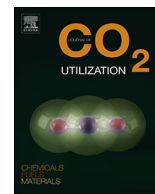




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# Mechanism of formation of engineered magnesite: A useful mineral to mitigate CO<sub>2</sub> industrial emissions

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## ABSTRACT

Magnesium carbonate production at the industrial scale is a realistic option to reduce the industrial emissions of CO<sub>2</sub>. Ultrabasic rocks and/or alkaline mine waste provide magnesium sources and are widely available in the Earth's crust. Here, we investigated the aqueous carbonation of magnesium hydroxide under moderate temperature (25–90 °C) and pressure (initial pressure of CO<sub>2</sub> = 50 bar) using NaOH as the CO<sub>2</sub> sequestering agent. From time-resolved Raman measurements, we demonstrate that the aqueous carbonation of magnesium hydroxide can be an effective engineered method to trap CO<sub>2</sub> into a solid material and produce large amounts of magnesite MgCO<sub>3</sub> (6 kg/m<sup>3</sup>h), or hydromagnesite Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O (120 kg/m<sup>3</sup>h) at 90 °C or nesquehonite MgCO<sub>3</sub>·3H<sub>2</sub>O (40 kg/m<sup>3</sup>h) at 25 °C. Higher production rates were measured for nesquehonite (at 25 °C) and hydromagnesite (at 60 and 90 °C). However, only the magnesite produced at 90 °C ensures a permanent CO<sub>2</sub> storage because this mineral is the most stable Mg carbonate under Earth surface conditions, and it could be co-used as construction material in roadbeds, bricks with fire-retarding property and granular fill. The use of specific organic additives can reduce the reaction temperature to precipitate magnesite. For example, ferric EDTA (ethylenediaminetetraacetic acid) reduces the temperature from 90 to 60 °C. However, more time is required to complete magnesite precipitation reaction at this lower temperature (15 h at 90 °C and 7 days at 60 °C). These results suggests that functionalized organic groups can reduce the energetic barriers during magnesite nucleation.

## 1. Introduction

CO<sub>2</sub> emissions have increased since the industrial revolution: about 36 Gt of CO<sub>2</sub> that originate from fossil fuel are annually emitted into the atmosphere with 30% from industrial activities and 70% from transport, agriculture and other sources [1]. These non-regulated emissions have led to concerns about global warming as a progressive increase of CO<sub>2</sub> concentration into atmosphere has been recorded in the last two centuries [1]. The energy transition (i.e., the use of carbon-free energy sources such as hydrogen, solar, wind, marine, hydraulic, geothermal) could significantly decrease CO<sub>2</sub> emissions. Some limitations, such as the supply of rare Earth elements, large amounts of water requirements and natural risks, have raised some concerns about how fast this transition will occur [2,3]. Moreover, conventional and unconventional fossil resources (gas, carbon and oil) are still available in geological formations [4], and their exploitation and resulting CO<sub>2</sub> emissions have been predicted to continue for 50–100 years [5]. Therefore, CO<sub>2</sub> capture from industrial sources and its transformation into re-usable

products (e.g. ethanol, syngas, etc.) and/or non-energetic materials (e.g. calcite, magnesite, siderite, etc.) has been proposed to reduce CO<sub>2</sub> emissions into the atmosphere [6–9]. CO<sub>2</sub> capture from industrial sources does not represent a technological or scientific obstacle, but the existing methods and technologies (including recovery of high-purity of CO<sub>2</sub> and its liquefaction) remain highly expensive. In this way, the improvement and optimization on the CO<sub>2</sub> capture units still represent important challenges. The goal of the present experimental study is to demonstrate that engineered magnesite (MgCO<sub>3</sub>) could be used as an effective option to store carbon dioxide within magnesite-rich solids. The obtained magnesite-rich solids could then be used as civil construction materials (e.g. roadbed materials, bricks, granular fill) [10]. Magnesite is the most stable carbonate mineral under typical Earth surface conditions, with the highest resistance to leaching and weathering [11]. The magnesite dissolution rate is 100–1000 times lower than that of calcite in a wide range of conditions, from ambient temperature to 150 °C and pH from 1 to 14 [11]. For this reason, anhydrous magnesium carbonates (magnesite and dolomite) have been considered

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**Table 1**Experiments of magnesium carbonates precipitation from Mg(OH)<sub>2</sub>-NaOH-H<sub>2</sub>O-CO<sub>2</sub> slurry under anisobaric conditions (initial CO<sub>2</sub> pressure of 50 bar).

