



Rapid precipitation of magnesite micro-crystals from Mg(OH)₂-H₂O-CO₂ slurry enhanced by NaOH and a heat-ageing step (from 20 to 90C)

German Montes-Hernandez, François Renard, Rodica Chiriac, Nathaniel Findling, François Toche

► To cite this version:

German Montes-Hernandez, François Renard, Rodica Chiriac, Nathaniel Findling, François Toche. Rapid precipitation of magnesite micro-crystals from Mg(OH)₂-H₂O-CO₂ slurry enhanced by NaOH and a heat-ageing step (from 20 to 90C). *Crystal Growth and Design*, American Chemical Society, 2012, 12 (11), pp.5233-5240. <10.1021/cg300652s>. <insu-00749133>

HAL Id: insu-00749133

<https://hal-insu.archives-ouvertes.fr/insu-00749133>

Submitted on 6 Nov 2012

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Rapid precipitation of magnesite micro-crystals from Mg(OH)₂-H₂O-CO₂ slurry enhanced by NaOH and a heat-ageing step (from ~20 to 90°C)

G. Montes-Hernandez^{a,*}, F. Renard^{a,c}, R. Chiriac^b, N. Findling^a, F. Toche^b

^a ISTERre, University of Grenoble I and CNRS, BP 53, 38041 Grenoble Cedex 9, France

^b Université de Lyon, Université Lyon 1, Laboratoire des Multimatériaux et Interfaces UMR CNRS 5615, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France

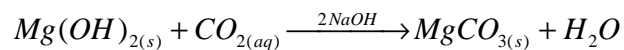
^c Physics of Geological Processes, University of Oslo, Norway

*Corresponding authors: G. Montes-Hernandez

E-mail address: german.montes-hernandez@ujf-grenoble.fr

Abstract

This study proposes a simple and novel synthesis route for rhombohedral single crystals (<2 μ m) of magnesite. This synthesis can be summarized by two main sequential reactions: (1) aqueous carbonation of synthetic brucite (Mg(OH)₂) by injection of CO₂ in a highly alkaline medium (2Molal of NaOH) at ambient temperature (~20°C), leading to precipitation of platy-compacted aggregates of dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) after 24h; (2) complete dypingite-to-magnesite transformation after 24h by a simple heat-ageing step from 20 to 90°C. The dypingite-to-magnesite transformation implies the simultaneous dehydration and carbonation of a brucitic layer of dypingite coupled with instantaneous formation of magnesite crystals. In this study, the NaOH played a catalytic role, i.e., it accelerated brucite carbonation by an increase in carbonate ion concentration with time and it promoted the formation of magnesite during the heat-ageing step as illustrated in the following global reaction:



At laboratory scale, magnesite is typically synthesized at high temperature (>90°C) and its synthesis requires several days or weeks depending on experimental conditions. For this reason, industrial-scale magnesite production has been limited. The proposed magnesite synthesis method, requiring only 48h and moderate temperature, could easily be extrapolated on an industrial scale. Moreover, a simple and novel synthesis route for the production of fine platy particles of hydromagnesite is reported, with synthesis requiring only 5h. Based on their chemical compositions and textural properties, there are potential applications for both minerals, for example as a mineral filler and/or as a flame-retardant.

Keywords: Magnesite; Hydrothermal synthesis; Precipitation; Brucite; Carbon dioxide; Hydromagnesite.

1. Introduction

The formation and textural properties of natural mineral Mg-carbonates have already been investigated in the past. However, various questions still remain unanswered concerning their formation in natural systems as well as their production at laboratory and industrial scales. Over the past two decades, the precipitation of Mg-carbonates from Mg-rich solutions or Mg-rich suspensions has been actively investigated with a view to the permanent storage of the captured anthropogenic CO₂ via ex-situ mineral carbonation; i.e., CO₂(gas)-to-carbonate(solid) transformation (e.g., 1-4). Such a carbonation reaction could therefore potentially be part of a Carbon Dioxide Capture and Storage (CCS) system, which attempts to capture CO₂ from industrial sources and store it permanently. The most successful implementation of this mineral carbonation process involves the extraction of magnesium from natural olivine or serpentines and/or Mg-rich solid waste in aqueous solutions and subsequent precipitation of Mg-carbonate under a CO₂ atmosphere (5-10). In addition, the reaction path for the MgO-H₂O-CO₂ system at ambient temperatures and at atmospheric CO₂ partial pressure is of both geological interest and practical significance. For example, if the reaction path in this system is known, this would lead to a better understanding of the low temperature alteration or weathering of mafic and ultramafic rocks. Moreover, exact knowledge of the reaction path in this system is important in order to assess the performance of geological repositories for nuclear waste where mineral periclase (MgO) and brucite (Mg(OH)₂) have been proposed as engineered barriers (e.g., 11).

Generally, in the MgO-H₂O-CO₂ or Mg(OH)₂-H₂O-CO₂ slurry systems a significant number of hydrated and basic (or hydroxylated) carbonates (e.g. nesquehontite, lansfordite, artinite, hydromagnesite, dypingite, pokrovskite, etc.) can be formed at ambient temperature and

at moderate CO₂ pressure (<55 bar) (1, 12-20, this study). All of these minerals are considered to be metastable compounds with respect to magnesite (anhydrous form: MgCO₃), which is the most stable form of Mg-carbonate. However, the low temperature precipitation of magnesite is kinetically inhibited by the preferential precipitation of some of the hydrated and/or hydroxylated Mg-carbonates mentioned above, possibly due to the high hydration nature of Mg²⁺ ions in solution (21). For this reason, the formation of magnesite at ambient temperature is virtually impossible (1). The minimum reported temperature for magnesite production is about 60-100°C, and its formation also requires a high CO₂ pressure (21-23). In various cases, the magnesite is obtained by transformation of pre-existing hydroxylated Mg-carbonate such as hydromagnesite (18, 24). This transition can be very slow; for example, below 150°C and at moderate pressures, its duration is often in the order of days. Higher temperatures, high salinity, high CO₂ pressure, low magnesium concentration (in a closed system) and the use of organic additives (ex. monoethylene glycol) are known to accelerate the hydromagnesite-to-magnesite transformation (18, 25). Reported transformation times are between 2h at 200°C in a solution saturated with NaCl, and over 100 days at 110°C at lower salinity in a closed system. Magnesite formation without any apparent hydromagnesite initially or at an intermediate stage has also been reported under high CO₂ pressures (100-150 bar) and at high temperatures (150-180°C), for experiments combining the dissolution of Mg-silicates with carbonate precipitation (23, 26-28). The requirement for high temperatures and high CO₂ pressures to precipitate the magnesite has limited its production at industrial scale. Moreover, magnesite used as a filler and pigment in paper, paint, rubber and plastics can sometimes be replaced by synthetic calcite that can be produced in a wide panel of lower temperatures and CO₂ pressures (29-31). Identifying novel and/or innovative synthesis methods for magnesite at low temperature and low CO₂ pressure still

remains a major scientific challenge to obtain a better understanding of its formation in natural systems and to facilitate its production on an industrial scale.

In this context, this study proposes a novel and simple synthesis route for the production of rhombohedral single crystals ($<2 \mu\text{m}$) of magnesite. This synthesis can be summarized by two main sequential reactions: (1) aqueous carbonation of synthetic brucite ($\text{Mg}(\text{OH})_2$) by injection of CO_2 (50 bar) in a highly alkaline medium (2Molal of NaOH) at ambient temperature ($\sim 20^\circ\text{C}$), leading to the precipitation of platy-compacted aggregates of dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$) after 24h; (2) complete dypingite-to-magnesite transformation after 24h by a simple heat-ageing step from 20 to 90°C . The NaOH plays a catalytic role, i.e., it accelerates brucite carbonation by increasing the concentration of carbonate ions and promoting the exclusive formation of magnesite during the heat-ageing step. Conversely, when the experiment was carried out in the absence of NaOH, incomplete carbonation of brucite was observed and the hydromagnesite became the dominant Mg-carbonate after the heat-ageing step. Here, the solid product contained only about 5% of magnesite, and is called hydromagnesite-magnesite-brucite composite hereafter. The specific P_{CO_2} -T conditions required to precipitate pure hydromagnesite as well as hydromagnesite-eitelite and hydromagnesite-magnesite-brucite composites from $\text{Mg}(\text{OH})_2$ - H_2O - CO_2 slurry in the presence/absence of NaOH are also reported. Various analytical tools such as X-ray diffraction (XRD), Field Emission Gun Scanning Electron Microscopy (FESEM), Thermogravimetric analyses (TGA) and N_2 adsorption isotherms were used to characterize the solid products.

