Phase evolution during accelerated CO₂ mineralization of brucite under concentrated CO₂ and simulated flue gas

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ABSTRACT

Experimental work on the carbonation of brucite has been carried out in the temperature and pressure ranges of 50-120°C and 1-10 bar respectively, using concentrated CO₂ and simulated flue gas. At 120°C hydromagnesite and trace amounts of magnesite were identified. Highly to semi-ordered dypingite like-phases and nesquehonite, coexisting with a possibly amorphous carbonate phase, were identified at 50°C. The dehydration temperatures and chemical composition of these amorphous phases are very close to those of crystalline, stoichiometric nesquehonite. This probably amorphous phase nourishes the late formation of dypingite. This latter mineral gradually undergoes a cell shrinkage due to the partial loss of molecular

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waters, becoming structurally more ordered as the carbonation reaction proceeds. It remains unclear whether nesquehonite formed directly from brucite or from the crystallization of an amorphous precursor. However, nesquehonite is precursor of dypingite and/or the possibly amorphous phase. Only crystalline carbonate phases were observed at 120°C. Concentrated CO₂ experiments yielded the highest amounts (up to 37 wt.%) of CO₂ sequestered at 10 bar and 16 hours of reaction, reaching an almost complete carbonation of brucite (>98%). On the other hand, flue gas experiments results showed higher amounts of CO₂ sequestered per unit of CO₂ partial pressure than with concentrated CO₂.

Keywords

Simulated flue gas; Mineral carbonation; CO₂ sequestration; Phase nucleation; Amorphous magnesium carbonates.

1. Introduction

Mineral carbonation is among the safest, environmentally benign and durable processes for carbon sequestration technologies [1–3], attempting to mimic the natural weathering of Ca/Mg-rich silicate rocks in an anthropic timescale [4]. The main interest of such an approach to CO₂ sequestration resides in and is justified by the fact that the CO₂ sequestration capacity of Mg-rich silicates in the Earth's crust far exceeds the total CO₂ that can be produced by burning the fossil fuel reserves [5].

The enhancement of the carbonation rate of silicate minerals can be achieved by maintaining the reaction in super-heated fluids at high pressures (~185°C, ~150 bar) [6,7]. This is based on the dissolution kinetics of Mg/Ca-rich minerals under slightly acidic conditions prompted by CO₂ dissolution in water [8–10]. However, such processes require reaction conditions that stray far from reality of post-combustion flue-gas conditions, making them difficult to implement at an industrial scale. [11,12].

Direct gas-solid carbonation (DGSC) of raw and pre-treated Mg-rich silicates has received little attention to date, as some early studies suggest that, in contrast with expectations from thermodynamic analysis [3,13], it is not an efficient mechanism for carbon sequestration [14–16]. However, there is a renewed

interest on DGSC under moist conditions, as more recent investigations [17–19] suggest that water vapor plays a critical role in carbonation reactions, allowing the chemical fixation of CO₂ through formation of reactive intermediates [10,20]. Other have suggested that for any DGSC to occur, a minimum amount of H₂O may be needed [16,21,22].

Brucite, Mg(OH)₂ is a relatively common mineral in ultramafic rocks [23] and is converted into magnesite, MgCO₃, through hydrothermal alteration of such materials in contact with CO₂-rich fluids [24–26]. The limited abundance of natural brucite does not make it, in principle, an attractive material to be used in carbon capture, utilization and storage (CCUS) strategies. Nevertheless, the presence of brucite plays a key role in the carbonation of industrial waste materials [27–29]. Alkaline residues are known to have a high carbonation potential (e.g. serpentine mine tailings or alkaline industrial wastes from steel production, alumina refining and coal-fired power generation) [30–34].

Brucite can be obtained from Mg-rich silicates and/or solid waste through the so-called ÅA route, and carbonation of this material has been investigated given its high MgO contents (up to 41 wt.%) [35–37] and fast reactions kinetics [28,38,39]. Recent research emphasized that this process is best applicable for phyllosilicates, such as serpentine minerals [40], considered to be the world's most abundant mineralization precursors [41]. Large mining sites worldwide produce or have produced easy-accessible, finely ground and highly reactive ultramafic mining wastes [29,42–45]. Previous approaches emphasize the extraction of reactive magnesium from Mg-bearing silicates as an essential first step [16,37,46] and agree that it is the most successful approach for ex-situ mineral carbonation processes [14,47]. The utilization of widely available above-ground alkaline industrial wastes avoids not only mining and milling but also consumption raw material. Moreover, the carbonation of brucite utilizes either flue gas or concentrated CO₂ in addition to its reaction products, which may substitute raw materials in various industries [32,48–50]. An energy and cost efficient carbonation process should be able to fix CO₂ from flue gas without need of capturing it in advance [51].

Direct carbonation of brucite to magnesite only occurs at high temperatures and pressures; at lower temperatures this reaction is kinetically inhibited by the formation of hydrated Mg carbonates [52,53]

during simultaneous carbonation and dehydroxylation [21,54,55]. Previous research has stated that the gas-solid carbonation of both MgO and Mg(OH)₂ takes place at a very slow rate, when compared with the “wet” route [19,21,56], and has emphasized the role of relative humidity on such reactions [17,19,55].

CO₂ mineralization processes should be able to reach feasible conversion rates when operating at temperatures and pressures near flue gas emissions [19,57]. However, the formation mechanisms of Mg carbonates under such conditions are poorly known. Previous studies have suggested the presence of an amorphous hydrated Mg carbonate phase (AMC) during carbonation and hydration of periclase, MgO [58]. Amorphous carbonates are precursors to crystalline phases and are known to play a key role in the precipitation of different hydrated or anhydrous carbonate phases. Nature takes advantage of the amorphous to crystalline transition in a variety of processes [59–61]. The transition of amorphous calcium carbonate (ACC) to crystalline phases have been thoroughly studied [62–65]. The formation of AMC and its transition to crystalline phases has received less attention, and it has been mainly discussed in the context of mixed Ca/Mg amorphous carbonate phases [64–67]. The presence of Mg²⁺ plays a key role on the crystallization of ACC, most probably because the slow dehydration of Mg²⁺ [69]. However, research interest is continuously increasing with regard to the accelerated formation of magnesium carbonates from Mg-rich oxides and silicates, since such processes has been proposed as a possible carbon sink for anthropogenic CO₂ [5,68]. Fukushi, et al., 2017 [65] suggested that AMC plays an important role on the formation of crystalline carbonate phases on the context of mixed Ca/Mg amorphous carbonate phases. Therefore, understanding the formation of AMC, its transition to crystalline phases and the role it plays during the evolution of carbonate phases during carbonation reaction is of paramount importance since it might provide important insights in the acceleration of carbonation reactions at conditions near to those of flue gas emissions, which are known to be kinetically challenging [1,11,12]. This is especially important for hydrated Mg carbonate minerals which occurs in several phases, such as nesquehonite, lansfordite, artinite, hydromagnesite, dypingite or barringtonite, each with different water contents [70]. The stability of amorphous materials is known to depend on size and water content [71]. AMC produced from Ca-Mg-CO₃ solutions are expected to be different to those that formed in Mg-CO₃ solutions [65].