Run	Temperature (°C)	Additive (1 g)	Real-time monitoring	Exp. Duration (h)	Mineral transient phase(s)	Final mineral phase(s)
1	25	–	Raman spectroscopy	72	none	nesquehonite
2	90	–	Raman spectroscopy	24	hydromagnesite	magnesite
3	90	–	pH probe	24	N/A	Magnesite and residual hydromagnesite
4	60	–	pH probe	24	N/A	hydromagnesite
5	60	citric acid	pH probe	24	N/A	hydromagnesite
6	60	aspartame	pH probe	24	N/A	hydromagnesite
7	60	EDTA	pH probe	24	N/A	hydromagnesite
8	60	EDTA	pH probe	72	N/A	magnesite and hydromagnesite
9	60	EDTA	pH probe	168	N/A	magnesite
10	25	EDTA	pH probe	168	N/A	nesquehonite

as relevant minerals to store permanently anthropogenic carbon dioxide. Magnesite and dolomite precipitation kinetics have been widely studied because their abiotic precipitation at ambient temperature (~25 °C) is virtually impossible within typical experimental time scales [12,13]. The strong solvation shells of magnesium ions in aqueous media produces this limitation [12]. However, the sole effect of Mg hydration might not be the only factor of inhibition of magnesite and/or dolomite formation. Recent studies claim that a more intrinsic crystallization barrier and the influence of fluid chemistry (e.g., relative size of the constituting cations) prevent the formation of a long-range ordered crystallographic structures at ambient conditions [14,15]. Conversely, a recent study has reported magnesite precipitation in batch reactors at room temperature after 77 days of reaction with the aid of carboxylated polystyrene microspheres [16]. Diluted ionic solutions (< 0.1 M) and microspheres coated with a high density of carboxyl groups at their surface allowed the binding and dehydration of Mg<sup>2+</sup> ions in solution, thereby minimizing the kinetic barrier and facilitating magnesite formation [16]. However, the reaction mechanism and the nature of precipitating minerals between 1 and 77 days remain to be identified, and whether precipitation occurred via the formation of transient phases or by a direct nucleation event is unknown. Moreover, this method needs to be up-scaled to produce high-amounts of magnesite in reasonable time (24 h). In order to overcome these limitations, the present study demonstrates magnesite precipitation at moderate temperature (60 and 90 °C) by aqueous carbonation of magnesium hydroxide (Mg(OH)<sub>2</sub>) under anisobaric conditions (initial CO<sub>2</sub> pressure = 50 bar). These conditions allow the production of high amounts of magnesite in only 15 h at 90 °C or 7 days at 60 °C. Herein, NaOH was used as a CO<sub>2</sub> sequestering agent and the ferric EDTA as a dehydration agent of Mg<sup>2+</sup> ions. Magnesium hydroxide was chosen because its engineered production from olivine and serpentine-rich materials was actively investigated for CO<sub>2</sub> mineralization purpose [17,18]. Magnesium oxide (MgO) and magnesium hydroxide (Mg(OH)<sub>2</sub>) may be produced from serpentine and other Mg-rich silicates. Both synthesized minerals have numerous industrial applications, and have been proposed as sinks to store anthropogenic carbon dioxide by transforming it into magnesium carbonate minerals [17,18].

## 2. Materials and methods

### 2.1. Magnesite precipitation using NaOH as sequestering agent of CO<sub>2</sub>

As already demonstrated in our group (e.g. [8,19]), the NaOH enhances the magnesite precipitation at 90 °C via aqueous carbonation process of magnesium hydroxide with compressed CO<sub>2</sub>. An initial CO<sub>2</sub> pressure of 50 bar ensures an excess of CO<sub>2</sub> with respect to Mg(OH)<sub>2</sub> in the reactor and ideal gas condition. In the present study, two new experiments were performed at 90 and 27 °C, respectively, and monitored by time-resolved in situ Raman spectroscopy as described in Montes-Hernandez and Renard, 2016 [19]. Herein, carbonate speciation and precipitated particles were monitored for 24 h with a 1-minute spectral

acquisition time. The Raman spectra were treated in order to estimate the position, full wide half maximum (FWHM) and integrated surface area as a function of time for specific stronger peaks in order to explain the reaction mechanism and kinetics of Mg carbonates precipitation and particularly magnesite (MgCO<sub>3</sub>).