2. Materials and Methods

The main experimental conditions required to synthesize magnesite, hydromagnesite and Mg-carbonate composites are summarized in Table 1 and the experimental procedures are described in detail in the following sections.

2.1. Synthesis of magnesite ($MgCO_3$)

One litre of high-purity water with electrical resistivity of 18.2 M Ω -cm, 2 mol of NaOH and 1 mol of synthetic brucite ($Mg(OH)_2$, with chemical purity >95%) were placed in a titanium reactor (autoclave with internal volume of two litres). This reactive suspension was immediately stirred during the reaction by means of a constant mechanical stirring system (400 rpm). The temperature of the suspension increased instantaneously to 26°C due to the exothermic dissolution of NaOH in the system. At this reference temperature, CO₂ (\approx 2 mol) was immediately injected in the system at a pressure of 50 bar. The carbonation reaction started instantaneously as attested by the continuous consumption of CO₂ (monitored by a pressure drop in the system) and an increase in temperature during the exothermic carbonation reaction (the maximum temperature reached was \approx 38°C after 1h of reaction ($\Delta T \approx 12^\circ C$)). After 24h of carbonation reaction at ambient (or room) temperature (16-20 °C) (including the exothermic period), a heat-ageing step was performed from ambient temperature to 90°C for a further 24h. Based on preliminary experiments, was found that the NaOH played a catalytic role, i.e., it accelerated brucite carbonation by an increase in carbonate ion concentration with time and promoted the formation of magnesite during the heat-ageing step. More details are provided in the Results and Discussion section.

At the end of the experiment, the autoclave was removed from the heating system and immersed in cold water. The residual CO₂ was degassed from the reactor during water-cooling period. After water cooling at 30°C (for about 15 minutes) the autoclave was disassembled, and the solid product was carefully recovered and separated by centrifugation (30 minutes at 12,000 rpm), decanting the supernatant solutions. The solid product was washed twice by re-dispersion/centrifugation processes in order to remove the soluble sodium carbonates formed during the synthesis. Finally, the solid product was dried directly in the centrifugation flasks at 80°C for 48 h. The dry solid product was manually recovered and stored in plastic flasks for subsequent characterization (FESEM, XRD, TGA and N₂ sorption isotherms).

2.2. Synthesis of hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$)

Two methods are reported in this study.

(i) Precipitation of hydromagnesite from Mg(OH)₂-H₂O-CO₂ slurry. One litre of high-purity water with electrical resistivity of 18.2 MΩ-cm and 1 mol of synthetic brucite (Mg(OH)₂) with chemical purity >95%) were placed in a titanium reactor (autoclave with internal volume of two litres). This reactive suspension was immediately stirred at 400 rpm and heated to 90°C. Once the temperature had stabilized, CO₂ was injected at a pressure of 50 bar and the total pressure in the system was immediately increased from 50 to 90 bar by argon injection. At these *T* and *P* conditions, the vapor phase primarily consists of a mixture of Ar + CO₂, with CO₂ in a supercritical state. The reaction time in this solid-liquid-gas thiphasic experiment (Mg(OH)₂-H₂O-CO₂ slurry) was typically 12 days in order to obtain high-purity hydromagnesite. The solid

product recovery/drying procedures were similar to those described above for the synthesis of magnesite.

(ii) Knowing the catalytic action of NaOH on brucite carbonation, a faster method was implemented to synthesize hydromagnesite. This simple method required only five hours of carbonation reaction. In fact, this method is very similar to the synthesis method for magnesite (see above) except for the reaction time in each carbonation step: only 3h for carbonation at ambient temperature (including the exothermic period) and 2h for the heat-ageing step at 90°C were required to obtain high-purity hydromagnesite. The solid product recovery/drying procedures were the same as described above for magnesite synthesis.

2.3. Synthesis of Mg-carbonate composites

Hydromagnesite-magnesite-brucite composite. This composite material was synthesized by making a simple modification to the synthesis method for magnesite (see above). More specifically, the carbonation reaction of brucite was carried out in the absence of NaOH, leading to the formation of hydromagnesite (dominant phase) and magnesite (minor phase). These Mg carbonates were intimately dispersed with residual (or unreacted) brucite forming a so-called hydromagnesite-magnesite-brucite composite. The solid product recovery/drying procedures were similar to those described above for the synthesis of magnesite, although in this case the solid product washing procedure to remove soluble Na carbonate was not necessary for this synthesis.

Hydromagnesite-eitelite composite. This composite material was synthesized by making simple modifications to the synthesis method for magnesite (see above). In this case, a heat-ageing step

at 45°C was performed immediately after CO₂ injection into the system. The reaction time in this Mg(OH)₂-H₂O-NaOH-CO₂ system was typically 10 days in order to obtain a hydromagnesite-eitelite binary composite. In this particular case, it was found that the sodium initially contained in NaOH reacted significantly to produce the eitelite mineral (Na₂CO₃·MgCO₃). So in this case, the NaOH had not just a catalytic affect because sodium was also incorporated in the mineral phase. The solid product recovery/drying procedures were the same as described above for magnesite synthesis.

2.4. Characterization of solid products

FESEM observations: magnesite, hydromagnesite and various Mg-carbonate composites were dispersed by ultrasonic treatment in absolute ethanol for five to ten minutes. One or two droplets of the suspension were then deposited directly on an aluminum support for SEM observations, and coated with platinum. The morphology of various selected powders was observed using a Zeiss Ultra 55 field emission gun scanning electron microscope (FESEM) with a maximum spatial resolution of approximately 1nm at 15kV.

XRD measurements: X-Ray Powder Diffraction (XRD) analyses were performed using a Siemens D5000 diffractometer in Bragg-Brentano geometry; equipped with a theta-theta goniometer with a rotating sample holder. The XRD patterns were collected using Cu k α ₁ ($\lambda_{k\alpha_1}=1.5406\text{\AA}$) and k α ₂ ($\lambda_{k\alpha_2}=1.5444\text{\AA}$) radiation in the range $2\theta = 10 - 70^\circ$ with a step size of 0.04° and a counting time of 6 seconds per step.

Thermogravimetric analyses: TGA for all Mg-carbonate samples were performed with a Mettler Toledo TGA/SDTA 851e instrument under the following conditions: sample mass of about 10

mg, 150 μ l alumina crucible with a pinhole, heating rate of $5^{\circ}\text{C min}^{-1}$, and inert N_2 atmosphere of 50 ml min^{-1} . Sample mass loss and associated thermal effects were obtained by TGA/SDTA. In order to identify the different mass loss steps, the TGA first derivative (rate of mass loss) was used. The TGA apparatus was calibrated in terms of mass and temperature. Calcium oxalate was used for the sample mass calibration. The melting points of three compounds (indium, aluminum and copper) obtained from the DTA signals were used for the sample temperature calibration.

N₂ sorption isotherms: N_2 sorption isotherms for magnesite, hydromagnesite and Mg-carbonate composites were obtained by using a sorptomatic system (Thermo Electron Corporation). The specific surface area of powdered samples was estimated by applying the Brunauer-Emmet-Teller (BET) equation in the $0.05 \leq P/P_0 \leq 0.35$ interval of relative pressure and based on a value of 16.2 \AA^2 for the cross-sectional area of molecular N_2 . A non-linear regression by the least-squares method was performed to fit the interval data (n_{ads} vs. P/P_0) in the experimental isotherms.