Recent research has also focused on the alternative to implement accelerated carbonation as an integrated capture and storage process [57,72–75]. This route will avoid prior CO₂ capture processes, which will significantly simplify the overall accelerated carbonation process. It has been observed that the reaction mechanisms and kinetics were similar to the ones obtained for pure CO₂ streams, indicating the high carbonation potential when using a gas composition similar to some industrial flue gas [74,75]. Moreover, the high-purity carbonate products are considered as a marketable product [72].

This work reports on the study of the evolution of carbonate phases during steam accelerated carbonation of magnesium hydroxide in a pressurized continuous flow reactor at moderate pressures (1 - 10 bar) and relatively low temperatures (50-120°C), using both simulated flue gas and concentrated CO₂.

2. Materials and methods

2.1. Experimental

Samples of 600 mg of magnesium hydroxide (>99% BioUltra, Sigma-Aldrich™, CAS number: 1309-42-8) were loaded into a purpose-designed reactor (35mL stainless steel) placed within a furnace with an integrated thermocouple (Figure S1), and heated up to the desired temperature (50°C to 120°C). Carbonation experiments were carried out in a pressurized continuous flow, using N₂ as a carrier gas. A summary of P, T, time and humidity conditions of all experiments is given in Table S1. A maximum temperature drift of ± 1 °C was measured inside the reactor in *operando* conditions. Flue gas composition was simulated with a 85% N₂ – 15% CO₂ mixture, following previous research [41,57,76,77]. Pressure was controlled with pressure reducers and back pressure regulators, until the desired conditions were achieved for a given flux. A drift of ± 0.2 bar in *operando* conditions was measured with 2 manometers located at the inlet and outlet of the reactor. Prior to introduction in the chamber, CO₂ was forced to flow through a ~50 mL bubbler containing water. Appropriate temperature and pressure were chosen to produce a gas mixture with relative humidities (RH) of 90% and 5 % for concentrated CO₂ and simulated flue gas experiments, respectively (Table S2). To avoid gas concentration changes due to the absorption of CO₂ in the bubbler, a continuous

flow of either concentrated CO₂ or CO₂ diluted with N₂ at the specific pressure and temperature conditions was maintained for at least 30 minutes before each experiment. Therefore, the water on the bubbler was saturated with CO₂ prior each experiment, inhibiting further absorption of CO₂. Conditions were kept isothermal during different reaction times. After the experiments, pressure was released and N₂ was used to stop the carbonation reaction while cooling.

2.2. Analytical

Raman spectra were obtained with an inVia Qontor™ confocal Raman microscope, equipped with a green laser with an excitation wavelength of 532 nm. Given the substantial heterogeneity of phase distribution at the microscale after reaction, a total of 40 measurements were averaged on each sample in order to obtain representative results. Infrared analyses were carried out with a Nicolet 6700™ Fourier Transform Infrared Spectrometer (FTIR). An attenuated total reflection (ATR) module was used to record spectra on a germanium crystal (mid-IR, from 750 – 4000 cm⁻¹), using 64 scans and 2 data point spacing. Mineral composition was determined with a Bruker D8™ X-Ray powder diffractometer (XRD), operated at 1deg/min scans over a scattering angle (2θ) from 10 to 80°, and a step size of 0.01°. A thermogravimetric analysis system (TA Instruments Q50™) was used to measure the mass losses upon decomposition of specific phases. Data were acquired at a heating rate of 10°C/min, from room temperature to 600°C, under a N₂ flow of 60mL/min. Scanning electron microscopy images of powder samples were obtained with a cross-beam work station Zeiss Neon 40™, equipped with an INCAPentaFET energy dispersive X-ray system for elemental analysis, operated at 5keV.

3. Results and discussion

3.1. Concentrated CO₂ experiments

Raman spectra of the solid products formed in the pressure range of 1 - 10 bar at 50 and 120 °C using concentrated CO₂ are shown in Fig. 1. Brucite is clearly identified as the starting material with its

characteristic peaks at 443 and 279 cm^{-1} [55,78]. Upon reaction at 50°C, two distinct peaks (1093.3 ± 1.1 , 1122.3 ± 0.1) are identified on the 1080-1125 cm^{-1} band, characteristic of the ν_1 symmetric stretching mode ($\nu_{1\text{sym}}$) of the carbonate ion (CO_3^{2-}) [79,80]. The intensity of the carbonate related peaks are in inverse proportion to the intensity of brucite peaks. At 120°C, two distinct peaks are identified within the $\nu_{1\text{sym}}$ band at 1094.6 ± 0.1 , and 1118.1 ± 0.5 ; these remain invariable upon reaction from 4 to 16 hours. An additional peak is observed at 328.3 ± 0.1 , especially at 7 and 10 bar.

FTIR analysis of the solid product of reaction also confirmed the presence of carbonates (Figure S2), showing characteristic peaks of the CO_3^{2-} and HCO_3^- ν_3 asymmetric stretching mode at 1405, 1470 and 1515 cm^{-1} [81–83]. However, different Mg carbonates cannot be differentiated due to the overlapping features among those phases on FTIR. Moreover, different Mg carbonates phases cannot be easily distinguished with the sole observation of the carbonate ion $\nu_{1\text{sym}}$ using Raman spectroscopy [79].

Fig. 1. Raman spectra of phase evolution after thermal treatments (50 – 120°C) in the 1-10 bar range (RH > 90%) from 4 to 16 hours. B: Brucite.

In order to provide additional insights on the differentiation of the distinct carbonate phases and their crystalline nature, an XRD study of the reaction products was carried out (Fig. 2). Brucite diffraction peaks are identified as the starting material and its relative peak intensity is progressively diminishing as pressure goes from 1 to 10 bar. At 120°C, crystalline hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is observed. [52,84]. At 50°C, broader peaks are identified (Figure S3a), probably indicating the presence of hydromagnesite-like phases such as dypingite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, as suggested by Hövelmann, et al., 2012 [38]. Dypingite and hydromagnesite are similar in composition, but the more hydrated carbonate has a more disordered structure with a variable amount of water molecules per formula unit [85–87]. This latter may serve as an explanation to the broader XRD features when compared to hydromagnesite (Figure S3b). At temperatures $\leq 50^\circ\text{C}$ the formation of hydromagnesite may be kinetically inhibited by the formation of highly hydrated Mg-carbonate phases, such as nesquehonite, $\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$, and dypingite [45,88,89].

Fig. 2. XRD of samples after thermal treatments at 50 and 120°C and 1 to 10 bar, maintained for 16h (RH > 90%). D/H: Dypingite/Hydromagnesite phase, H: Hydromagnesite, B: Brucite.

