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Synthesis of Calcium Magnesium Acetate (CMA) Deicer from Dolomite

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Calcium magnesium acetate (CMA) is an environmentally friendly alternative to sodium and/or calcium chloride for the use of de-icing salt on highways. Owing to the several advantages such as low corrosion for asphalt and concrete structures and multi-purpose availability, it is highly preferred for the use of road-salt. In this study, dolomitic rocks were investigated to synthesize the CMA in laboratory conditions. For this purpose, the initial size of rocks was manually reduced and the dolomitic materials with a particle size range of less than 0.5 mm were prepared for experimental studies. The prepared materials were utilized in leaching tests where dilute acetic acid (CH_3COOH) solutions at a specific concentration of 40% were used for the dissolution of dolomite minerals. During leaching tests, the effects of leaching time (T, min), temperature (t, °C) as well as the ratio of solid to liquid (S/L) on the variations in dolomite dissolution were investigated. As a result of these investigations, it was determined that the average of dolomite dissolution rate were found to be 74.60% under the conditions of T = 180 min, t = 80 °C and S/L = 10%. The chemical constituents of the CMA as a final product was determined by crystallizing and evaporating of leach solutions at 80 – 90 °C with a heating control procedure. X-Ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyses were used for the characterization of CMA products and the results showed that the CMA mainly comprises three main phases with different quantities: calcium magnesium acetate (59.7% – 66.1%), calcium acetate (25.7% – 31.5%) and magnesium acetate (8.2% – 9.3%).

Keywords: Road-Salt, Calcium Magnesium Acetate, Synthesis, Dolomitic Rocks.
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1. Introduction

Road salt is a conventional choice when dealing with deicing management of highways. However, it has been experienced from practical applications that the adverse effects of rock salt on road and concrete structures may outweigh its short-term benefits. In general, road salt refers sodium chloride (NaCl) in most cases and no matter how widely it is used, it could not be benefited effectively if the temperature is lower than -7 °C since NaCl has an endothermic nature [1]. In parallel with the ineffectiveness of NaCl in colder regions, the extent of chloride ions in salty solution penetrating into concrete structures results in a remarkable deterioration in such infrastructures of highways and bridges [2].

Therefore, researchers have attempted to focus on investigations with relation to more effective natural and/or artificial deicing salts. The deicers are generally divided into three main categories, which are sorted as chloride-based, acetate-based and inorganic-based ones [3, 4]. Common chloride-based deicers are NaCl, calcium chloride ($CaCl_2$) and magnesium chloride ($MgCl_2$) whereas, acetate-based deicers are Calcium-Magnesium Acetate (CMA) and Potassium Acetate (KAc). Inorganic-based deicers are mainly of sodium monohydrate and/or dehydrate phosphates [5]. Apart from these kinds of deicers, a complementary agent in deicing management could be mentioned as carbohydrate-based ones. Liquid carbohydrate-based agents mainly composed of cane or beet sugar do not aid in melting ice, however, they allows for diminishing the freezing point of ice [6]. Alternatives to road-salt are listed in Table 1 with their possible environmental impacts. Accordingly, calcium chloride ($CaCl_2$) with an effective temperature of -32 °C could be a leading hygroscopic alternative, capturing moisture from the contact environment and accelerating the melting procedure.

Table 1. Environmental impacts of several de-icers [modified after 2, 13].

Environm. Impact	**Rock salt (NaCl)**	**Calcium magnesium acetate (CMA)**	**Calcium Chloride ($CaCl_2$)**	**Magnesium Chloride ($MgCl_2$)**
Soil	Excessive Na^+ ions may corrupt the soil structure.	Potential substitutions of Ca^{++} and Mg^{++} ions may be observed in soils.	Chloride-based constituents may lead to heavy metal contamination in the long-term.	Similar to the one of CMA.
Ground water	Chloride loading or accumulation in groundwater may result in anoxia.	Acetate degradation can decrease the oxygen availability.	Heavy metal contamination could be stimulated if it mixes into groundwater.	Similar to the ones of NaCl and $CaCl_2$.
Vegetation	The use of NaCl around vegetated areas may influence up to 120 m downwind from commonly used roadways, which may result in a decrease of biodiversity.	Little or no remarkable effects are expected.	It could be worthwhile to plant growth.	Similar to the one of $CaCl_2$.
Highway infrastructure	Initiating and accelerating the rate of corrosion in concrete structures, it acts adversely.	It is less corrosive then chloride-based de-icers.	It could be a potential corrosive agent when stayed longer on wet surfaces.	Owing to the Mg-related reactions, infrastructures may deteriorate.
Effective temp. (°C)	-7	-27	-32	-18