3. Results and Discussion

3.1. Magnesite precipitation: Physicochemical steps and reaction mechanism

The precipitation of magnesite at low temperature is kinetically inhibited by the preferential precipitation of hydrated and/or hydroxylated Mg-carbonates (e.g., nesquehontite, lansfordite, artinite, hydromagnesite, dypingite, pokrosvskite, etc.), possibly due to the high hydration nature of Mg^{2+} ions in solution (21). Based on this assumption, the formation of magnesite at ambient temperature is virtually impossible (1).

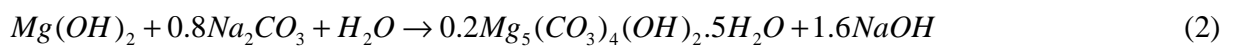
A simple and novel synthesis route for the formation of rhombohedral single crystals (<2μm) of magnesite is described here. The precipitation process requires only 48h and can be summarized by two main sequential steps (see Fig. 1):

(1) Aqueous carbonation of synthetic brucite (Mg(OH)₂) by injection of CO₂ in a highly alkaline medium (2Molal of NaOH) at ambient temperature (~20°C). This physicochemical step led to the precipitation of platy-compacted aggregates of dypingite ($Mg_5(CO_3)_4(OH)_2 \cdot 5H_2O$) after 24h of fluid-solid interaction as attested by XRD and FESEM observations on the solid (see Fig. 1 and 2). Moreover, a moderate specific surface area (9 m²/g) was deduced from the N₂ adsorption isotherm (Table 2).

Assuming that CO₂ absorption in the highly alkaline solution of NaOH is faster and greater than in water via the following exothermic reaction:

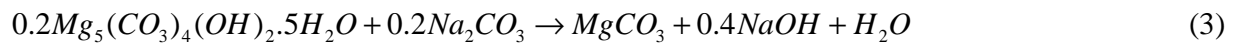


the carbonation of brucite leading to the precipitation of dypingite can be written as follows:

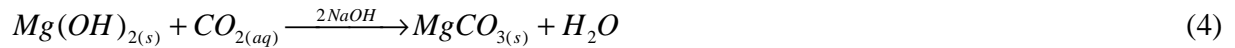


These two coupled reactions take place at ambient temperature (~20°C) for the first 24 hours. However, as observed in the experiments, these reactions are exothermic, with the suspension temperature reaching a maximum value of 38±1°C after about 1h of reaction. The maximum value of temperature remains constant for about 2h and then it decreases slowly to ambient temperature (~20°C).

(2) A heat-ageing step from 20 to 90°C was performed to obtain complete transformation of dypingite to magnesite after 24 hours. This assumes a solid state transition implying the simultaneous dehydration and carbonation of a brucitic layer of dypingite precursor coupled with instantaneous formation of magnesite crystals. However, the dissolution of the dypingite precursor coupled with magnesite precipitation cannot be excluded. The general reaction for the dypingite-to-magnesite transformation can be written as follows:



In this study, NaOH played a catalytic role, i.e., it accelerated brucite carbonation by an increase in carbonate ion concentration with time. The catalytic role can be verified by adding reactions 1 to 3. The presence of NaOH also promoted magnesite formation during the heat-ageing step. In this way, the precipitation of magnesite, enhanced by NaOH and a heat-ageing step, can be illustrated by the following global carbonation reaction:

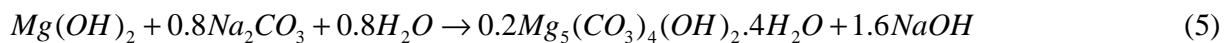


This reaction takes place exclusively when NaOH is used as a catalytic agent. Conversely, if the same experiment is carried out in the absence of NaOH, incomplete carbonation of brucite is observed and hydromagnesite is the dominant Mg-carbonate after the heat-ageing step. In such case, the hydromagnesite-magnesite-brucite composite obtained contains only about 5% of magnesite (see Fig. 3).

3.2. Synthesis of hydromagnesite

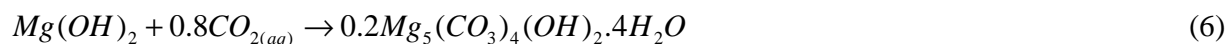
Hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$) is a naturally occurring compound found in magnesium-rich minerals such as serpentine and altered magnesium-rich igneous rocks. It is also produced by alteration of brucite in periclase marbles. In view of its potential use in industrial applications, several scientific studies, technical reports and patents have been published concerning its synthesis at laboratory scale (e.g., 19).

Two different methods for synthesizing hydromagnesite under laboratory conditions are reported here; both methods can be used to synthesize high-pure hydromagnesite as attested by X-ray diffraction observations on the powder products where the experimental XRD patterns successfully match with the ICDD card # 070-0361 (see Fig. 4). Platy fine particles with moderate specific surface area ($>20m^2/g$) were obtained for both methods (see Table 2 and FESEM image for synthesis S3 in Fig. 5). However, the synthesis time is drastically reduced from 12 days to 5 hours when NaOH is used as catalyst and/or additive in the $Mg(OH)_2$ - H_2O - CO_2 system. Similarly to the synthesis of magnesite, the NaOH-rich solution accelerates brucite carbonation by an increase in carbonate ion concentration with time. For this case, the general reaction for hydromagnesite precipitation, i.e., an intermediate hydroxylated (or basic) Mg-carbonate with respect to magnesite, can be written as follows:



As mentioned above, this carbonation reaction of brucite takes only five hours. Conversely, the hydrothermal carbonation of brucite in the absence of NaOH takes about 12 days to obtain hydromagnesite with similar textural properties. The hydrothermal carbonation of brucite to form

hydromagnesite at 90°C, 90 bar, and in the absence of NaOH can be described by the following global reaction.



In conclusion, the use of NaOH as a catalyst is a powerful option to accelerate the production of hydromagnesite (only five hours) with potential industrial applications given its advantageous textural properties and composition, as reported in Table 2.

3.3. Synthesis of Mg-carbonate composites

As mentioned in the Introduction, magnesite is considered to be the most stable Mg-carbonate compound. However, its precipitation at low temperature is kinetically inhibited by the preferential precipitation of hydrated and/or hydroxylated Mg-carbonates, possibly due to the high hydration nature of Mg^{2+} ions in solution (21). Based on these concepts, the formation of anhydrous Mg-carbonates (e.g., magnesite and dolomite) at ambient temperature is virtually impossible (1). However, anhydrous eitelite ($Na_2CO_3 \cdot MgCO_3$) can be formed at low-temperature (32). This mineral is not found in large quantities in natural sedimentary environments but its anhydrous form is certainly of interest for understanding how Mg in solution can be dehydrated to form anhydrous Mg carbonates at low temperature.

In the present study, the catalytic role of NaOH has been demonstrated for rapid precipitation of magnesite (reactions 1 to 4) and hydromagnesite (reaction 5) (see also Tables 1 and 2). However, under specific conditions (see S4 in Table 1), the sodium dissolved during the carbonation process may react significantly after 10 days to form an atypical hydromagnesite-

eitelite composite at low temperature (45°C), both minerals were clearly identified by X-ray diffraction on the solid product and the experimental XRD pattern obtained successfully matched the ICDD cards #070-0361 for hydromagnesite and #024-1227 for eitelite (see S4 in Fig. 6). FESEM observations have revealed irregular fine aggregates (S4 in Fig. 5) and a moderate specific surface area (11 m²/g) was deduced from the N₂ adsorption isotherm (see also Table 2). It is assumed that hydromagnesite is initially formed in this system, according to reaction (5), followed by the precipitation of eitelite. In such a case, two explanations are possible: (i) dissolution of hydromagnesite (so-called precursor) coupled with eitelite precipitation or (ii) a solid state transition implying the simultaneous dehydration and carbonation of a brucitic layer of hydromagnesite precursor coupled with the progressive formation of eitelite crystals. The general reaction for hydromagnesite-to-eitelite transformation can be written as follows:



This reaction cannot be completed because only 1mol of Na₂CO₃ can be produced in the system, see reaction (1). For this reason, the solid recovered after 10 days of reaction contains mainly hydromagnesite and eitelite minerals, the so-called hydromagnesite-eitelite composite in the present study.