No differences are identified when comparing the baseline of the XRD patterns from the starting material with the carbonated products obtained at 120°C, 10 bar (Fig. S3b). However, when comparing the baseline between the carbonated products obtained at 50 and 120°C and 10 bar, a plateau is observed from 24 to 54 $2\theta^\circ$ and with center near 31 $2\theta^\circ$ (Fig S3c). This plateau is almost identical to the one observed for an amorphous Mg carbonate with chemical composition $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$ [65,90–92]. The latter is possibly indicating the coexistence between an amorphous component with poorly-ordered dypingite [62,91,93,94].

A comparison between the Full Width Half Maximum (FWHM) of the Raman ν_{lsym} peaks as well as the two more intense XRD peaks of the carbonated products was carried to provide more insights on the nature of the observed carbonate phases (Figure 3). Calculated data from 120 °C experiments fits very well with reference data corresponding to hydromagnesite. The FWHM of the two more intense XRD peaks from the

carbonated products are very similar to reference hydromagnesite, indicating a well-defined structure, in agreement with above observations. Moreover, the minor peak observed at 1094.6 ± 0.1 (Figure 1, 120°C treatments) fits very well with reference magnesite, and its presence is correlated with the emergence of the 328.3 ± 0.1 peak, which is also characteristic of magnesite [79,95,96]. Only traces amounts are observed of this latter mineral, which explains its relative inexistence on the XRD patterns (Figure 2, 120°C treatments). The formation of magnesite could come from the transformation of hydromagnesite or directly from brucite [53,55,97].

The calculated Raman data (Figure 3a) from the 50°C experiments shows that the peak located at 1122.3 ± 0.1 fits well with reference dypingite. Moreover, the identified two more intense XRD peaks (Figure 3b) have very similar positions when compared to reference hydromagnesite XRD peaks but with higher FWHM, indicating a more disordered structure, as previously discussed. The Raman peak located at 1093.3 ± 1.1 has a much higher FWHM than the other identified and reference carbonate phases, as well as higher peak position variability, indicating a possibly highly disordered or amorphous carbonate phase. Some studies have also observed this peak and its presence is related to dypingite [84,98]. The disordered to semi-disordered structure of dypingite is reflected on the difficulties to obtain good quality Raman spectra [98]. The possible coexistence of semi-ordered dypingite-like phases with a possible amorphous phase increases the difficulties to associate Raman spectra to pure dypingite phases. It is not clear if this peak (1093.3 ± 1.1) whether belongs to the semi-ordered dypingite or it is prompted by the vibration of $\nu_{1\text{sym}}$ peaks of coexisting highly to semi-ordered disordered dypingite-like phases with a possible amorphous carbonate phase [84,98]. Therefore, the nature of the hydrated Mg carbonate that generates the 1093.31 ± 1.1 Raman peak is yet unknown. This “unknown Mg-carbonate” (UMC) may be associated with the amorphous component observed with XRD (Figure S3c, S4).

Figure 3. FWHM vs peak position of (a) Raman $\nu_{1\text{sym}}$ peaks and (b) two more intense XRD peaks of the carbonated products reacted at 50 and 120°C, 1-10 bar. M: Magnesite, N: Nesquehonite, H: Hydromagnesite, D: Dypingite. The FWHM and peak position of reference minerals were calculated from Lafuente, et al., 2015 [99].

Microstructural changes occurring upon carbonation have been studied by SEM (Figure 4). The starting material consists of well-defined hexagonal crystals of brucite ($< 1\mu\text{m}$; Figure 4a), similar to those previously studied by Pang et al. (2011). After 16 h at 50°C, only some sub-euhedral brucite grains can be identified and the microstructure is dominated by an irregularly-shaped massive material (Figure 4b) that might be associated with UMC. Energy dispersive spectrometry (EDS) analysis of such material reveals the presence of a carbonate component, different from the carbon-free (brucite) starting material (Figure S5). When temperature reaches 120°C, characteristic hydromagnesite plates of maximum sizes of $\sim 1\mu\text{m}$ are observed (Figure 4c), with morphological features similar to those identified by Zhang et al. (2006). Fully developed hydromagnesite plates are observed at 10 bar (Figure 4d), as well as rhombohedral magnesite [103]. This latter constituting a minor phase (Figure 4d, inset).

Figure 4. Representative SEM images of the progressive carbonation stages, from (a) brucite starting material (euhedral hexagonal crystals $\leq 1\mu\text{m}$) to (b) relict subhedral brucite immersed in a massive carbonate matrix (see Figure S5) formed at 50°C , (c) well developed hydromagnesite plates ($\sim 1\mu\text{m}$) appearing at 120°C with some residual brucite and (d) euhedral hydromagnesite plates ($\leq 10\mu\text{m}$) and rhombohedral magnesite ($\leq 1\mu\text{m}$) formed at 120°C and 10 bar. Bru: Brucite, Mg': massive irregularly shaped carbonate, Hmg: Hydromagnesite, Mag: Magnesite.

The reaction products obtained at 120°C are composed of crystalline carbonate phases. At 50°C temperatures, possibly amorphous and semi-ordered phases emerge providing challenges for predicating and controlling the evolution of such minerals for long term-storage since the properties of amorphous Mg-carbonates are not well established [104].

3.1.1. Evolution of carbonate phases at 50°C

In order to provide more insights on the identification of the carbonate phases, a systematic characterization of the reaction products of experiments carried at 50°C, 10 bar from 7 minutes to 120 hours (Figure 5) was carried out. Figure S6 summarizes the variation of Raman peak intensity of the reaction products for each experiments plotted against reaction time. Dypingite was already identified after 7-minute reaction (Figure 5a, S7) together with a minor Raman peak associated with UMC. From 15 minutes to 2 hours, another Raman peak emerges with position 1101.1 cm^{-1} (Figure 5a) as well as new XRD peaks (Figure 5b, S7) characteristic of nesquehonite [81,105]. UMC and dypingite are also identified (Figure 5, S8). Analogous comparison of the XRD analysis baselines as performed in section 3.1 (Figure S3 and S4) show the appearance of previously observed plateau (Fig S7b, c), suggesting the possible presence of an amorphous component.

Figure 5. (a) Raman and (b) XRD analysis of the carbonated product of reactions from 7 minutes to 120 hours. B: Brucite, D/H: Dypingite/Hydromagnesite phase, N: Nesquehonite.

Nesquehonite is no longer identified at 4 hours of reaction and UMC and dypingite are the only identified carbonate phases (Figure 5a, S7). It is known that at temperatures 50°C and below, nesquehonite and dypingite are commonly formed under carbonation reaction. Nesquehonite often acts as a precursor for hydromagnesite and hydromagnesite like-phases, such as dypingite [84,86]. Such transformation might undergo the presence of an amorphous precursor [106]. It remains unknown if nesquehonite formed directly from brucite or if it underwent intermediate precursors. However, our results show that nesquehonite acted as a precursor of dypingite and/or UMC.