Even if the alternatives to Rock salt listed in Table 1 can be consistent with the issues with respect to snow management, chloride-based de-icers have significant disadvantages such as corrosion and deterioration in concrete structures, potentially endangering the life [7 – 12].

Calcium Magnesium Acetate (CMA), a non-chloride deicing agent, was firstly introduced by DOT Company in the USA in the 1980s after an extensive research program initiated by the Federal Highway Administration (FHWA) [14]. The CMA has highly efficient at lower temperatures because of its eutectic temperature of −27 °C that is nearly 20 °C lower than that of rock salt [15]. The advantages of CMA can be summarized as follows:

•Utilization as a deicer in special engineering structures such as bridges, airports etc.
•Less corrosive to highway-related metals and concretes,
•Less endangering the soil, groundwater and biodiversity.

The only disadvantage of the CMA is expensiveness. The CMA approximately costs 10 – 20 times more than that of rock salt. The CMA is a physical mixture of magnesium acetate ($MgAc_2{\cdot}4H_2O$) and, calcium acetate ($CaAc_2{\cdot}H_2O$) both in their stable hydrated forms. Hence, it is possible to be synthesized considering rocks with different Ca/Mg bearing constituents. It was documented that acetic acid with different concentrations could be used to produce the CMA in laboratory conditions [16]. In terms of raw materials such as limestone, dolomite or dolomitic lime, the CMA production could be described by the following equation;

$CaMg(CO_3)_2 + 4HAc = CaAc_2 + MgAc_2 + 2CO_2 + 2H_2O$ (1)

In this study, dolomitic rocks were leached in dilute acetic acid solutions to produce the CMA. During experimental studies, the effects of leaching time (T, min), leaching temperature (t, °C) and solid-to-liquid ratio (S/L) on dolomite dissolution were investigated. As a result of leaching tests, the CMA as a product was characterized through X-Ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyses.

2. Materials and methods

Representative dolomitic rocks to produce CMA were obtained from Nasdur Mining Company located in Hatay province in Turkey. The dolomitic rocks were crushed by a laboratory jaw crusher and then milled to a size of -0.5 mm with a ball mill. CMA synthesis was performed using -0.5 mm sized dolomite sample. The chemical constituents of dolomitic rocks were determined using a Minipal 4 Panalytical XRF (X-Ray Fluorescence) apparatus and the results are given in Table 2.

Table 2. Chemical analysis results of the dolomitic rocks used in this study.