On the other hand, as mentioned in sub-section 3.1, the carbonation of brucite in the absence of NaOH, leads to incomplete brucite carbonation after a heat-ageing step (S2 synthesis) where the mineral composition of the recovered solid was hydromagnesite, magnesite and residual brucite (see Fig. 3 and 6). More specific information on the experimental conditions, composition and textural properties are provided in Tables 1 and 2. For this case, the hydromagnesite formation is in agreement with reaction (6) where a small proportion of hydromagnesite was transformed into

magnesite by the following classical reaction:



In general, higher temperatures (>150°C), high salinity, high CO₂ pressure, low magnesium concentration (in a closed system) and the use of organic additives (e.g., monoethylene glycol) are known to accelerate the hydromagnesite-to-magnesite transformation (18, 25).

3.4. Potential industrial applications

In general, anhydrous Mg-carbonates (e.g., magnesite, eitelite, dolomite, etc.) and intermediate basic magnesium carbonates (e.g., dypingite, hydromagnesite, artinite, pokrosvskite, etc.) with controlled morphology and particle size and moderate-to-high specific surface area, have great potential for use in applications such as mineral filler and pigment in paper, paint, rubber and plastics, and could also be used as flame-retardants. Unfortunately, the production at industrial scale has been limited because high pressures, high temperatures and long production times are frequently required. The present study shows how high-purity magnesite can be produced after 48h of reaction and how high-purity hydromagnesite can be produced after 5h of reaction. Based on its composition and textural properties, the magnesite could be used as a mineral filler in paper and pigments. Moreover, additional applications such as a flame-retardant in electrical and electronic parts, construction materials, etc., can be envisaged for hydromagnesite because their dehydration-dehydroxylation-decarbonation processes consume significant amount of energy in a broad interval of temperature (see Fig. 7). Moreover, the platy fine particles and moderate specific surface area (28 m²/g) of hydromagnesite can facilitate its dispersion/distribution when used as a mineral filler or flame-retardant.

4. Conclusion

This study proposes simple and novel synthesis routes for the production of rhombohedral single crystals ($<2\mu\text{m}$) of magnesite and platy fine particles of hydromagnesite. It also demonstrates the catalytic action of NaOH during the carbonation process of brucite mineral, leading to fast precipitation of high-purity magnesite after 48h of reaction and fast precipitation of high-purity hydromagnesite after only 5h of reaction. For each case, a global reaction mechanism has been proposed. Finally, it is worth noting that both minerals could have good potential for use as mineral filler and/or as flame-retardant.

Acknowledgements

The authors are grateful to the French National Center for Scientific Research (CNRS) and the University Joseph Fourier in Grenoble for providing financial support.

References

- (1) Hanchen, M.; Prigiobbe, V.; Baciocchi, R.; Mazzotti, M. *Chem. Eng. Sci.* **2008**, 63, 1012.
- (2) Saldi, G. D.; Jordan, G.; Schott J.; Oelkers, E. H. *Geochem. Cosmochem. Acta* **2009**, 73, 5646.
- (3) Zhao, L.; Sang, L.; Chen, J.; Ji, J.; Teng H. H. *Environ. Sci. Technol.* **2010**, 44, 406.
- (4) Benezeth, P.; Saldi, G. D.; Dandurand, J.-L., Schott, J. *Chem. Geol.* **2011**, 286, 21.
- (5) IPCC (Intergovernmental Panel on Climate Change) Special Report on Carbon Dioxide Capture and Storage. *Cambridge University Press*, **2005**, Cambridge, UK, New York.
- (6) O'Connor, W. K.; Dahlin, C. L.; Rush, G. E.; Gerdemann, S. J.; Penner, L. R.; Nilsen, D. N. Final report aqueous mineral carbonation: mineral availability, pretreatment, reaction parametrics, and process studies. *Technical Report DOE/ARC-TR-04-002*, **2005**, Albany Research Center.
- (7) Munz, I. A.; Kihle, J.; Brandvoll, O.; Machenbach I.; Carey, J. W.; Haug, T. A.; Johansen, H., Eldrup, N. *Energy Procedia* **2009**, 1, 4891.
- (8) Lin, P.-C.; Huang, C.-W.; Hsiao, C.-T.; Teng, H. *Environ. Sci. Technol.* **2008**, 42, 2748.
- (9) Sun, Y.; Parikh, V.; Zhang, L. *J. Hazard. Mater.* **2012**, 209-210, 458.
- (10) Bobicki, E. R.; Liu, Q.; Xu, Z.; Zeng, H. *Progress in Energy and Combustion Science* **2012**, 38, 302.
- (11) Xiong, Y.; Lord, A. S. *Appl. Geochem.* **2008**, 23, 1634.

- (12) Langmuir, D. *The Journal of Geology* **1965**, 73, 730.
- (13) Oh, K. D.; Morikawa, H.; Iwai, S.-I.; Aoki, H. *American Mineralogist* **1973**, 58, 339.
- (14) Hales, M. C.; Frost, R. L.; Martens, W. J. *Raman Spectrosc.* **2008**, 39, 1141.
- (15) Deelman, J. C. *Neues Jahrbunch Für Mineralogy, Monatshefte* **1999**, 7, 289.
- (16) Deelman, J. C. *Notebooks on Geology* **2003**, Letter 2003/03 (CG2003_L03_JCD).
- (17) Zhang, Z.; Zheng, Y.; Ni, Y.; Liu, Z., Chen, J.; Liang X. *J. Phys. Chem. B* **2006**, 110, 12969.
- (18) Sandengen, K.; Josang, L. O.; Kaasa, B. *Ind. Eng. Chem. Res.* **2008**, 47, 1002.
- (19) Pohl, M.; Rainer, C., Esser, M. *European Patent Application* **2011**, EP 2 322 581 A1.
- (20) Fournier, J. *Research Center, Richmond, Virginia* **1992**, Report 2022153401.
- (21) Deelman, J. C. *Chemie Der Erde-Geochemistry* **2001**, 61, 224.
- (22) Usdowski, E. *Naturwissenschaften* **1989**, 76, 374.
- (23) Giammar D. E.; Bruant Jr., R. G.; Peters, C. A. *Chem. Geol.* **2005**, 217, 257.
- (24) Stevula, L.; Petrovic, J.; Kubranova, M. *Chemicke Zvesti* **1978**, 32, 441.
- (25) Zhang, L. *Sandia National Laboratories, Albuquerque, USA* **2000**, Technical Report SAN099-19465.
- (26) Bearat, H.; Mckelvy, M. J.; Chizmeshya, A. V. G.; Gormley, D., Nunez, R.; Carpenter, R. W., Squires, K.; Wolf, G. H. *Environ. Sci. Technol.* **2006**, 40, 4802.

- (27) Wolf, G. H.; Chizmeshya, A. V. G.; Diefenbacher, J.; Mckelvy, M. J. *Environ. Sci. Technol.* **2004**, 38, 932.
- (28) O'Connor, W. K., Dahlin, D. C.; Rush, G. E.; Dahlin, C. L.; Collins, W, K. *Mineral & Matallurgical Processing* **2002**, 19, 95.
- (29) Montes-Hernandez, G.; Renard, F.; Geffroy, N.; Charlet, L.; Pironon, J. *J. Cryst. Growth* **2007**, 308, 228.
- (30) Montes-Hernandez, G.; Fernandez-Martinez, A.; Renard, F. *Cryst. Growth Des.* **2009**, 9, 4567.
- (31) Montes-Hernandez, G.; Daval, D.; Chiriac, R.; Renard, F. *Cryst. Growth Des.* **2010**, 10, 4823.
- (32) Deelman, J. C. *Neues Jahrbunch Für Mineralogy, Monatshefte* **1984**, H10, 468.

