

## Influence of acetate on the carbonation of brucite (Mg(OH)<sub>2</sub>)

N. Kamala Ilango<sup>1\*</sup>, H. Nguyen<sup>1,2</sup>, F. Winnefeld<sup>2</sup> and P. Kinnunen<sup>1</sup>

<sup>1</sup> Fibre and Particle Engineering Research Unit, University of Oulu, Oulu, Finland

Email: [nirrupama.kamalailango@oulu.fi](mailto:nirrupama.kamalailango@oulu.fi); [hoang.nguyen@oulu.fi](mailto:hoang.nguyen@oulu.fi); [paivo.kinnunen@oulu.fi](mailto:paivo.kinnunen@oulu.fi)

<sup>2</sup> Empa, Swiss Federal Laboratories for Material Science and Technology, Laboratory for Concrete and Asphalt, Dübendorf, Switzerland

Email: [frank.winnefeld@empa.ch](mailto:frank.winnefeld@empa.ch)

### ABSTRACT

Magnesium-rich minerals can capture and store CO<sub>2</sub> as stable magnesium carbonate minerals and can be utilized to produce construction materials with low or even negative carbon footprints. Organic ligands influence the growth and morphology of the magnesium carbonates. Among these ligands, acetate is known to enhance the formation of carbonates. However, there is no clear link between the influence of this ligand and the hydration of MgO, which potentially leads to a different pathway of mineralization. To address this gap, we investigated the influence of Mg-acetate on the properties of brucite precipitated by hydrating MgO in aqueous solution (w/s = 20). Subsequently, carbonation of precipitated brucite under different temperature (80 and 202 °C), steam pressure (0 and 15 bar) and CO<sub>2</sub> pressure of 20 bar was also studied. The phase assemblage and the morphology of the carbonated mineral was measured. Data reveals that the addition of Mg-acetate results in a poorly crystalline brucite, and alters the morphology and the composition of the precipitate as evident from scanning electron microscopy, X-ray diffraction and thermogravimetry analyses. The characteristics of the (hydrated) magnesium carbonates formed seem to depend on the properties of the brucite seed as precursor and the reaction conditions. This work gives insights on role of organic ligands in modifying the properties of brucite and tailoring the properties of minerals to maximize the carbon capture efficiency.

**KEYWORDS:** *Brucite, Hydrothermal, Low carbon cements, (hydrated) magnesium carbonates, Mineral carbonation.*

### 1. Introduction

With more than 10 000 Gt of Mg/Ca-rich minerals (Sanna et al. (2014)) available, it offers immense potential for carbon mineralization and to the development of low-carbon or negative carbon binders. Carbon storage and utilization (CSU) has been recognized as a key step towards achieving climate goals put forward by Intergovernmental Panel on Climate Change (IPCC). The need to reduce the carbon footprint of cement industry which presently accounts for ~8% of global CO<sub>2</sub> emissions along with the increasing demand for construction materials due to increase in population, infrastructure development projects around the globe offers high-volume application for the carbonated minerals. The key challenges in using Mg-based minerals for carbon mineralization are low reactivity of Mg-silicates. However, recent development in technologies for extraction of MgO or brucite from Mg-silicates has opened new opportunities (Nduagu et al. (2012) and Scott et al. (2021)).

Many studies have focused on the development of hydrated magnesium carbonate (HMCs) binders (Dung et al. (2017), Kuenzel et al. (2018), Winnefeld et al. (2019) and Nguyen et al. (2021)). Primary challenge in using MgO or brucite as precursor is the formation of the reaction products as a passivation layer over the surface of the mineral, hindering further reaction. Organic ligands have proved to be effective chelating agents that can steer the reaction pathways and kinetics of MgO-based binders. Several works from Dung et al. (2017) have shown increased carbonation potential and mechanical performance for

reactive magnesium cements when Mg-acetate was used as hydration agent. The increase in the formation of carbonate phases in the presence of Mg-acetate was attributed to increased formation of magnesium hydroxide, which in turn carbonates to form HMCs. However, there is no clear understanding on the role of acetate on the hydration of MgO to form brucite with varying mineral properties, which could in turn lead to a different pathway of mineralization and is the focus of this study. To this end, the hydration of MgO in an aqueous environment with 0.1 M Mg-acetate solution as the hydrating agent has been done. Further, the hydrated precipitates (brucite) were carbonated in a high-pressure reactor at two different temperatures (80 and 202 °C), and at constant CO<sub>2</sub> pressure of 20 bar. The findings of this work will contribute to a better understanding of role of ligands and mineral properties on different mineralization pathways and in turn can maximize carbon sequestration potential.

## **2. Materials and Methods**

### **2.1 Materials**

MgO was prepared in the laboratory by calcining magnesium hydroxide (Mg(OH)<sub>2</sub>) purchased from VWR chemicals (assay ~99.7%) at 900 °C for 6 hours to produce reactive magnesia. The median particle size was about 8 μm as measured from laser diffraction spectroscopy. Magnesium acetate tetrahydrate (Mg(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O) was obtained from Sigma-Aldrich (assay ≥ 99%) and used without further treatment to prepare 0.1M solution in deionized water.