Contents	CaO	MgO	Fe_2O_3	LOI
%	30.43	21.86	0.51	46.38

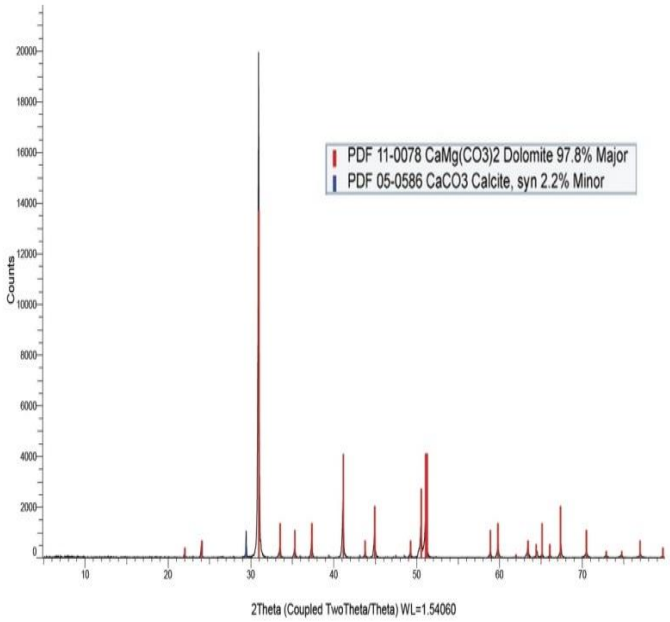

Figure 1. *XRD pattern of the dolomitic rocks*

For leaching tests, acetic acid solution with a specific concentration of 40% was prepared by diluting analytical grade glacial acetic acid (100% purity, Merck) in distilled water. The tests were executed in a 500-mL glass beaker. The leach slurry was mixed by a digital magnetic stirrer (MTOPS) at 400 rpm equipped with a temperature controller hot plate (MTOPS - MSDSM).

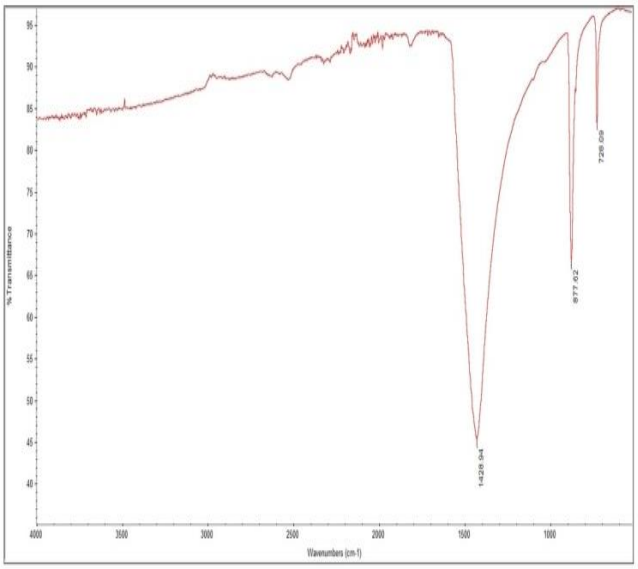

Figure 2. *FTIR pattern of the dolomitic rocks*

For each experiment, the required volume of distilled water was transferred into the reactor and following this procedure, it was heated to the desired temperature before adding ore sample to commence the leaching process. Once the leaching process has been completed, solid-liquid separation was conducted. The CMAs were synthesized from the obtained solutions with a heat-controlled procedure around 80 – 90 °C.

All the tests were duplicated and conducted at 1 atm pressure.

In order to characterize the CMA as product, the Bruker Discover D8 XRD device was used for XRD analyses. In addition, Nicolet 6700 FTIR with ATR (Attenuated Total Reflection) apparatus was used for FTIR analyses. The representative XRD and FTIR patterns of dolomitic rocks are given in Figure 1 and Figure 2, respectively.

3. Results and discussion

3.1. The effects of leaching temperature

For the evaluation of varying temperature effect on dolomite dissolution, 20 g of prepared sample was used in the experiments under the conditions of mixing speed of 400 rpm, acetic acid concentration of 40% (in total of 100 mL leach solution), and 1 h of leach duration. Under these conditions kept stable, leaching tests were performed at different temperatures (i.e. 25 °C, 40 °C, 60 °C and 80 °C).

The effect of temperature on the dissolution of dolomite was found to be significantly high. Particularly, in the experiment carried out at 80 °C, the dissolution rate of dolomite were more than two times than that of room temperature (25 °C) (Figure 3).