### 2.2. Magnesite precipitation using NaOH and organic additives

Magnesite precipitation was also investigated at 60 °C in the presence of three organic molecules (Aspartame, ferric EDTA, and citric acid tri-sodium salt), expecting a dehydration effect of Mg<sup>2+</sup> ions or a chelation effect. In these experiments, 15 g of Mg(OH)<sub>2</sub>, provided by Sigma-Aldrich with chemical purity of 99%, 20 g of NaOH, 1 g of organic additive, and 500 mL of high-purity water were mixed in the reactor (total internal volume of 960 mL). The slurry was immediately dispersed by mechanical agitation (400 rpm) and gaseous CO<sub>2</sub>, provided by Linde Gas S.A., was injected at 50 bar into the reactor. About 3 min at 25 °C were required to reach the pre-defined pressure. The agitation speed was kept to 400 rpm using a rotor with two blades (Parr reactor) that ensured homogeneous dispersion of reacting and precipitating solids and fast dispersion of the injected CO<sub>2</sub> in the system. Following injection, the system was heated to 60 °C, the pH of the solution and the CO<sub>2</sub> consumption (pressure drop) were monitored in-situ during mineral formation for 24, 72 or 168 h.

At the end of the experiment, the residual CO<sub>2</sub> was degassed from the reactor by opening the gas line valve for five minutes. The solid product was recovered by centrifugation and washed twice with ultrapure water and then was dried directly in the centrifugation flasks at 60 °C for 48 h. The dry solid products were stored in plastic flasks for subsequent characterization by Raman spectroscopy, Field Emission Gun Scanning Electron Microscopy (FESEM) and powder X-ray diffraction (XRD). All ten performed experiments are summarized in Table 1.

### 2.3. Ex situ characterization of precipitates

XRD analyses were performed using a Siemens D5000 diffractometer in Bragg-Brentano geometry, equipped with a theta-theta goniometer with a rotating sample holder. Diffraction patterns were collected using Cu Kα<sub>1</sub> (λ<sub>Kα1</sub> = 1.5406 Å) and Kα<sub>2</sub> (λ<sub>Kα2</sub> = 1.5444 Å) radiation in the range 2θ = 10 - 70°, with a step size of 0.04° and a counting time of 6 s per step. For high-resolution imaging, the solid products 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 and coated with platinum. The morphology of the crystals was imaged using a Zeiss Ultra 55 FESEM with a maximum spatial resolution of approximately 1 nm at 15 kV.

## 2.4. Calculation of production rate

The production rate of a given magnesium carbonate was calculated as follows:

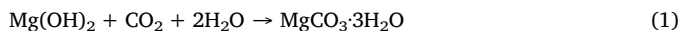
$$P_{\text{rate}} = (\lambda * \text{Mol}_{\text{Mg(OH)}_2} * M_{\text{MgCarbonate}}) / (t_{\text{max}} * V_{\text{reactor}})$$

where  $\lambda$  is the chemical conversion factor for Mg carbonate phases determined from Raman spectroscopy when peak intensity is constant for a given time-interval. The value  $\lambda = 1$  is reached when the peak intensity for a given Mg carbonate is constant and only a single mineral is detected.  $\text{Mol}_{\text{Mg(OH)}_2}$  is the initial amount (in mol) of  $\text{Mg(OH)}_2$  (complete transformation was determined from ex-situ XRD measurements in recovered solid products);  $M_{\text{MgCarbonate}}$  is the molar mass of a given Mg carbonate;  $t_{\text{max}}$  is the time where only one mineral phase exists and the peak intensity is constant;  $V_{\text{reactor}}$  is the effective volume of the reactor which is equal to 0.6 L (runs 1–2) or 1 L (runs 3–10). This calculation using time-resolved experimental measurements could allow a realistic extrapolation to pilot and/or industrial scale assuming roughly proportional dimensions and equivalent precipitation times.