Table 1. Summary of experimental conditions for the synthesis of anhydrous and hydroxylated Mg-carbonates.

| Exp. Label | System | Use of NaOH | T _i (°C) | P _i (bar) | Heat-ageing step | t _r | Isobaric/Anisobaric | Mineral |
|------------|---|-------------|---------------------|----------------------|------------------|----------------|---------------------|-----------------|
| S0 | Mg(OH) ₂ -H ₂ O-CO ₂ | Yes | Ambient (~26*) | 50 | not | 24 hours | Anisobaric | Dypingite |
| S1 | Mg(OH) ₂ -H ₂ O-CO ₂ | Yes | Ambient (~26*) | 50 | From 20 to 90 °C | 48 hours | Anisobaric | Magnesite |
| S2 | Mg(OH) ₂ -H ₂ O-CO ₂ | Not | Ambient (~20) | 50 | From 20 to 90 °C | 48 hours | Anisobaric | H-M-B composite |
| S3 | Mg(OH) ₂ -H ₂ O-CO ₂ | Not | 90 | 50 | not | 12 days | Isobaric** | Hydromagnesite |
| S4 | Mg(OH) ₂ -H ₂ O-CO ₂ | Yes | Ambient (~26*) | 50 | From 26 to 45 °C | 10 days | Anisobaric | H-E composite |
| S5 | Mg(OH) ₂ -H ₂ O-CO ₂ | Yes | Ambient (~26*) | 50 | From 38 to 90 °C | 5 hours | Anisobaric | Hydromagnesite |

T_i: Temperature at which the CO₂ gas was injected; P_i: Initial CO₂ pressure in the system; t_r: total reaction time (including heat-ageing step); *: Temperature of suspension (including exothermic dissolution of NaOH in water); **: synthesis at constant gas (CO₂+Ar) pressure (90 bar), the consumption of CO₂ was regulated by automatic argon injection; H: Hydromagnesite; M: Magnesite; B: Brucite; E: Eitelite.

Table 2. Mineral composition, morphology and specific surface area (S_{BET}) for synthesized Mg-carbonates deduced from XRD, TGA, FESEM and N_2 adsorption isotherms.

| Exp. Label | Main Mineral(s) | Formula | Minor mineral(s) (<5%) | Morphology | S_{BET} (m^2/g) |
|------------|-----------------|---|-------------------------|----------------------------|--|
| S0 | Dypingite | $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ | Eitelite | Platy-compacted aggregates | 9 |
| S1 | Magnesite | MgCO_3 | Eitelite+hydromagnesite | Rhombohedral crystals | 3 |
| S2 | Hydromagnesite | $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ | Not detected | Platy-compacted aggregates | 6 |
| | Magnesite | MgCO_3 | | Rhombohedral crystals | |
| S3 | Brucite | $\text{Mg}(\text{OH})_2$ | | Hexagonal crystals | 23 |
| | Hydromagnesite | $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ | Brucite | Platy fine particles | |
| S4 | Hydromagnesite | $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ | Brucite | Irregular aggregation | 11 |
| | Eitelite | $\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3$ | | | |
| S5 | Hydromagnesite | $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ | Brucite | Platy fine particles | 28 |

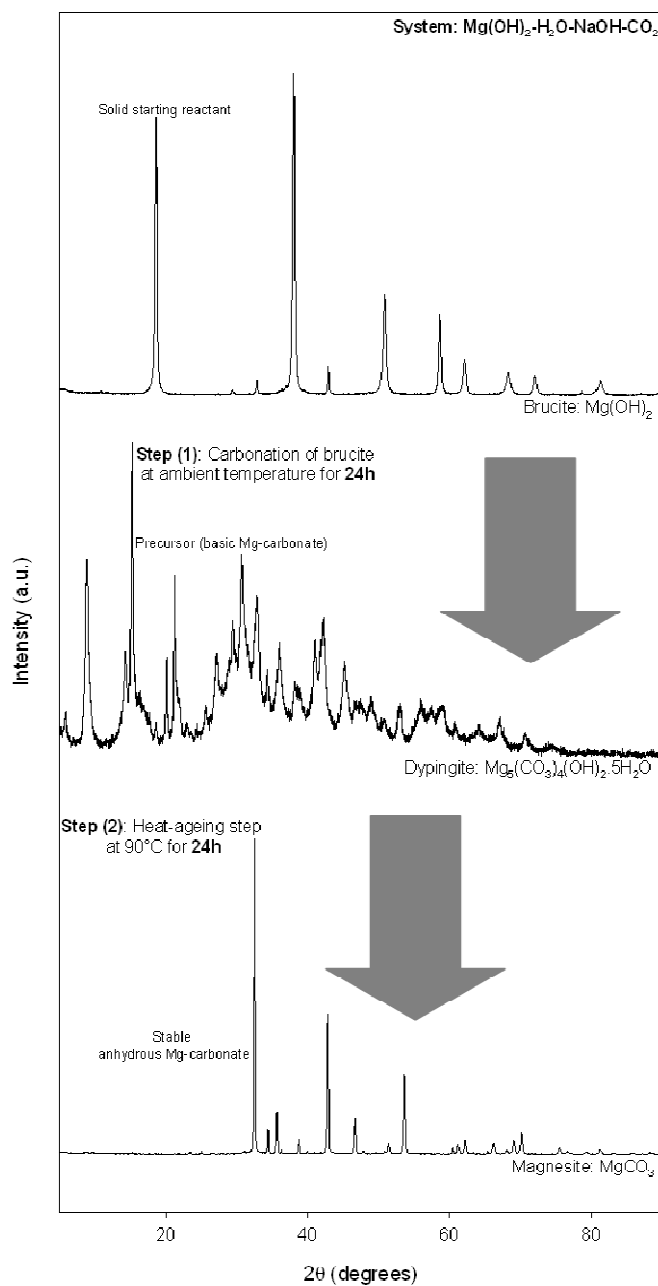


Figure 1. Fast precipitation of magnesite from $\text{Mg(OH)}_2\text{-H}_2\text{O-CO}_2$ slurry, enhanced by NaOH and a heat-ageing step from ambient temperature to 90°C. Only 48h were required to produced high-purity magnesite as attested from the XRD pattern (ICDD # 086-2346). Precursor or basic Mg-carbonate was identified as dypingite from the XRD pattern (ICDD # 023-1218). High-purity synthetic brucite was used as solid starting reactant as attested from the XRD pattern (ICDD # 083-0114).