### **2.2 Sample preparation**

Synthetic brucite was prepared by reaction calcined MgO with 0.1 M Mg-acetate at water to solid ratio of 20. MgO was hydrated in a closed beaker and the solution was continuously stirred with a magnetic rotor at 250 rpm for 6 hours and further allowed to react at static condition till 24 hours. The precipitates were then collected through vacuum filtration (2μm filter paper, 90 cm diameter) followed by washing with isopropanol and diethyl ether and drying at 40 °C for 15 minutes. In this study, laboratory-grade brucite was used as reference.

The carbonation of the brucites was done using a 2.5 L high pressure reactor (RVD-2-250, with maximum pressure of 250 bar, and 250 °C temperature). The precursor was homogeneously mixed with 20% (by wt.) of water and was subjected to carbonation at constant CO<sub>2</sub> pressure (P<sub>CO<sub>2</sub></sub>) of 20 bar and at two different temperatures (80 and 202 °C). The samples were placed inside the autoclave and was heated to the desired temperature. A water source (100 ml) was placed at the bottom of the reactor. This enabled 100% relative humidity in the case of 80 °C and at 202 °C the presence of water built a steam pressure (P<sub>steam</sub>) of 15 bar. CO<sub>2</sub> was flushed with pressurized-CO<sub>2</sub> for about 2 min after the desired temperature was reached. The reaction conditions were maintained for 15 minutes, and the pressure was immediately released, and the system was cooled down with a heat exchanger with the cooling rate of about 3 °C/min. The solid precipitates were then collected and dried at 40 °C for 2.5 hours.

### **2.3 Methods**

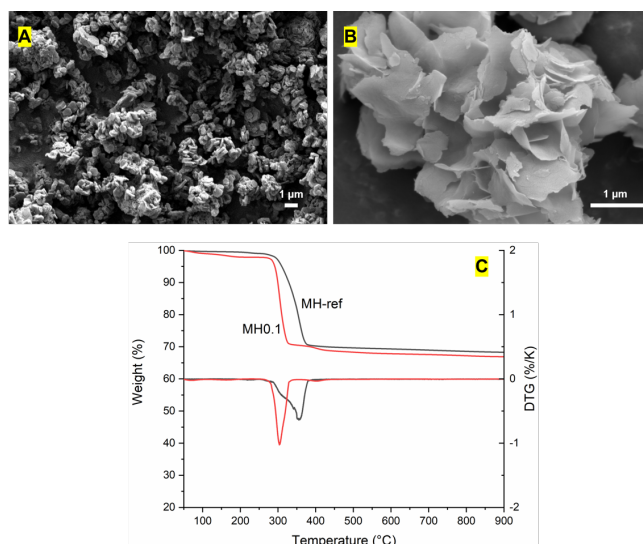
Thermal analysis of the precipitates was measured using TG, Precisa (prepASH 129, TEOPAL). The temperature was increased from 30 °C to 1000 °C with a ramp of 10 K/min. About 0.45 to 0.5 g of sample were loaded in an alumina crucible, and N<sub>2</sub> atmosphere was used. The morphologies of the hydrated and carbonated samples were studied using JEOL field emission scanning electron microscopy (FESEM). An accelerating voltage of 5 kV and a working distance of about 10-15 mm were used. The images were taken using secondary electron mode. Platinum coating at 40 mA for 40 s was done to reduce charging.

## **3. Results and Discussion**

The influence of acetate on the properties of brucite precipitated from 0.1 M Mg-acetate solution and the subsequent carbonation of the precipitates at different temperature and steam pressure is discussed in this section.

### 3.1 Hydration

The morphology of the reference brucite and brucite formed in 0.1 M Mg-acetate solution (synthesized brucite) is shown in Fig. 1. It can be noted that the presence of acetate leads to the formation of thin sheet-like layers with larger diameter than the regular hexagonal morphology of brucite. The thermal decomposition of the reference and synthesized brucite is presented in Fig. 1c. It could be noted that MgO has completely reacted with 0.1 M Mg-acetate solution to form brucite. The dehydroxylation of synthesized brucite is at about 300 °C. The shift in the thermal decomposition of brucite to lower temperature compared to reference indicates lower particle size and/or lower crystallinity of brucite that is formed in the presence of Mg-acetate.



**Fig. 1. Morphology of reference brucite (A), brucite synthesized in 0.1 M Mg-acetate (B) and the thermogravimetric analysis of the both the brucite samples (C).**

### 3.2 Carbonation

The morphology and the thermal decomposition of reference and synthesized brucite carbonated in the high-pressure reactor at 80 °C and CO<sub>2</sub> pressure of 20 bar for 15 mins is shown in Fig. 2. It is evident that the reference brucite reacts with CO<sub>2</sub> at 80 °C to form hydromagnesite. However, no clear HMCs could be identified for synthesized brucite. The dehydroxylation/ dehydration around 180 °C, however, indicate the presence of unknown reaction product.