Brucite is no longer identified after 48 h. However, dypingite is still forming as the UMC Raman peaks and XRD baseline plateau are diminishing. The Dypingite/UMC ratio of $\nu_{1\text{sym}}$ Raman peak intensity (Figure S6b) shows that UMC is forming at a similar rate to dypingite at reaction times of 24 hours or shorter. However, at longer reaction times (48 and 120 hours), dypingite formation is increased relative to UMC, suggesting that UMC nourished dypingite growth (Figure S6a). This differential behavior might suggest that dypingite and UMC related peak behave like two different carbonate phases, being UMC the most disordered or possibly amorphous.

The carbonation reaction probably proceeds through an amorphous precursor that is converted into a structurally semi-ordered phase (dypingite) that over time slowly becomes more organized, following the Ostwald step rule, where the transformation of phases often evolves to a structurally similar phase rather than a thermodynamically more stable phase [107].

FWHM vs Peak position of the reaction products shows that the nesquehonite Raman and XRD peaks fit very well with the reference mineral. Dypingite peaks are continuously approaching the calculated hydromagnesite reference over longer reaction times (7 minutes to 120 hours), indicating a more organized structure and possibly with less molecular water per unit. UMC calculated data remained on the same region as identified on Figure 3a (1093 ± 2.05).

Previous studies have identified the presence of an AMC after 0.4 minutes of reaction a peak emerged with position 1082 cm^{-1} and FWHM 8 cm^{-1} which was associated with AMC [97]. It should be noted that there are several disordered precursors and unnamed Mg-carbonate phases that could possibly have played

a role during our carbonation experiments [84]. However, the AMC Raman peak identified by Montes-Hernandez, et al., 2016 [97] has a very low FWHM which is often associated with ordered materials [93] and its peak position different from any known Mg-carbonate and very close to calcium carbonates, which are characterized by a lower $\nu_{1\text{sym}}$ peak position than Mg carbonates [79].

Figure 6. FWHM vs peak position of (a) Raman $\nu_{1\text{sym}}$ peaks and (b) two more intense XRD peaks of the carbonated products reacted at 50 °C, 10 bar from 7 minutes to 120 hours. N: Nesquehonite, H: Hydromagnesite, D: Dypingite. The FWHM and peak position of reference minerals were calculated from Lafuente, et al., 2015 [99]. Dashed line represents the evolution of different phases over time.

The SEM study (Figure 7) reveals that reaction products obtained from 30 minutes treatments consist of platy dypingite crystals ($\leq 1\mu\text{m}$) [89,108], organized in agglomerates with brucite hexagonal crystals (Figure 7a). Nesquehonite rod crystals of about $10\mu\text{m}$ in length is observed after 1 hour of reaction, showing etch pits and overgrowths of platy dypingite crystals, producing a “house of cards” texture [84,109] (Figure 7b). Almost complete covered nesquehonite rod by etch pits and overgrowths of dypingite, exhibiting a well-developed “house of cards” texture is observed at 2 hours of reaction (Figure 7c). Moreover, a massive carbonate layer has been observed to partially cover residual pristine nesquehonite (Figure 7c inset). The edges between this massive layer and nesquehonite are irregular. This layer is similar to the one observed

for an amorphous hydrated Mg carbonate identified in Zhang, et al., 2018 [58], suggesting that it may be amorphous and may be associated with the presence of UMC. The “house of cards” texture is often interpreted as resulting from a dissolution-recrystallization self-assembly growth mechanism. The overgrowth of dypingite crystals act as nucleation points, analogous to the transformation of nesquehonite into hydromagnesite [84,109]. It is likely that such transformation involves multiple semi/ordered crystalline and/or amorphous precursors [84]. Such behavior is a good example of the Ostwald step rule [107]. A former nesquehonite rod-like structure is observed replaced by platy dypingite crystals which is partially covered by a massive carbonate layer (Figure 4d). Well-developed dypingite plates are observed after 120 hours of reaction (Figure S9).

Figure 7. Representative SEM images of the progressive carbonation stages performed at 50°C and 10 bar. (a) brucite euhedral hexagonal crystals ($\leq 1\mu\text{m}$) and dypingite characteristic plates (30 min); (b) nesquehonite rod crystal ($\sim 10\mu\text{m}$) showing etch pits and overgrowths of platy dypingite crystals $\sim 10\mu\text{m}$, producing a “house of cards” texture (1h); (c) well developed “house of card texture”, inlet shows a naked

section of nesquehonite being covered by a massive and irregularly shaped carbonate (Mg'; 2h); (d) former nesquehonite rod that has been replaced with dypingite plates, which itself is covered by a massive carbonate matrix (4h). Bru: brucite, Nsq: nesquehonite, Dyp: dypingite and Mg': massive irregularly shaped carbonate.

The CO₂:H₂O ratio of the carbonation products was estimated with the aid of TGA (Figure S10-S14). Figure 8 shows the CO₂:H₂O ratio of the reaction products from section 3.1 (Figure 8a) and 3.1.1 (Figure 8b). At 120°C the reaction products have a hydration level consistent with stoichiometric hydromagnesite (Figure 8a). At 50°C, the hydration level of the carbonated products is more like that of stoichiometric dypingite and, in some experiments, it reached the level of stoichiometric nesquehonite.

Experiments carried at 50°C, 10 bar from 7 minutes to 120 hours (Figure 8b) show that initially the carbonate product has a hydration level very close to stoichiometric nesquehonite but, over longer reaction times, it starts to dehydrate, reaching a hydration level below that of stoichiometric hydromagnesite (48 and 120 hours). Such partial dehydration is related with a more structurally ordered dypingite (Figure 6), suggesting a cell shrinkage with less waters of crystallization.

Figure 8. CO₂:H₂O (wt.%) ratios as estimated with TGA of the solid product of reaction at (a) 50 – 120 °C, 1 - 10 bar from 4 to 16 hours and at (b) 50°C, 10 bar, 7 minutes to 120 hours. Error bars were estimated

on the average of three different experiments. Dashed line represents the evolution of the $\text{CO}_2\cdot\text{H}_2\text{O}$ (wt.%) ratio from reaction performed at 7 minutes until 120 hours.

Figure S14 shows the TGA patterns of the reaction products of experiments carried at 50°C, 10 bar from 7 minutes to 120 hours. Dehydration temperature ranges of dypingite starts at room temperature (rT) and continues steadily up to 380°C. However, many differences are observed among different studies [110–112]. Such discrepancies may be related with the possible coexistence of highly to semi-ordered dypingite-like phases with a possible amorphous phase. The mass loss from rT to 180°C is diminishing as the mass loss from 180°C to 380°C is increasing upon longer reaction times. Comparison of Raman, XRD and TGA shows that there is a strong correlation between the initial mass loss (up to 180°C) with the UMC peak and the possible amorphous component. Such dehydration temperature ranges are also characteristic of nesquehonite [113]. Therefore, UMC might have similar composition and thermal dehydration temperature ranges to that of nesquehonite. Zhang et al., 2018 [58] have identified a hydrated AMC which have thermal dehydration behavior similar to nesquehonite [59, 60]. Moreover, White, et al., 2014 [70] identified a hydrated AMC with very similar molecular water per unit as nesquehonite.