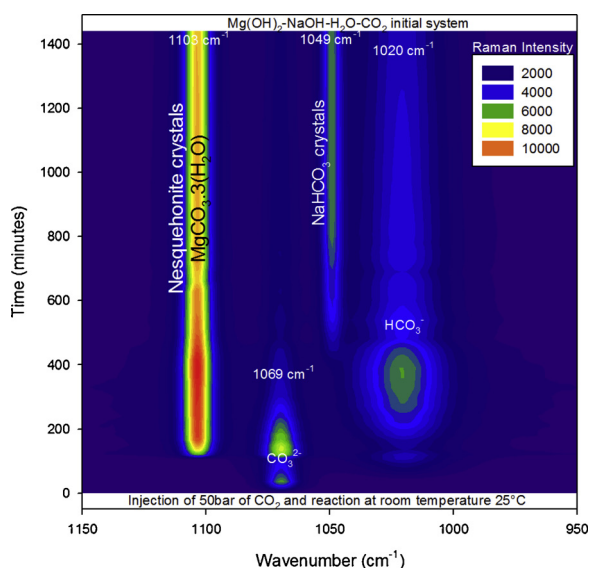
## 3. Results and discussion

### 3.1. Magnesite precipitation at 90 °C: Reaction mechanism and kinetics

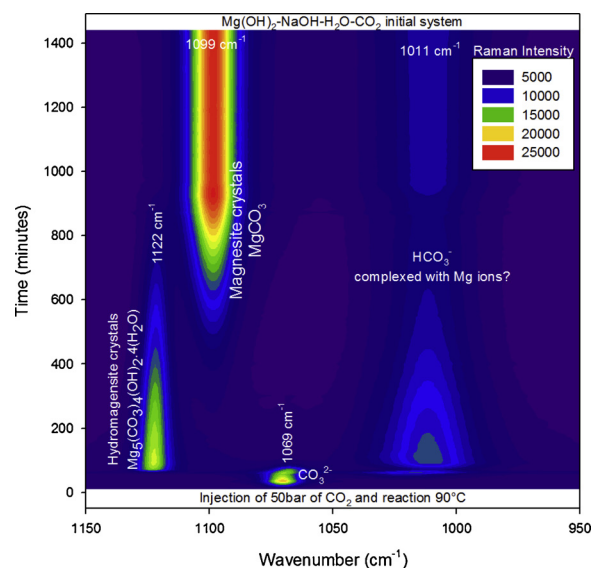
Carbonation of  $\text{Mg(OH)}_2$  at 25 °C leads the precipitation of nesquehonite, with the following global reaction:



The successive events involved during magnesium hydroxide carbonation are displayed in Fig. 1. Dissolved NaOH enhanced the rate and amount of sequestration of injected CO<sub>2</sub> (initial  $P_{\text{CO}_2} = 50$  bar). The carbon dioxide dissolved into interacting alkaline solution ( $\text{CO}_{2(\text{gas})} \leftrightarrow \text{CO}_{2(\text{aq})}$ ) was rapidly dissociated into  $\text{CO}_3^{2-}$  ( $\text{CO}_{2(\text{aq})} + 2\text{NaOH} \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} + 2\text{Na}^+$ ). A fraction of the carbonate ions was protonated after about 60 min ( $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$ ) producing a pH change in the interacting solution, and simultaneously enhancing the dissolution of magnesium hydroxide ( $\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} + 2\text{OH}^-$ ). All these combined reactions led to the precipitation of nesquehonite ( $\text{Mg}^{2+} + \text{HCO}_3^- + 3\text{H}_2\text{O} \rightarrow \text{MgCO}_3 \cdot 3\text{H}_2\text{O} + \text{H}^+$ ) with a nucleation induction time of 105 min. This mineral grew by continuous dissolution



**Fig. 1.** Time-lapse Raman spectroscopy monitoring of the aqueous carbonation of magnesium hydroxide at 25 °C under anisobaric conditions. The positions of the Raman peaks and the corresponding aqueous or mineral species are indicated on the figure.

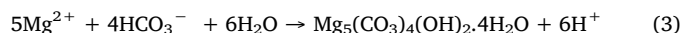


**Fig. 2.** Time-lapse Raman spectroscopy monitoring of the aqueous carbonation of magnesium hydroxide at 90 °C under anisobaric conditions. The positions of the Raman peaks and the corresponding aqueous or mineral species are indicated on the figure. The same data are shown on Fig. SI-2 in the form of spectra.