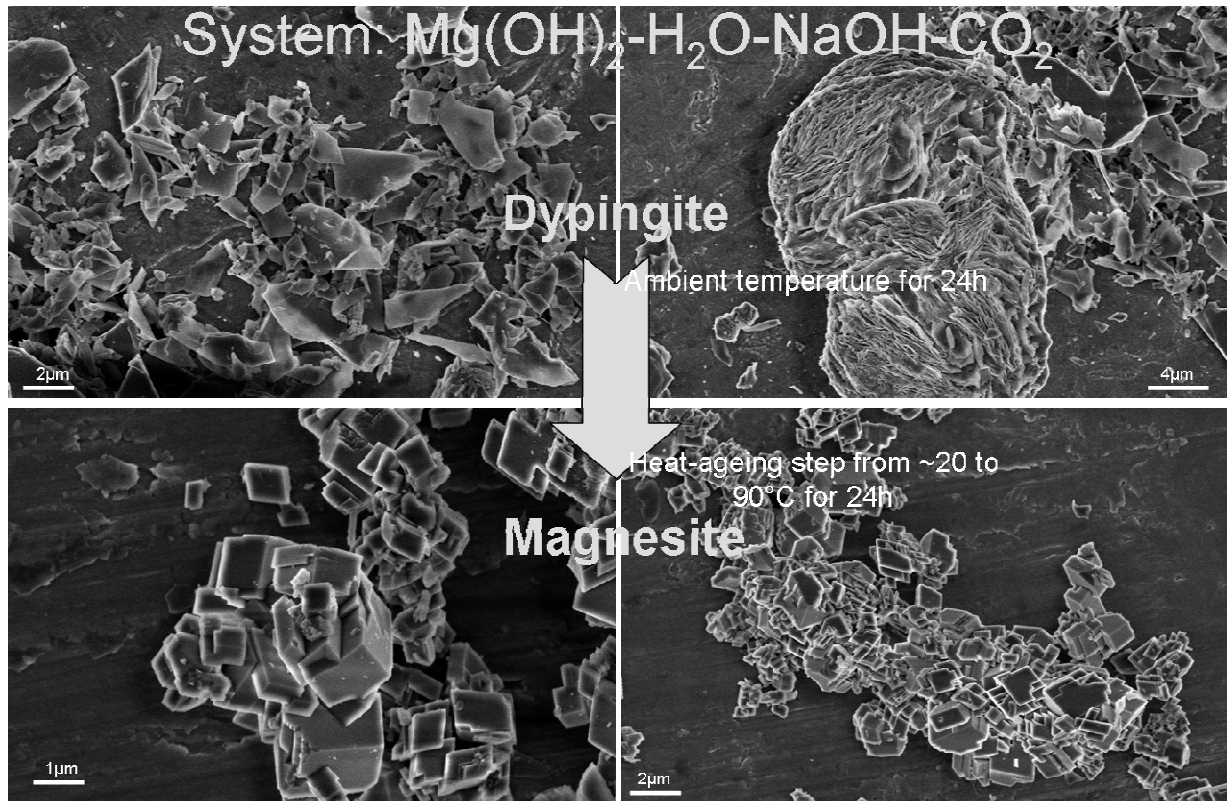


Figure 2. FESEM images showing the morphology of the dypingite precursor and magnesite crystals precipitated from the $\text{Mg}(\text{OH})_2\text{-H}_2\text{O-NaOH-CO}_2$ system at ambient temperature and after a heat-ageing step at 90°C, respectively.

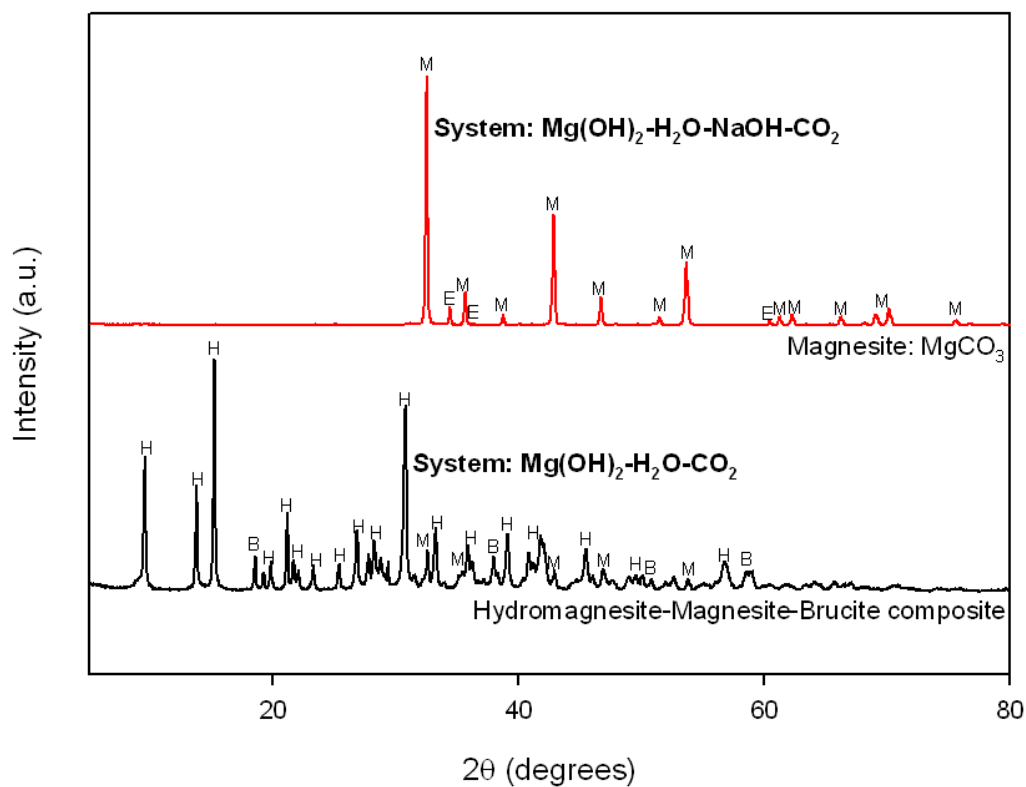


Figure 3. XRD patterns showing the aqueous carbonation of brucite Mg(OH)_2 in the presence and absence of NaOH. The sodium hydroxide played a catalytic role to precipitate the magnesite after only 48h of reaction. Experimental XRD patterns matching magnesite (M: ICDD # 086-2346), hydromagnesite (H: ICDD # 070-0361), eitelite (E: ICDD # 024-1227) and brucite (B: # 044-1482).

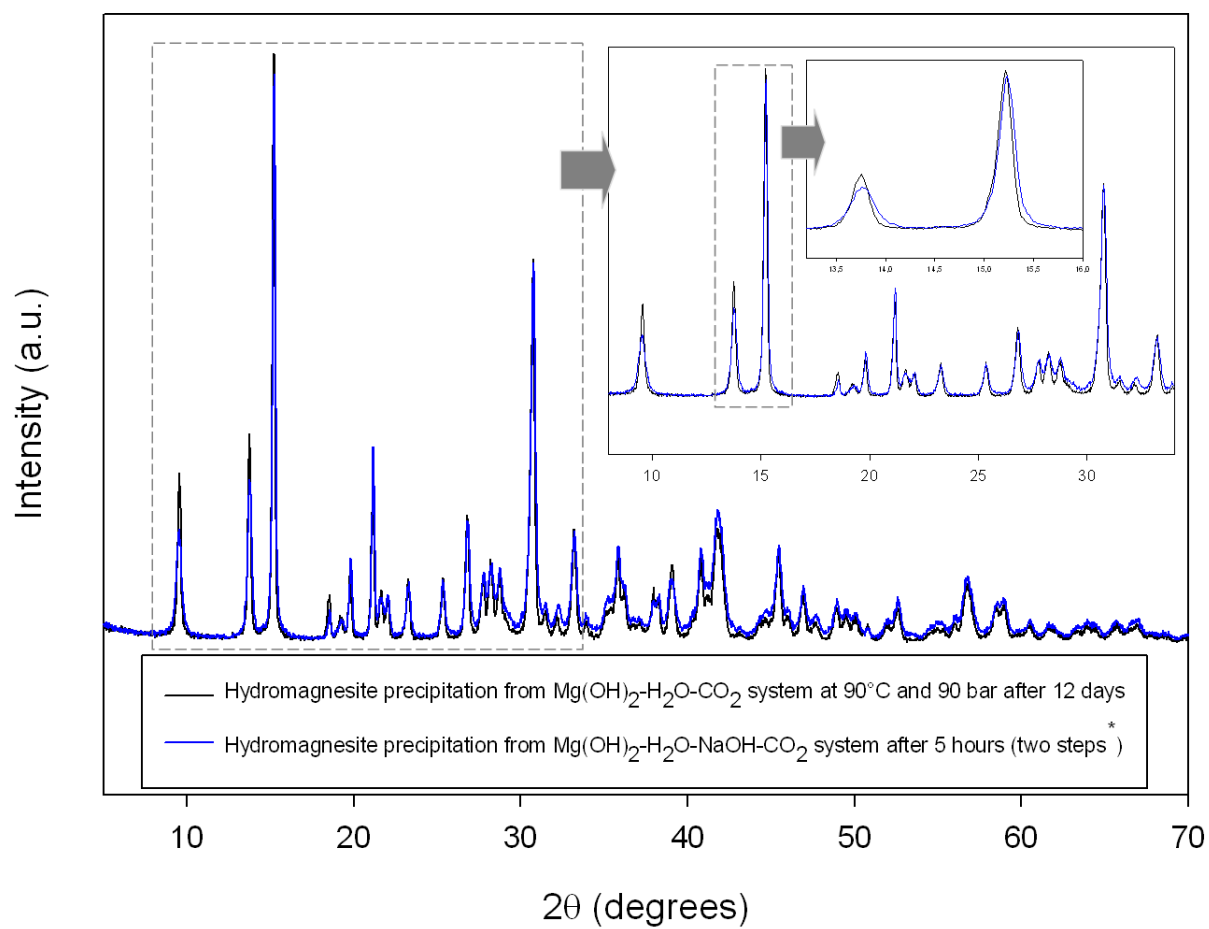


Figure 4. Experimental XRD patterns corresponding to hydromagnesite (ICDD # 070-0361) synthesized from the $\text{Mg}(\text{OH})_2\text{-H}_2\text{O-CO}_2$ system in the absence and presence of NaOH, S2 and S5 syntheses in tables 1 and 2, respectively. *: (1) carbonation of brucite without external heating for 3h followed by (2) heat-ageing step from 38 to 90°C for 2h.