The possible coexistence of a highly disordered and/or possibly amorphous component with semi-ordered dypingite-like phases together with the TGA, Raman, XRD and SEM observations may indicate that the wide $\nu_{1\text{sym}}$ Raman peak is associated to this amorphous component. It is unclear whether early dypingite was formed from UMC or directly from brucite, however, it was observed the UMC nourishes the late formation of dypingite. Analogous behavior was also previously reported from the transformation of AMC to a hydromagnesite-like phases [65,69]. The possible AMC was observed to play an important role during the formation of highly-disordered dypingite-like phases. White et al., 2014 [70] proposed that the atomic structure of AMC is heterogeneous, where regions rich in Mg^{2+} and CO_3^{2-} are interspersed with small “pores” of water molecules. Regions rich in H_2O might be less tightly bound in the disordered matrix. As discussed by the authors, such heterogeneity might play an important role on the dehydration mechanisms responsible for the transition of hydrated AMC to anhydrous AMC. Such heterogeneity might also play an important role on its transition to a highly disordered dypingite-like phase, since the regions

rich in Mg^{2+} and CO_3^{2-} might tend to be more organized (under carbonation conditions) crystallizing into a highly-disordered and less-hydrated dypingite-like phase. Only partial dehydration will occur on such process, which might be explained by the slow dehydration of Mg^{2+} [69]. Over time, shrinkage of dypingite structure occurs, caused by the loss of molecular water, producing a more organized structure. On the other hand, the early formation of nesquehonite remains also unclear. However, nesquehonite was observed to nourish UMC and/or dypingite growth, following the Ostwald rule. The proposed reaction pathway is shown in Figure 9.

Research on brucite carbonation in the presence of moisture have speculated on the formation of an hydrous AMC coexisting with crystalline carbonate phases [17,19,55]. However, the difficulties associated to the characterization of coexistent amorphous phases with poorly to well-organized crystalline phases makes difficult the differentiation of such intermediate phases. Our results suggest that a hydrous precursor AMC was probably formed upon carbonation. Moreover, it also provides new insights on the role that plays the possible AMC and/or highly disordered Mg-carbonate phases on the phase evolution of carbonate phases during accelerated carbonation of brucite under moderately low temperature and pressure conditions.

Amorphous carbonate phases play a key role on the nucleation of different hydrated crystalline phases, as they possibly control the level of hydration of the crystalline carbonates. An example being the formation of monohydrocalcite, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (MHC), which requires simultaneous formation of MHC and a $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$ phase, which was previously associated to nesquehonite [114]. However, more recent research has suggested that this $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$ phase might correspond to an amorphous hydrous Mg carbonate instead of nesquehonite [65,66,115]. Fukushi et al., 2017 [65] suggested that AMC coats MHC surface, inhibiting the ability of MHC to form spherical morphology, and possibly passivating the MHC transformation to a more stable calcium carbonate. Recent research has emphasized the importance of an amorphous precursor in order to produce crystalline calcium carbonates [93]. Understanding the processes that take place during accelerated carbonation is of paramount importance for accelerating such reactions and the nucleation of preferential carbonate phases

Figure 9. Scheme of the carbonate phases evolution during carbonation reactions performed at 50°C, 10 bar during 7 minutes to 120 hours. Bru: Brucite, Dyp', Dyp* and Dyp represent the evolution of dypingite-like phases from early highly disordered to late semi-ordered, Nsq: nesquehonite, UMC: possible amorphous Mg carbonate that might have played an important role on the nucleation and/or partial crystallization of semi-ordered dypingite.

3.2. Flue gas experiments

The solid products of the reaction carried at 120°C using simulated flue gas (SFG) at 1 and 10 bar experiments yield to products with similar carbonate mineralogy to that found when using concentrated CO₂ (CC) at 120°C. Calculated FWHM vs peak position data of both XRD and Raman peaks correlates well with reference hydromagnesite (Figure 10, S15). Brucite remained detectable after each experiment. Only traces of hydromagnesite were identified with Raman from experiments at atmospheric pressure (Figure 10a); this low abundance probably explains the apparent lack of this phase in the XRD patterns

(Figure 10b). Increasing the pressure enhances significantly the carbonation of brucite, as evidenced by the formation of hydromagnesite. This latter phase constitutes the most abundant mineral in each experiment carried from 4 to 10 bar.

The $\text{CO}_2\text{:H}_2\text{O}$ ratio, calculated from TGA data (Figure S16-18), shows that the SFG reaction products are less hydrated than those obtained with CC and reference hydromagnesite (Figure S19).

Figure 10. (a) Raman and (b) XRD analysis of phase evolution treatments at 120°C, 1 and 10 bar using SFG. H: hydromagnesite, B: Brucite

3.3. Time-resolved carbonation efficiency

The extent of carbonation (expressed as $\text{g CO}_2 / 100 \text{ g}$ of sample) and the estimated carbonate content achieved after CC and SFG experiments are summarized in Figure 11. During experiments at 120°C it was possible to sequester more CO_2 than at 50°C when using CC (Figure 11a), and was always favored by pressure especially in the range of 1 to 4 bar. On the other hand, experiments carried using SFG yielded a similar amount of CO_2 sequestered to the experiments at 50°C, using CC. Carbonation at atmospheric pressure with SFG was nearly negligible. However, when using CC, a total of 11.5 to 22.1 $\text{g CO}_2 / 100 \text{ g}$ sample (depending on temperature and reaction time) was successfully sequestered by carbonate minerals.

The increase of pressure plays a significant role on the acceleration of the carbonation reaction during SFG experiments.

The comparison between CO₂ sequestered/100g sample normalized by the CO₂ partial pressure is shown in Figure S20. Carbonation using CC at pressures of 4 bar and higher have significantly lower CO₂ fixation capacity per unit of pressure when compared to experiments at 1bar. Therefore, the carbonation process is very efficient (defined as the capacity to fix CO₂) at atmospheric pressure and this efficiency is greatly decreased with increasing pressure (from 4 to 10 bar). CC experiments exhibit higher amounts of CO₂ sequestered than SFG experiments. However, SFG experiments results shows high CO₂ fixation capacity per unit of pressure when compared to the CC experiments at 4 to 10 bar. On the other hand, it was observed a successful carbonation of brucite using SFG at pressures 4 bar and higher. Our results highlight the importance of the CO₂ partial pressure during brucite accelerated carbonation at moderately low temperature and pressures, providing insights on the utilization of industrial flue gas as an alternative to implement accelerated carbonation as in integrated capture and storage processes.