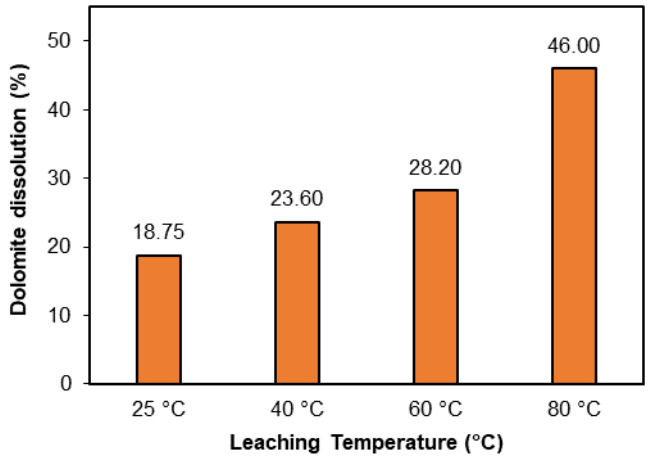

Figure 3. *Dissolution rates of dolomite with respect to varying temperatures.*

3.2. The effects of leaching time

In this evaluation, sample weight (20 g) mixing speed (400 rpm) and acetic acid concentration (40%) were the same as previously described, however, leaching temperature of 80 °C was adopted and under these conditions additional tests were conducted. Leaching tests were conducted up to 3 h and at each hour dolomite, dissolution rates were recorded. As seen in Figure 4, dolomite dissolution gradually increased with increasing leach duration. In the subsequent times, dolomite dissolution continued relatively slow. In other words, after a leach duration of 3h, the dolomite dissolution rate proportionally increased at a rate of 12% when compared the one obtained after 1h leach duration.

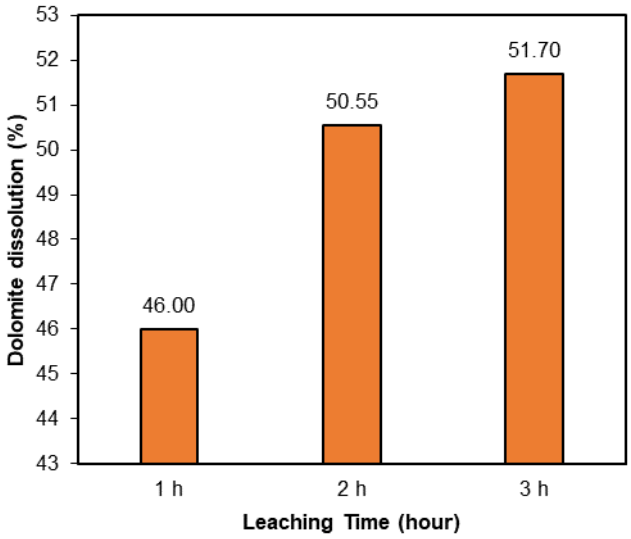

Figure 4. *Dissolution values at different leaching times*

3.3. The effects of solid weight

The dissolution tests were performed at three different S/L ratios (i.e. S/L ranging from 10% to 20%) when the concentration of the acetic acid was 40%, at a temperature of 80 °C, stirring speed of 400 rpm, and leaching duration of 180 min. The decrease in the S/L ratio resulted in an increase in the dissolution values. The maximum dolomite dissolution yielded in the experiments when S/L ratio of 10% was in charge (Figure 5).

3.4. Crystallization tests

After the solid-liquid separation, the leach solutions were gradually heated up to 80 – 90 °C in a 500 mL beaker. The CMAs were obtained at the bottom of the beaker by crystallization and evaporation. After an effective crystallization has been achieved, the CMAs were obtained from the beaker and prepared for the characterization tests. As a result of XRD and FTIR patterns of CMAs, more than 60% of the materials obtained were found as calcium magnesium acetate and the remainder are calcium acetate and magnesium acetate (Figure 6 and Figure 7). Furthermore, it was determined that FTIR analysis results are in a good agreement with the study of [16].

