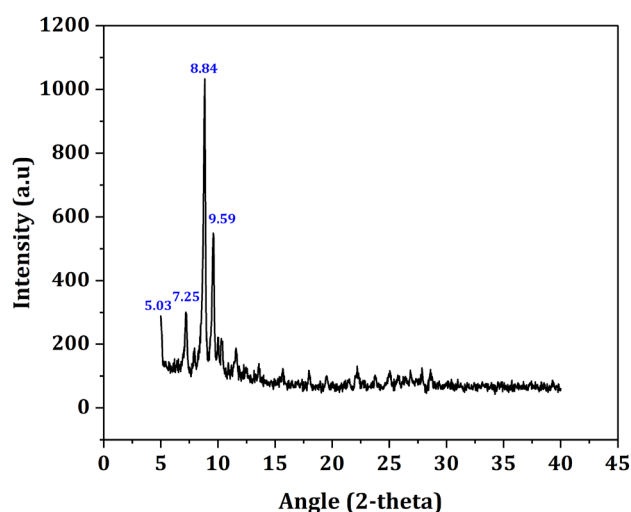


Fig. 3. XRD graph of CMA.

crystalline calcium magnesium acetate in the sample. These peaks match with the JCPD standards. From the present structural analysis data, it can safely be stated that the concentration of CMA was high enough in the sample. A lower concentration of calcium acetate also occurred along with CMA, as is clear from the lower peaks. The results obtained are in good agreement with those obtained in [7].

FT-IR analysis

Fig. 4 shows the FT-IR spectrum of CMA sample. The absorption bands between $3200 - 3400 \text{ cm}^{-1}$ are formed due to the overlap of $-\text{OH}$ stretching vibration and $-\text{CH}$ saturation associated with the formation of a hydrogen bond. The absorption band occurring near 1600 cm^{-1} is due to the $\text{C}=\text{O}$ stretching vibration. On

the other hand, the absorption band in the region of 1200 - 1300 cm^{-1} is based on C–O stretching vibration. Moreover, the spectral region of 1200 - 1600 cm^{-1} is dominated by CH_3 bending and C–O stretching vibrations. The absorption band at 1000 cm^{-1} depicts the stretching vibration of methyl group (CH_3). Lastly, the intense peak at 672 cm^{-1} occurs due to the presence of calcium acetate, which depicts the anti-symmetric and symmetric twisting and rocking of the O–C–O fragment. The obtained results closely match that in [4].

Deicing Performance of CMA

The deicing performance of CMA and NaCl for initial 5 h is shown in Fig. 5. The overall deicing effect of CMA and NaCl after 24 h is shown in Fig. 6. The performance of both salts was also compared with the use of no deicing agent. It can be observed that application of CMA over frozen water melted almost 29 % of ice in 5 h. On the other hand, NaCl melted almost 36 % of ice in the same duration, which was about 20 % or 1.2 times higher than that of CMA. In the same scenario, if no deicing agent was used, only 11 % of the ice melted. After 24 h, 15 %, of ice melted, when no deicing agent was used. Likewise, 49.4 %, and 66.4 % of ice melted, when CMA and NaCl were used as deicing agents, respectively. Thus, the rate of ice melting increased by 70 % and 77.4 %, with CMA and NaCl respectively. A similar study conducted by McElroy et. al. concluded that about 772 g of CMA is required to melt the same quantity of ice as 454 g of NaCl [15]. So, the results of present study are much encouraging as compared to the literature. Although the cost and dosage of CMA for deicing may seem on higher side as opposed to NaCl, yet the absence of chlorine in CMA makes it an excellent choice for saving the precious environment. CMA eliminates the risk of corrosion of roads and bridge concrete, reduces the impact on plant growth, and minimizes the damage to groundwater and soil.