The reaction proceeded similarly for either CC or SFG experiments (section 3.2), in agreement with previous research [74,75]. However, it was observed faster reaction kinetics during CC experiments, especially for the low-pressure experiments (1 and 4 bar). Research on brucite carbonation in the presence of moisture has suggested that such reaction is favored when working near 100% RH, by allowing the formation of hydrated intermediates [19]. The lower carbonation kinetics when using SFG when compared to CC might be explained by the lower RH during SFG experiments. Moreover, a more recent research has also identified different CO₂ uptakes when using different CO₂ partial pressures during carbonation of heat activated serpentine [72]. It was also suggested that there is an optimal CO₂ partial pressure for carbonation of heat activated serpentine.

Figure 11. (a) CO₂ sequestered (gCO₂/100g sample) of experiments carried using concentrated CO₂ (50, 120°C) and simulated flue gas (120°C) from 1 to 10 bar at 4, 8 and 16 hours. Error bars estimate the average between three analogous experiments (b) calculated carbonate content based on the sequestered CO₂. Error bars represent the estimated carbonate content based on the different carbonate mineralogy (Figure S13).

Carbonate contents were calculated on the basis of CO₂ sequestered/100g sample for different carbonate phases (Figure 11b). Experiments using CC at 120°C, 10 bar and 16 hours of reaction yield to almost complete carbonation of brucite (*ca.* 98%). For SFG, the final carbonate contents reached values of 53-70 %, depending on pressure conditions. Such carbonate contents are similar to those obtained at 50°C treatments using CC. The high-purity of the products obtained when using CC could have an important sale value, thus, it will contribute to overcome the carbonation processing cost, which is already reduced by the low temperature and pressure conditions [72]. Further brucite carbonation acceleration is required when using SFG in order to obtain high-purity carbonate products. Highfield et al., 2016 [19] reported similar extents of brucite carbonation under moderately low temperature and pressures ($\leq 120^{\circ}\text{C}$, ≤ 10 bar) in the presence of water vapor to those obtained in this research.

Typical temperatures of flue gas from coal-fired power plants range from 160 to 180°C [116], therefore no additional heating and/or prior CO₂ capture processes would be needed to consider the reactions discussed

in this work for CO₂ sequestration. Moreover, results from experiments at atmospheric pressure show a higher carbonation potential when using SFG; however, further carbonation acceleration is needed. Results from this work are reported on reactions that have occurred below the typical temperatures of flue gas, therefore, an increase in the amount of water vapor and/or temperature may probably play a significant role on enhancing the carbonation reaction using SFG at atmospheric pressure [16,21,22].

Magnesite is the preferred Mg-carbonate for mineral carbonation processes, since it has the highest CO₂ sequestration capacity (Mg/C=1), is the most stable, least soluble and lighter Mg carbonate phase, therefore, leading to lower transportation and processing costs [18]. At pressure and temperature conditions near to those of flue gas emission, its formation is kinetically inhibited by the formation of hydrated carbonates [19,117]. It is also worth considering that the hydrated carbonates formed during SFG experiments do not require the addition of any water since typical flue gas may contain up to 8 mol % of water vapor [77]. In this study only traces of magnesite were identified. Therefore, further research is needed to accelerate the either direct or indirect formation of magnesite at conditions near to those of flue gas emissions. Swanson et al., 2014 [117] demonstrated that the nucleation of magnesite can be accelerated by seeding the reactive material with magnesite particles.

Reaction maintained at 50°C from 7 minutes to 120h using CC shows a continuous increment of the CO₂ sequestered/100 g sample over time until it reaches 48h (Figure S21). At this time a complete carbonation of brucite to hydrated carbonate phases is observed.

4. Conclusions

The carbonation of brucite been studied experimentally in the temperature and pressure ranges of 50-120°C and 1-10 bar using concentrated CO₂ (CC) and simulated flue gas (SFG). At 120°C hydromagnesite was identified with trace amounts of magnesite. At 50°C, coexistent nesquehonite, highly to semi-ordered dypingite-like phases with possibly an amorphous carbonate phase were observed. A Raman peak located at 1093 ± 2.05 with high FWHM, that doubles any crystalline reference Mg-carbonate, might be associated

with the possible amorphous component, which has similar composition and dehydration temperature ranges to those of nesquehonite. It is unclear whether early dypingite was formed from the crystallization of the possible amorphous phase or directly from brucite. However, our results suggest that this possible amorphous phase nourishes the late formation of dypingite, following the Ostwald rule. It also remains unclear whether nesquehonite forms directly from brucite or if underwent an amorphous precursor. However, nesquehonite is observed to be precursor of dypingite and/or possibly the amorphous phase. This latter phase nourishes the late-formation of dypingite, which over longer reaction times losses molecular water and becomes structurally more ordered.

Concentrated CO₂ (CC) experiments results gave higher amounts of CO₂ sequestered (CO₂/100g sample) compared to the experiments carried using simulated flue gas (SFG). A maximum of *ca.* 37wt%. of CO₂ was successfully sequestered at 120°C, 10 bar during 16 hours using CC, reaching an almost complete brucite carbonation (>98%). However, SFG experiments were able to utilize more efficiently the CO₂ partial pressure, especially at 4 to 10 bar. For both SFG and CC experiments carried at 120°C, only crystalline hydrated carbonate phases were observed. Ongoing research is focused on the further enhancement of the carbonate reactions at atmospheric pressure using SFG. Results from this work may provide additional insights on the CO₂ utilization from flue gas and concentrated CO₂ streams, through the formation of Mg-carbonates, in the optimization of carbon sequestration technologies focused on the carbonation of brucite.

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Highlights for: Phase evolution during accelerated CO₂ mineralization of brucite under concentrated CO₂ and simulated flue gas

- Nesquehonite, dypingite and a possible amorphous phase were identified at 50°C
- Hydromagnesite and traces of magnesite were identified at 120°C
- The amorphous phase has composition and dehydration behavior akin to nesquehonite
- Concentrated CO₂ experiments yielded to up to 37 wt.% of CO₂ sequestered
- Higher amounts of CO₂ were fixed per unit of CO₂ partial pressure using flue gas

Mag: Magnesite
Hmg: Hydromagnesite
Dyp: Dypignite

Nsq: Nesquehonite
UMC: Possibly an amorphous carbonate

Phase evolution during accelerated CO₂ mineralization of brucite under concentrated CO₂ and simulated flue gas

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ABSTRACT

Experimental work on the carbonation of brucite has been carried out in the temperature and pressure ranges of 50-120°C and 1-10 bar respectively, using concentrated CO₂ and simulated flue gas. At 120°C hydromagnesite and trace amounts of magnesite were identified. Highly to semi-ordered dypingite like-phases and nesquehonite, coexisting with a possibly amorphous carbonate phase, were identified at 50°C. The dehydration temperatures and chemical composition of these amorphous phases are very close to those of crystalline, stoichiometric nesquehonite. This probably amorphous phase nourishes the late formation of dypingite. This latter mineral gradually undergoes a cell shrinkage due to the partial loss of molecular

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waters, becoming structurally more ordered as the carbonation reaction proceeds. It remains unclear whether nesquehonite formed directly from brucite or from the crystallization of an amorphous precursor. However, nesquehonite is precursor of dypingite and/or the possibly amorphous phase. Only crystalline carbonate phases were observed at 120°C. Concentrated CO₂ experiments yielded the highest amounts (up to 37 wt.%) of CO₂ sequestered at 10 bar and 16 hours of reaction, reaching an almost complete carbonation of brucite (>98%). On the other hand, flue gas experiments results showed higher amounts of CO₂ sequestered per unit of CO₂ partial pressure than with concentrated CO₂.