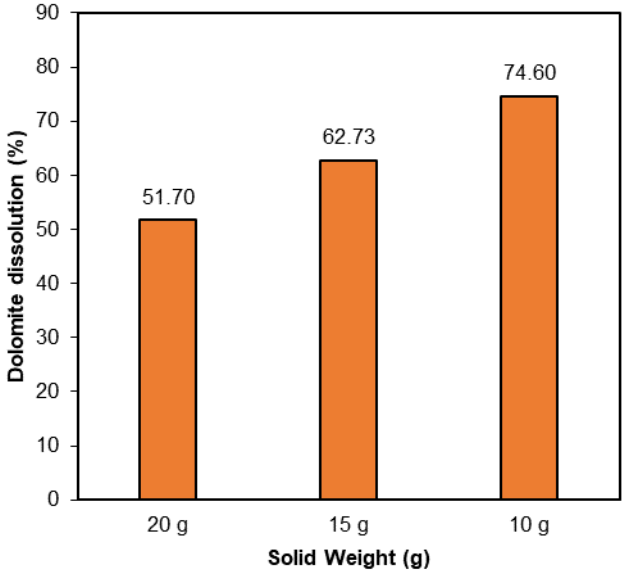

Figure 5. *Dissolution values at different solid ratios (in 100 mL solution)*

4. Conclusions

This research demonstrated that CMAs could be synthesized from the dolomite mineral after the leaching process with acetic acid. The experimental results showed that the dolomite dissolution was the highest when the concentration of the acetic acid was 40%, at a temperature of 80 °C, a solid/liquid ratio of 100 g/L, stirring speed of 400 rpm, a size fraction of – 0.5 mm, and leaching duration of 180 min. Under these conditions, 74.60% of dolomite was dissolved. The CMAs were synthesized from the leach solutions and characterized by XRD and FTIR analyses.

Significant CO_2 emissions were observed during during leaching operations. This released CO_2 can be stored attempted to extablish a closed-loop system in order to attain dry ice as byproduct. In future studies, it should be planned to investigate CMA production after calcination of dolomite. In this regard, positive/negative effects of calcination process on CMA production might be revealed.

5. Acknowledgement

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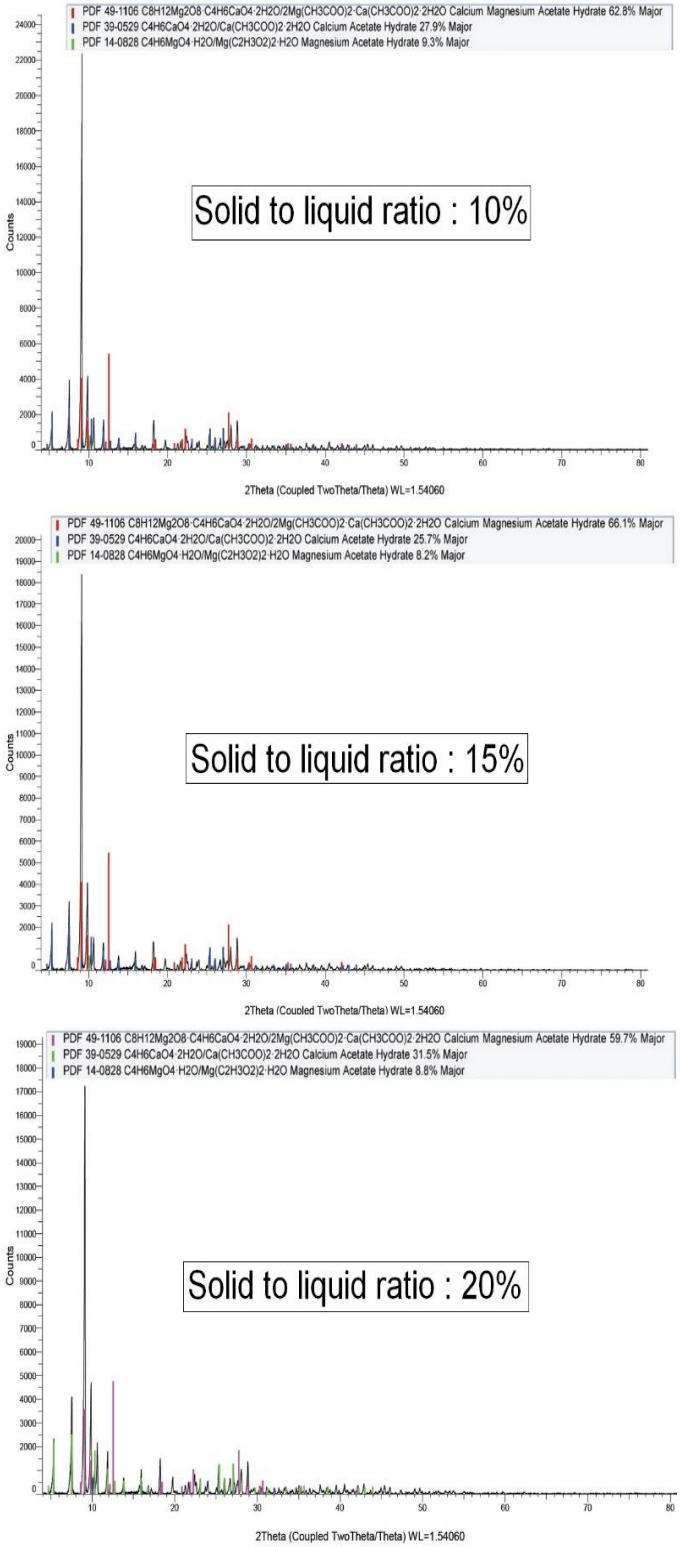