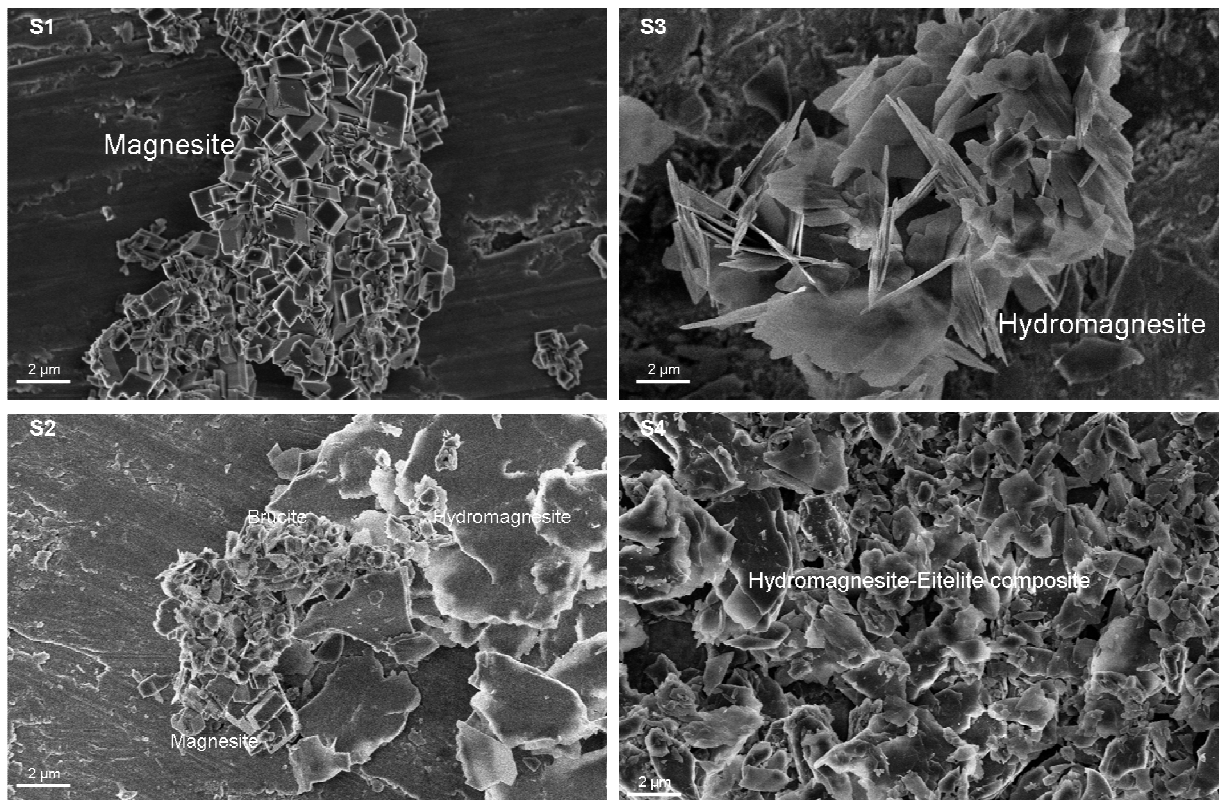


Figure 5. FESEM images showing the morphology of magnesite (S1), hydromagnesite (S3), hydromagnesite-magnesite-brucite composite (S2) and hydromagnesite-eitelite composite (S4) precipitated from the $\text{Mg}(\text{OH})_2\text{-H}_2\text{O-CO}_2$ system in the presence/absence of NaOH. Specific experimental conditions for these syntheses are reported in Table 1.

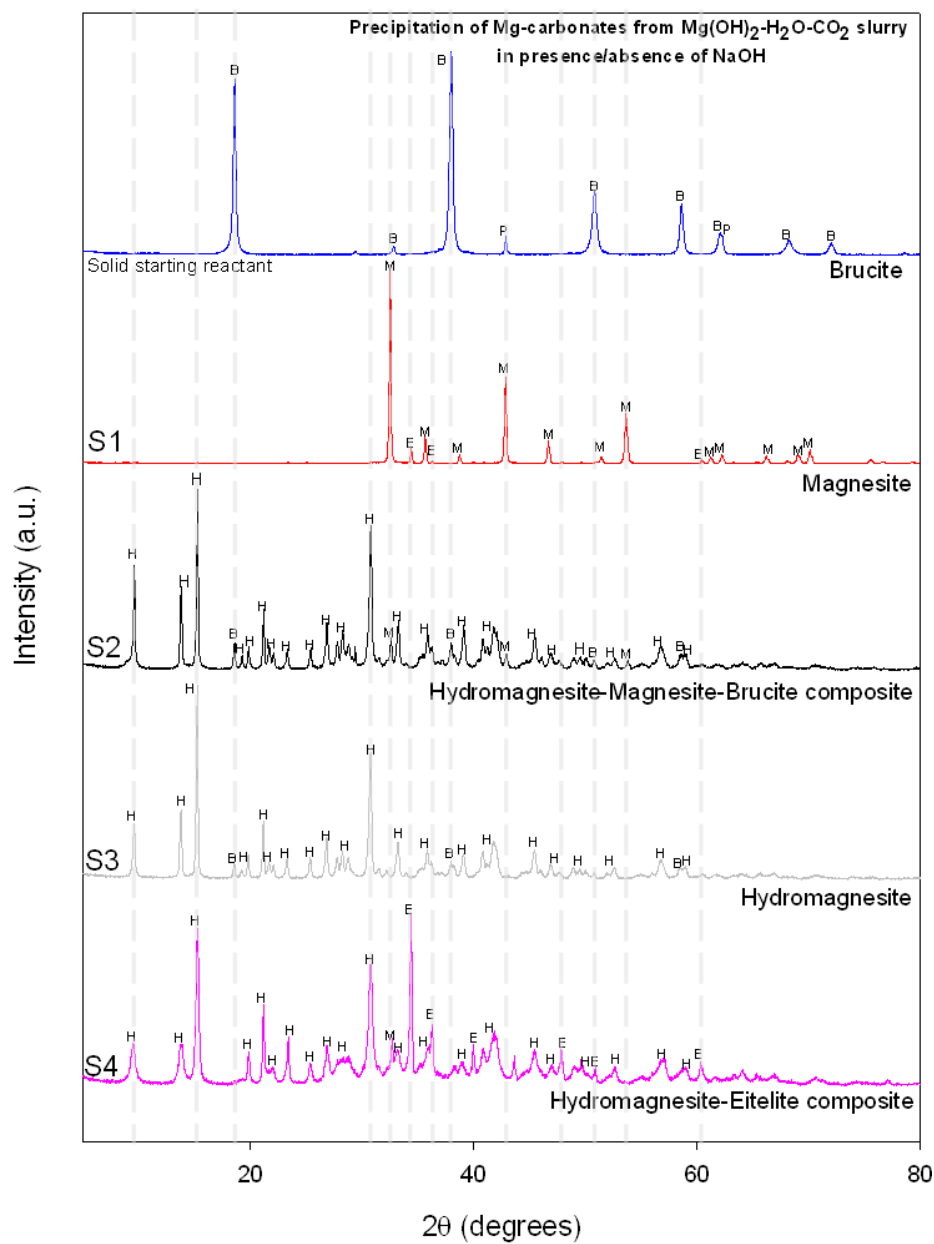


Figure 6. Characterization by X-ray diffraction of the solid starting reactant (brucite) and the solid products recovered after brucite carbonation in the presence or absence of NaOH (syntheses: S1, S2, S3 and S4). Experimental XRD patterns matching magnesite (M: ICDD # 086-2346), hydromagnesite (H: ICDD # 070-0361), eitelite (E: ICDD # 024-1227) and brucite (B: # 044-1482).