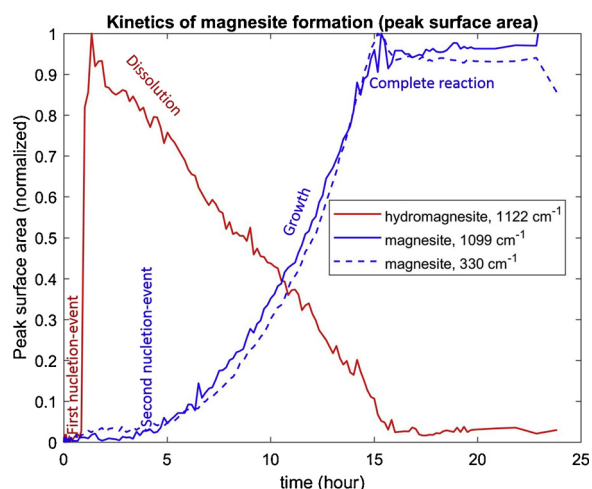
of magnesium hydroxide until complete consumption in the reactor. Nesquehonite remained stable in the interacting solution until the end of experiment (72 h). Ex-situ FESEM images revealed micrometric crystals of prismatic elongated morphology (Fig. SI-1). Time-resolved Raman measurements and ex-situ characterization of solid confirm that magnesite precipitation was inhibited by nesquehonite precipitation at 25 °C. Conversely, magnesite formation was rapidly obtained at 90 °C and only 15 h were required to produce high-purity magnesite ( $\sim 6$  kg/m<sup>3</sup>h) as monitored by Raman spectroscopy (Fig. 2). The global reaction summarizes the process:



A complete aqueous carbonation reaction was obtained at 90 °C exclusively when NaOH was used as the CO<sub>2</sub> sequestering agent, in agreement with previous results [8]. In the present study, a more detailed reaction mechanism and kinetics are demonstrated from the time-resolved in-situ Raman spectroscopy measurements and all temporal reaction events are shown in Fig. 2 and Fig. SI-2. Similar to the nesquehonite case, the aqueous carbon dioxide ( $\text{CO}_{2(\text{gas})} \leftrightarrow \text{CO}_{2(\text{aq})}$ ) was rapidly dissociated into  $\text{CO}_3^{2-}$  ( $\text{CO}_{2(\text{aq})} + 2\text{NaOH} \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} + 2\text{Na}^+$ ), but this reaction remained active only during the first 100 min. Then, carbonate ions were rapidly protonated, forming bicarbonate ions ( $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$ ) that may complex with  $\text{Mg}^{2+}$ , leading to a shift of the maximum of the Raman peak of  $\text{HCO}_3^-$  from 1020 cm<sup>-1</sup> (Fig. 1) to 1011 cm<sup>-1</sup> (Fig. 2). After 150 min, aqueous carbon dioxide and bicarbonate ions were the dominant species in the reactor, which induced a significant pH change in the interacting solution as suggested from carbonate speciation in relation with pH (inorganic carbonate fraction vs pH diagram). Under these conditions, the dissolution of magnesium hydroxide ( $\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} + 2\text{OH}^-$ ) was enhanced, and the release of magnesium ions generated oversaturation states with respect to several magnesium carbonates. Consequently, the nucleation of hydromagnesite was detected in-situ after 60 min of reaction (first nucleation-event).

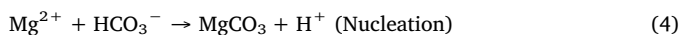


Hydromagnesite formed as a transient mineral phase that reached a maximum spectral intensity after 120 min. Then, this mineral dissolved in a destabilization processes through a decrease of spectral peak



**Fig. 3.** Kinetics of nucleation and growth of hydromagnesite and magnesite during aqueous carbonation of magnesium hydroxide at 90 °C measured by Raman spectroscopy. The peak surface area is calculated as a function of time for one Raman peak of hydromagnesite and two Raman peaks for magnesite, from the data shown in Figs. 2 and SI-2.

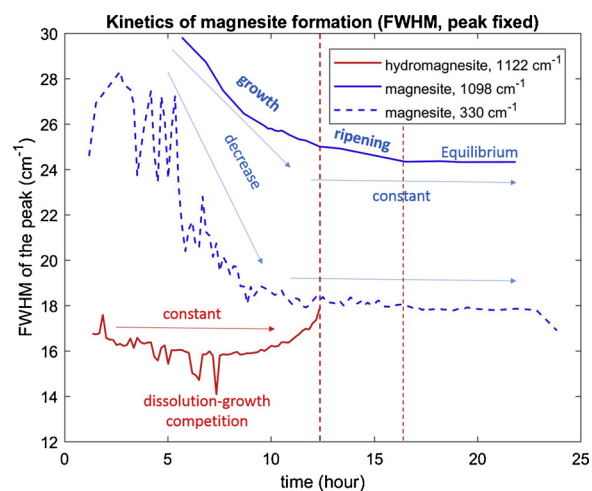
surface area (i.e., Fig. 3) progressively before the nucleation of magnesite that was detected after 240 min of reaction (second nucleation-event).