Keywords

Simulated flue gas; Mineral carbonation; CO₂ sequestration; Phase nucleation; Amorphous magnesium carbonates.

1. Introduction

Mineral carbonation is among the safest, environmentally benign and durable processes for carbon sequestration technologies [1–3], attempting to mimic the natural weathering of Ca/Mg-rich silicate rocks in an anthropic timescale [4]. The main interest of such an approach to CO₂ sequestration resides in and is justified by the fact that the CO₂ sequestration capacity of Mg-rich silicates in the Earth's crust far exceeds the total CO₂ that can be produced by burning the fossil fuel reserves [5].

The enhancement of the carbonation rate of silicate minerals can be achieved by maintaining the reaction in super-heated fluids at high pressures (~185°C, ~150 bar) [6,7]. This is based on the dissolution kinetics of Mg/Ca-rich minerals under slightly acidic conditions prompted by CO₂ dissolution in water [8–10]. However, such processes require reaction conditions that stray far from reality of post-combustion flue-gas conditions, making them difficult to implement at an industrial scale. [11,12].

Direct gas-solid carbonation (DGSC) of raw and pre-treated Mg-rich silicates has received little attention to date, as some early studies suggest that, in contrast with expectations from thermodynamic analysis [3,13], it is not an efficient mechanism for carbon sequestration [14–16]. However, there is a renewed

interest on DGSC under moist conditions, as more recent investigations [17–19] suggest that water vapor plays a critical role in carbonation reactions, allowing the chemical fixation of CO₂ through formation of reactive intermediates [10,20]. Other have suggested that for any DGSC to occur, a minimum amount of H₂O may be needed [16,21,22].

Brucite, Mg(OH)₂ is a relatively common mineral in ultramafic rocks [23] and is converted into magnesite, MgCO₃, through hydrothermal alteration of such materials in contact with CO₂-rich fluids [24–26]. The limited abundance of natural brucite does not make it, in principle, an attractive material to be used in carbon capture, utilization and storage (CCUS) strategies. Nevertheless, the presence of brucite plays a key role in the carbonation of industrial waste materials [27–29]. Alkaline residues are known to have a high carbonation potential (e.g. serpentine mine tailings or alkaline industrial wastes from steel production, alumina refining and coal-fired power generation) [30–34].

Brucite can be obtained from Mg-rich silicates and/or solid waste through the so-called ÅA route, and carbonation of this material has been investigated given its high MgO contents (up to 41 wt.%) [35–37] and fast reactions kinetics [28,38,39]. Recent research emphasized that this process is best applicable for phyllosilicates, such as serpentine minerals [40], considered to be the world's most abundant mineralization precursors [41]. Large mining sites worldwide produce or have produced easy-accessible, finely ground and highly reactive ultramafic mining wastes [29,42–45]. Previous approaches emphasize the extraction of reactive magnesium from Mg-bearing silicates as an essential first step [16,37,46] and agree that it is the most successful approach for ex-situ mineral carbonation processes [14,47]. The utilization of widely available above-ground alkaline industrial wastes avoids not only mining and milling but also consumption raw material. Moreover, the carbonation of brucite utilizes either flue gas or concentrated CO₂ in addition to its reaction products, which may substitute raw materials in various industries [32,48–50]. An energy and cost efficient carbonation process should be able to fix CO₂ from flue gas without need of capturing it in advance [51].

Direct carbonation of brucite to magnesite only occurs at high temperatures and pressures; at lower temperatures this reaction is kinetically inhibited by the formation of hydrated Mg carbonates [52,53]

during simultaneous carbonation and dehydroxylation [21,54,55]. Previous research has stated that the gas-solid carbonation of both MgO and Mg(OH)₂ takes place at a very slow rate, when compared with the “wet” route [19,21,56], and has emphasized the role of relative humidity on such reactions [17,19,55].

CO₂ mineralization processes should be able to reach feasible conversion rates when operating at temperatures and pressures near flue gas emissions [19,57]. However, the formation mechanisms of Mg carbonates under such conditions are poorly known. Previous studies have suggested the presence of an amorphous hydrated Mg carbonate phase (AMC) during carbonation and hydration of periclase, MgO [58]. Amorphous carbonates are precursors to crystalline phases and are known to play a key role in the precipitation of different hydrated or anhydrous carbonate phases. Nature takes advantage of the amorphous to crystalline transition in a variety of processes [59–61]. The transition of amorphous calcium carbonate (ACC) to crystalline phases have been thoroughly studied [62–65]. The formation of AMC and its transition to crystalline phases has received less attention, and it has been mainly discussed in the context of mixed Ca/Mg amorphous carbonate phases [64–67]. The presence of Mg²⁺ plays a key role on the crystallization of ACC, most probably because the slow dehydration of Mg²⁺ [69]. However, research interest is continuously increasing with regard to the accelerated formation of magnesium carbonates from Mg-rich oxides and silicates, since such processes has been proposed as a possible carbon sink for anthropogenic CO₂ [5,68]. Fukushi, et al., 2017 [65] suggested that AMC plays an important role on the formation of crystalline carbonate phases on the context of mixed Ca/Mg amorphous carbonate phases. Therefore, understanding the formation of AMC, its transition to crystalline phases and the role it plays during the evolution of carbonate phases during carbonation reaction is of paramount importance since it might provide important insights in the acceleration of carbonation reactions at conditions near to those of flue gas emissions, which are known to be kinetically challenging [1,11,12]. This is especially important for hydrated Mg carbonate minerals which occurs in several phases, such as nesquehonite, lansfordite, artinite, hydromagnesite, dypingite or barringtonite, each with different water contents [70]. The stability of amorphous materials is known to depend on size and water content [71]. AMC produced from Ca-Mg-CO₃ solutions are expected to be different to those that formed in Mg-CO₃ solutions [65].

Recent research has also focused on the alternative to implement accelerated carbonation as an integrated capture and storage process [57,72–75]. This route will avoid prior CO₂ capture processes, which will significantly simplify the overall accelerated carbonation process. It has been observed that the reaction mechanisms and kinetics were similar to the ones obtained for pure CO₂ streams, indicating the high carbonation potential when using a gas composition similar to some industrial flue gas [74,75]. Moreover, the high-purity carbonate products are considered as a marketable product [72].