Figure 6. *The results of XRD analyses for the synthesized samples*

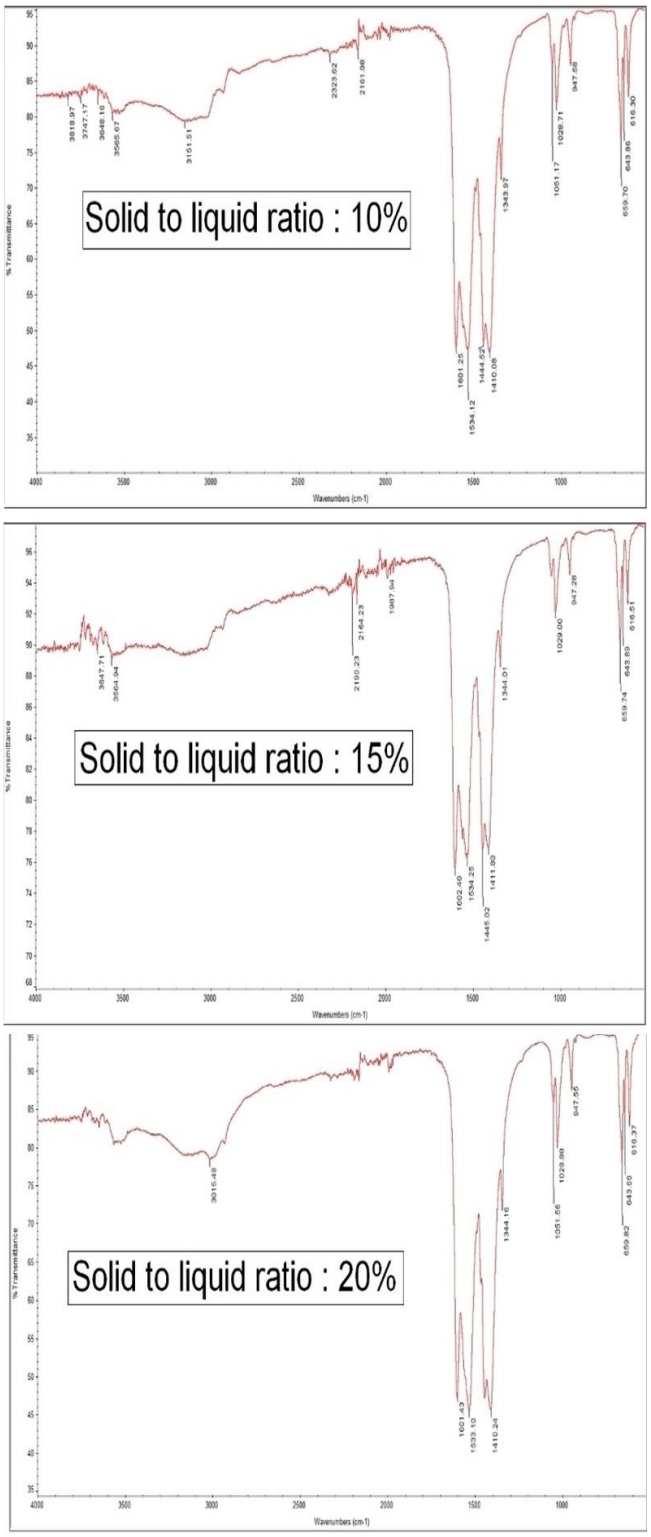

Figure 7. *The results of FTIR analyses for the synthesized samples*

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