After this magnesite nucleation event, the growth of magnesite was mainly nourished by progressive dissolution of hydromagnesite. The temporal evolution of peak surface areas and Full Width Half Maximum (FWHM) for hydromagnesite and magnesite minerals (Figs. 3 and 4) suggest that this reaction included coupled dissolution-reprecipitation. Hydromagnesite was completely consumed after 13 h. An Ostwald ripening process could explain the growth in the following two hours. Equilibrium was reached after 15 h of reaction, as demonstrated by the constant FWHM of magnesite after this time (Fig. 4). FESEM images revealed rhombohedral single crystals with sizes < 5 μm (Fig. SI-3), in agreement with previous work [8].

### 3.2. Role of temperature and organic additives

Several complementary experiments were performed in order to



**Fig. 4.** Crystal growth mechanism of magnesite (blue) at 90 °C, nourished by hydromagnesite dissolution (red) and measured by the Full Width at Half Maximum (FWHM) of the Raman peaks shown in Figs. 2 and SI-2.

assess the evolution of pH in-situ, the dehydration effect of organic additives around Mg ions, and the role of reaction temperature (Table 1, Fig. 5). For all of these experiments, the pH decreased from 12.4 to 9 in the first 10 min and then continued to decrease at a slower rate until stabilization to a value in the range 5.5–6 after 1 h of reaction. This result indicates that the pH was mainly controlled by inorganic carbonate speciation and CO<sub>2</sub> pressure (Figs. SI-4 and 5), and that organic additives had a little or undetected influence. This result is in agreement with time-lapse Raman measurements where a protonation process of carbonate ions was also detected, indicating a pH change in the interacting solution (Figs. 1,2). Conversely, organic additive has significant effect on the texture (crystal size) and structural water content of the mineral produced, as identified in recovered suspensions by Raman ex-situ measurements (Fig. 5). Hydromagnesite was the main mineral phase precipitated at 60 °C for 24 h in the absence or presence of organic additive. However, both the mineral texture, measured by the Full Width Half Maximum (FWHM) of the largest Raman peak, and the structural water content, measured by the position of largest Raman peak, were slightly different with respect to the reference of the hydromagnesite precipitated in a solution free of additive. In addition, some traces of magnesite were detected after 24 h of reaction when ferric EDTA or citric acid tri-sodium salt were used. For the EDTA additive, slow hydromagnesite-to-magnesite transformation was detected and about 7 days were required to obtain high-purity magnesite at 60 °C. Only nesquehonite was detected at 25 °C in the presence of EDTA (Fig. 5). This result confirms that magnesite precipitation from the aqueous carbonation of magnesium hydroxide at room temperature was inhibited, or strongly retarded, by the precipitation of nesquehonite.

### 3.3. Environmental implications

Magnesite formation at room temperature (< 30 °C) from the aqueous carbonation of magnesium hydroxide remains a scientific challenge. This formation could make the magnesite precipitation an economical issue to store permanently the CO<sub>2</sub> with important environmental advantages:

- (1) reduce CO<sub>2</sub> emissions from the industrial sector (e.g. steel and cement industry, coal-fired power),
- (2) obtain magnesite-rich or high-purity magnesite materials with an aggregate value (e.g. fabrication of roadbed materials, bricks, granular fill, fire-retardant building material) at low or moderate temperature and reduced time (< 24 h) and,
- (3) use of mine solid wastes (e.g., mines in ultrabasic rocks) or widely available Mg-silicates as a magnesium source to capture CO<sub>2</sub>.

In practice, the residual alkaline-solution obtained during magnesite production (Na + bi-carbonate solution) could be recycled for future carbonation experiments or re-used in other chemical processes, but these options were not assessed in the present study.

In this context, the production of magnesite material as an effective solution to reduce the industrial CO<sub>2</sub> emission may be a serious option at industrial scale as now proposed by Cambridge Carbon Capture (<http://www.cacaca.co.uk/#news>).