**Fig. 2. Morphology and thermogravimetric analysis of brucite after carbonation at 80 °C and CO<sub>2</sub> pressure of 20 bar. (A) reference brucite, (B) brucite synthesized in 0.1 M Mg-acetate and (C) TG-DTG showing the formation of hydromagnesite and unreacted brucite in the case of reference brucite and possible hydrated magnesium carbonate phases in synthesized brucite.**

Fig. 3 shows the morphology and the thermal behaviour of samples reacted at 202 °C. The increase in temperature to 202 °C builds a steam pressure of 15 bar in the reactor in addition to the CO<sub>2</sub> pressure (20 bar). The effect of the steam pressure on the carbonate products formed is evident. In this condition, brucite both reference and synthesized, react to form anhydrous magnesium carbonate (MgCO<sub>3</sub>).

However, it could be noted that the rate of reaction of synthesized brucite is higher. The amount of  $\text{MgCO}_3$  formed as calculated from the mass loss between 480 °C to 650 °C is about 10% for reference and 26% for acetate modified brucite.

**Fig.**

**3. Morphology and thermogravimetric analysis of brucite after carbonation at 202 °C with steam pressure of 15 bar along with  $\text{CO}_2$  pressure of 20 bar. (A) reference brucite, (B) brucite synthesized in 0.1 M Mg-acetate and (C) TG-DTG showing the formation of magnesite along with unreacted brucite for both cases.**

#### 4. Conclusions

In this study, the influence of acetate on the properties of precipitated brucite in aqueous solution and the subsequent carbonation of the dried precipitates at different temperatures and steam pressure (constant  $P_{\text{CO}_2}$ ) was elucidated. It was observed that the acetate alters the morphology and the crystallinity of the precipitated brucite. The synthesized brucite when subjected to carbonation showed to have a profound influence on the carbon mineralization pathway. At 80 °C, unknown carbonate phases formed compared to the formation of hydromagnesite in the case of reference brucite. With increased temperature and steam pressure, though magnesite was the main carbonate mineral to form in both precursors, the rate of reaction of synthesized brucite was higher than the reference. Further, the effect of steam pressure on the phases formed is also evident. The result from this study is a step towards enhanced  $\text{CO}_2$  sequestration by tailoring mineral properties. Further, it paves way for the utilization of the resulting carbonated mineral with controlled morphologies and properties (Carbon capture and utilization, CCU) to produce low carbon construction material.

#### Acknowledgements

The authors would like to acknowledge the financial support from the University of Oulu & The Academy of Finland Profi5 326291, as well as the Academy of Finland project 329477. A part of the material characterization was carried out with the support from the Centre for Material Analysis, University of Oulu, Finland.

#### References

- Dung, N.T. and Unluer, C. (2017) "Sequestration of  $\text{CO}_2$  in reactive MgO cement-based mixes with enhanced hydration mechanisms", *Construction and Building Materials*, 143: 71–82.
- Kuenzel, C., Zhang, F., Ferrándiz-Mas, V., Cheeseman, C.R. and Gartner, E.M. (2018) "The mechanism of hydration of MgO-hydromagnesite blends", *Cement and Concrete Research*, 103: 123–129.
- Nduagu, E., Björklöf, T., Fagerlund, J., Wärnå, J., Geerlings, H. and Zevenhoven, R. (2012) "Production of Magnesium Hydroxide from Magnesium Silicate for the Purpose of  $\text{CO}_2$  Mineralisation- Part 1: Application to Finnish Serpentine", *Minerals Engineering*, 30: 75-86.
- Nguyen, H., Santos, H., Sreenivasan, H., Kunther, W., Carvelli, V., Illikainen, M. and Kinnunen, P. (2022) "On the carbonation of brucite: Effects of Mg-acetate on the precipitation of hydrated magnesium carbonates in aqueous environment", *Cement and Concrete Research*, 153: 106696.
- Sanna, A., Uibu, M., Caramanna, G., Kuusik, R. and Maroto-Valer, M. M. (2014) "A Review of Mineral Carbonation Technologies to Sequester  $\text{CO}_2$ ", *Chem. Soc. Rev.*, 43 (23): 8049–8080.
- Scott, A., Oze, C., Shah, V., Yang, N., Shanks, B., Cheeseman, C., Marshall, A. and Watson, M. (2021) "Transformation of Abundant Magnesium Silicate Minerals for Enhanced  $\text{CO}_2$  Sequestration", *Communications Earth and Environment*, 2 (1): 1–6.
- Winnefeld, F., Epifania, E., Montagnaro, F. and Gartner, E.M. (2019) "Further studies of the hydration of MgO-hydromagnesite blends", *Cement and Concrete Research*, 126: 105912.