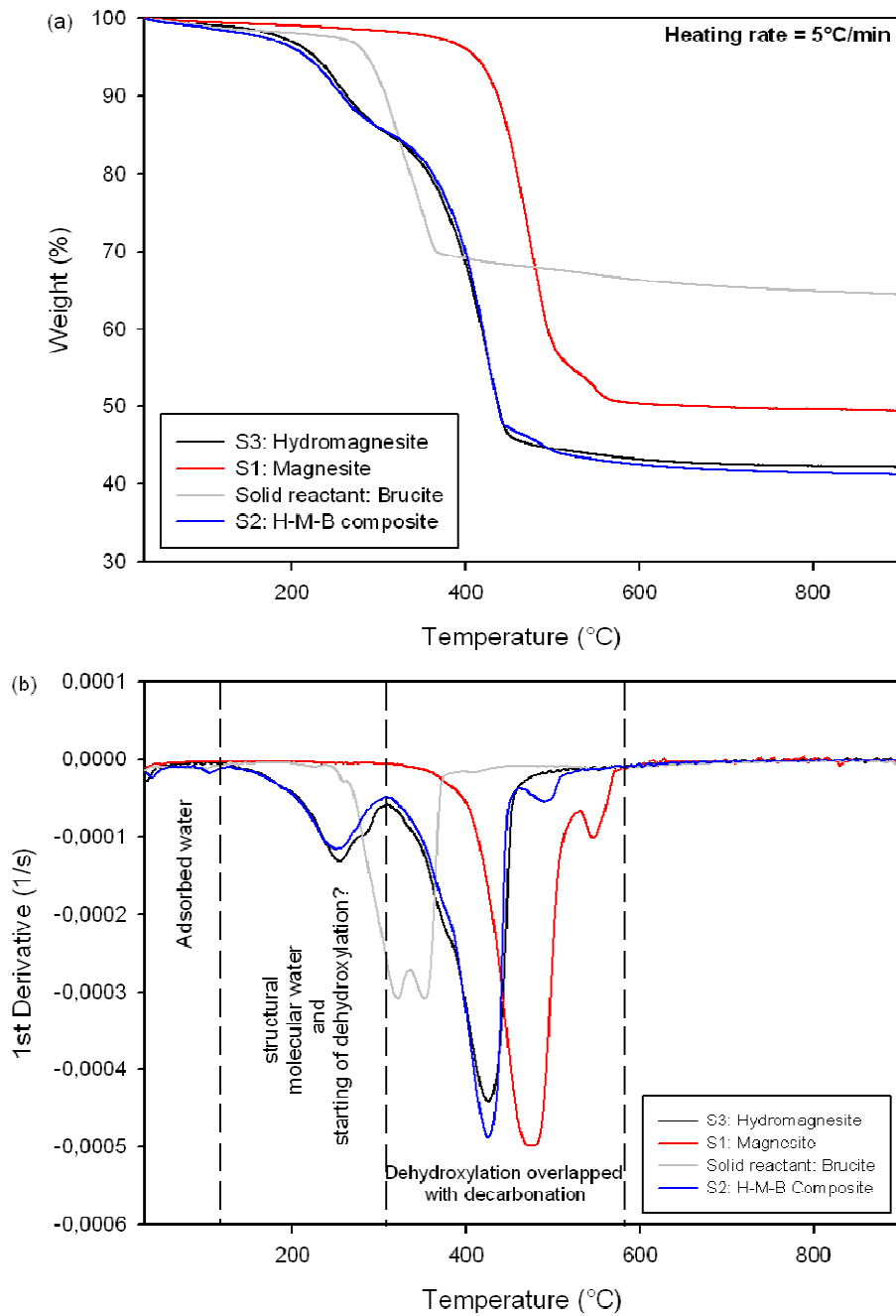
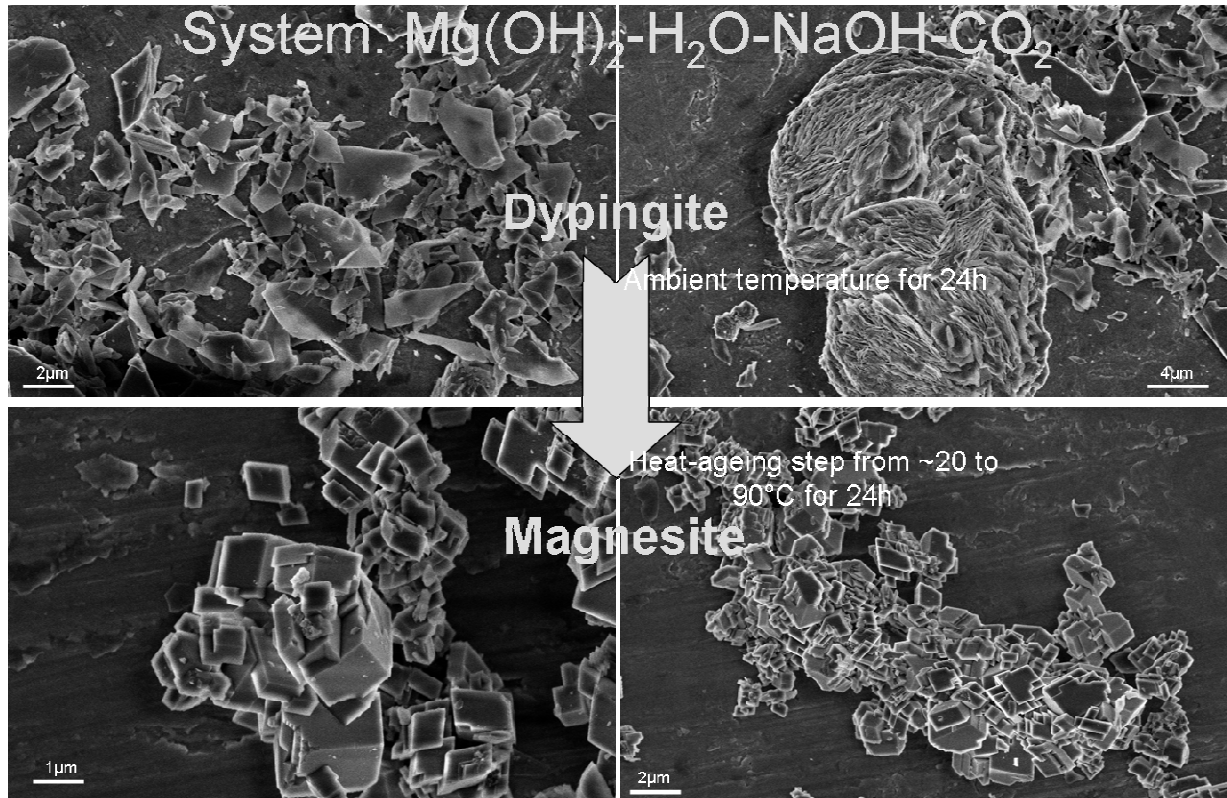


Figure 7. Thermogravimetric analyses (TGA on top graph and differential TGA on bottom graph) of synthesized magnesite (S1), hydromagnesite (S3), and hydromagnesite-magnesite-brucite composite (S2).

Table of Content Graphic

Rapid precipitation of magnesite micro-crystals from $\text{Mg}(\text{OH})_2\text{-H}_2\text{O-CO}_2$ slurry enhanced by NaOH and a heat-ageing step (from ~ 20 to 90°C) by Montes-Hernandez et al.



Synopsis: We propose simple and novel synthesis routes for the production of rhombohedral single crystals ($<2\mu\text{m}$) of magnesite and platy fine particles of hydromagnesite. It also demonstrates the catalytic action of NaOH during the carbonation process of brucite mineral, leading to fast precipitation of high-purity magnesite after 48h of reaction and fast precipitation of high-purity hydromagnesite after only 5h of reaction. For each case, a global reaction mechanism has been proposed.