CONCLUSIONS

In the present study, Calcium Magnesium Acetate (CMA) was synthesized from the dolomitic limestone of Abbottabad region, Pakistan. It is commonly used as a deicing agent in place of conventional materials like rock salt (NaCl). The use of NaCl as a deicer is known to pose

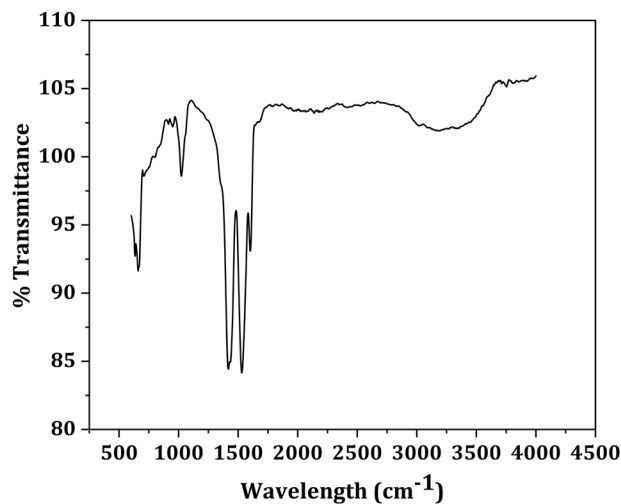


Fig. 4. FT-IR Spectrum of CMA.

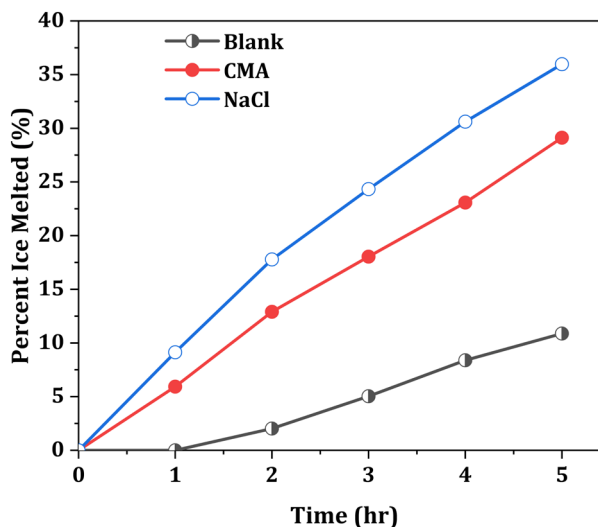


Fig. 5. Deicing performance of CMA and NaCl in initial 5 h.

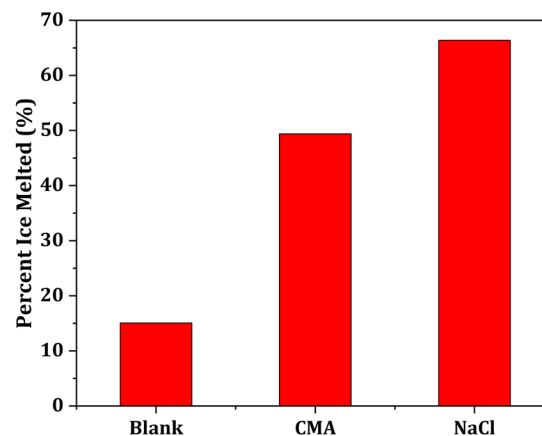


Fig. 6. Deicing performance of CMA and NaCl after 24 h.

a number of environmental threats including damage to plants, vegetation, automobiles, road infrastructure and concrete bridges. In contrast, CMA is a much safer alternative to NaCl as it is chlorine free and environment friendly. The synthesized samples of CMA were characterized through various instrumental techniques like SEM-EDX, XRD, and FTIR. The deicing performance of CMA was compared with NaCl. It was found that 15 % of ice melted 24 hours, when no deicing agent was used. On the other hand, when CMA and NaCl were used as deicing agents, 49.4 %, and 66.4 % of ice melted after 24 hours, respectively. Although, the melting rate of NaCl was found to be higher, yet its use as a deicing agent could not be recommended due to its serious environmental concerns. The analysis showed that CMA could successfully be produced from dolomitic limestone of Abbottabad, and the same may be applied for deicing applications.

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