## 4. Conclusion

In the present study, we demonstrated that high-purity magnesite can be produced from the carbonation of magnesium hydroxide at a rate of about 6 kg/m<sup>3</sup>h, and thus a mineralization rate of CO<sub>2</sub> into magnesite of about 3 kg/m<sup>3</sup>h. Higher productions were estimated for hydromagnesite (120 kg/m<sup>3</sup>h) and nesquehonite (40 kg/m<sup>3</sup>h), but these minerals are thermodynamically less stable at Earth surface conditions than magnesite.

Our time-resolved Raman measurements allowed a detailed description of reaction mechanism and kinetics of carbonation of magnesium hydroxide in batch reactor conditions. This experimental setup offers new possibilities for investigating mineral condensation from



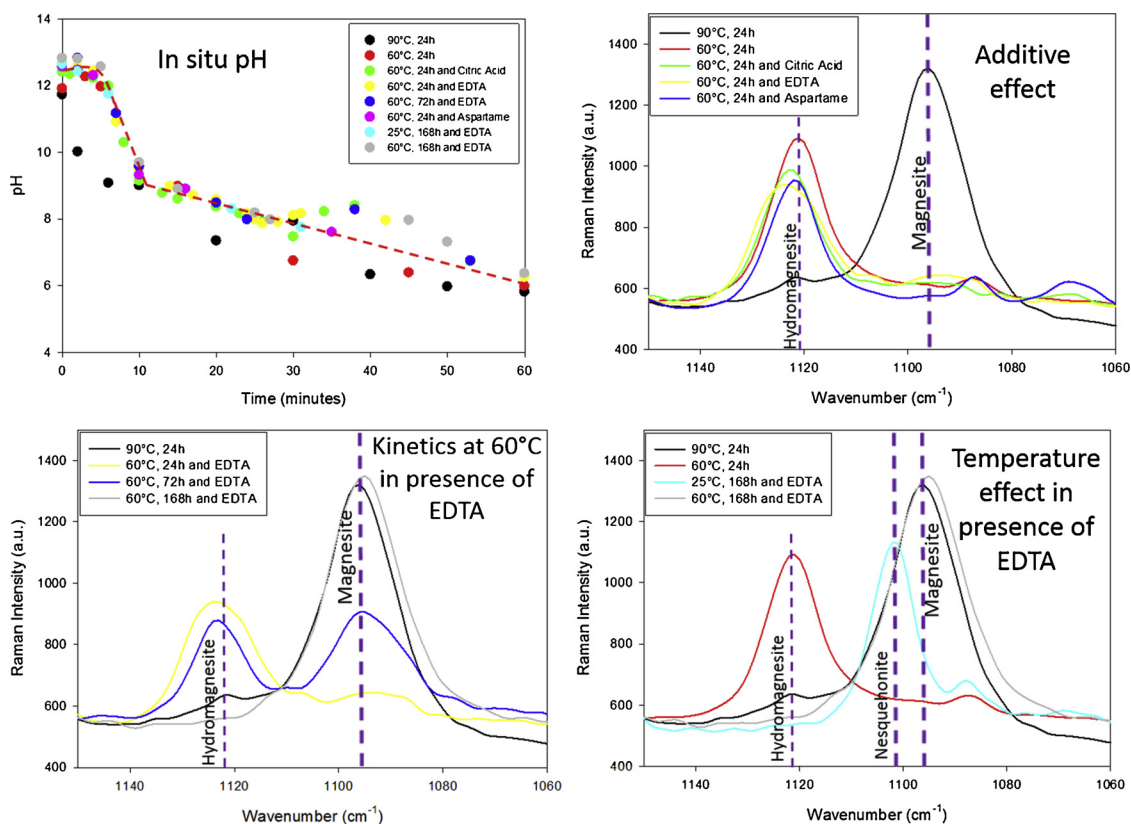


Fig. 5. pH measured in-situ during aqueous carbonation of magnesium hydroxide in eight experiments (Table 1), with or without additive. Influence of organic additives and temperature on the aqueous carbonation of magnesium hydroxide ( $\text{Mg}(\text{OH})_2\text{-NaOH-H}_2\text{O-CO}_2$  slurry) under anisobaric conditions.

ionic solutions and slurries, and for investigating other chemical reactions at the solid-fluid interfaces.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2019.10.006>.

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