This work reports on the study of the evolution of carbonate phases during steam accelerated carbonation of magnesium hydroxide in a pressurized continuous flow reactor at moderate pressures (1 - 10 bar) and relatively low temperatures (50-120°C), using both simulated flue gas and concentrated CO₂.

2. Materials and methods

2.1. Experimental

Samples of 600 mg of magnesium hydroxide (>99% BioUltra, Sigma-Aldrich™, CAS number: 1309-42-8) were loaded into a purpose-designed reactor (35mL stainless steel) placed within a furnace with an integrated thermocouple (Figure S1), and heated up to the desired temperature (50°C to 120°C). Carbonation experiments were carried out in a pressurized continuous flow, using N₂ as a carrier gas. A summary of P, T, time and humidity conditions of all experiments is given in Table S1. A maximum temperature drift of ± 1 °C was measured inside the reactor in *operando* conditions. Flue gas composition was simulated with a 85% N₂ – 15% CO₂ mixture, following previous research [41,57,76,77]. Pressure was controlled with pressure reducers and back pressure regulators, until the desired conditions were achieved for a given flux. A drift of ± 0.2 bar in *operando* conditions was measured with 2 manometers located at the inlet and outlet of the reactor. Prior to introduction in the chamber, CO₂ was forced to flow through a ~50 mL bubbler containing water. Appropriate temperature and pressure were chosen to produce a gas mixture with relative humidities (RH) of 90% and 5 % for concentrated CO₂ and simulated flue gas experiments, respectively (Table S2). To avoid gas concentration changes due to the absorption of CO₂ in the bubbler, a continuous

flow of either concentrated CO₂ or CO₂ diluted with N₂ at the specific pressure and temperature conditions was maintained for at least 30 minutes before each experiment. Therefore, the water on the bubbler was saturated with CO₂ prior each experiment, inhibiting further absorption of CO₂. Conditions were kept isothermal during different reaction times. After the experiments, pressure was released and N₂ was used to stop the carbonation reaction while cooling.

2.2. Analytical

Raman spectra were obtained with an inVia Qontor™ confocal Raman microscope, equipped with a green laser with an excitation wavelength of 532 nm. Given the substantial heterogeneity of phase distribution at the microscale after reaction, a total of 40 measurements were averaged on each sample in order to obtain representative results. Infrared analyses were carried out with a Nicolet 6700™ Fourier Transform Infrared Spectrometer (FTIR). An attenuated total reflection (ATR) module was used to record spectra on a germanium crystal (mid-IR, from 750 – 4000 cm⁻¹), using 64 scans and 2 data point spacing. Mineral composition was determined with a Bruker D8™ X-Ray powder diffractometer (XRD), operated at 1deg/min scans over a scattering angle (2θ) from 10 to 80°, and a step size of 0.01°. A thermogravimetric analysis system (TA Instruments Q50™) was used to measure the mass losses upon decomposition of specific phases. Data were acquired at a heating rate of 10°C/min, from room temperature to 600°C, under a N₂ flow of 60mL/min. Scanning electron microscopy images of powder samples were obtained with a cross-beam work station Zeiss Neon 40™, equipped with an INCAPentaFET energy dispersive X-ray system for elemental analysis, operated at 5keV.

3. Results and discussion

3.1. Concentrated CO₂ experiments

Raman spectra of the solid products formed in the pressure range of 1 - 10 bar at 50 and 120 °C using concentrated CO₂ are shown in Fig. 1. Brucite is clearly identified as the starting material with its

characteristic peaks at 443 and 279 cm^{-1} [55,78]. Upon reaction at 50°C, two distinct peaks (1093.3 ± 1.1 , 1122.3 ± 0.1) are identified on the 1080-1125 cm^{-1} band, characteristic of the ν_1 symmetric stretching mode ($\nu_{1\text{sym}}$) of the carbonate ion (CO_3^{2-}) [79,80]. The intensity of the carbonate related peaks are in inverse proportion to the intensity of brucite peaks. At 120°C, two distinct peaks are identified within the $\nu_{1\text{sym}}$ band at 1094.6 ± 0.1 , and 1118.1 ± 0.5 ; these remain invariable upon reaction from 4 to 16 hours. An additional peak is observed at 328.3 ± 0.1 , especially at 7 and 10 bar.

FTIR analysis of the solid product of reaction also confirmed the presence of carbonates (Figure S2), showing characteristic peaks of the CO_3^{2-} and HCO_3^- ν_3 asymmetric stretching mode at 1405, 1470 and 1515 cm^{-1} [81–83]. However, different Mg carbonates cannot be differentiated due to the overlapping features among those phases on FTIR. Moreover, different Mg carbonates phases cannot be easily distinguished with the sole observation of the carbonate ion $\nu_{1\text{sym}}$ using Raman spectroscopy [79].

Fig. 1. Raman spectra of phase evolution after thermal treatments (50 – 120°C) in the 1-10 bar range (RH > 90%) from 4 to 16 hours. B: Brucite.

In order to provide additional insights on the differentiation of the distinct carbonate phases and their crystalline nature, an XRD study of the reaction products was carried out (Fig. 2). Brucite diffraction peaks are identified as the starting material and its relative peak intensity is progressively diminishing as pressure goes from 1 to 10 bar. At 120°C, crystalline hydromagnesite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, is observed. [52,84]. At 50°C, broader peaks are identified (Figure S3a), probably indicating the presence of hydromagnesite-like phases such as dypingite, $\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, as suggested by Hövelmann, et al., 2012 [38]. Dypingite and hydromagnesite are similar in composition, but the more hydrated carbonate has a more disordered structure with a variable amount of water molecules per formula unit [85–87]. This latter may serve as an explanation to the broader XRD features when compared to hydromagnesite (Figure S3b). At temperatures $\leq 50^\circ\text{C}$ the formation of hydromagnesite may be kinetically inhibited by the formation of highly hydrated Mg-carbonate phases, such as nesquehonite, $\text{Mg}(\text{HCO}_3)(\text{OH}) \cdot 2(\text{H}_2\text{O})$, and dypingite [45,88,89].

Fig. 2. XRD of samples after thermal treatments at 50 and 120°C and 1 to 10 bar, maintained for 16h (RH > 90%). D/H: Dypingite/Hydromagnesite phase, H: Hydromagnesite, B: Brucite.

No differences are identified when comparing the baseline of the XRD patterns from the starting material with the carbonated products obtained at 120°C, 10 bar (Fig. S3b). However, when comparing the baseline between the carbonated products obtained at 50 and 120°C and 10 bar, a plateau is observed from 24 to 54 $2\theta^\circ$ and with center near 31 $2\theta^\circ$ (Fig S3c). This plateau is almost identical to the one observed for an amorphous Mg carbonate with chemical composition $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$ [65,90–92]. The latter is possibly indicating the coexistence between an amorphous component with poorly-ordered dypingite [62,91,93,94].

A comparison between the Full Width Half Maximum (FWHM) of the Raman ν_{sym} peaks as well as the two more intense XRD peaks of the carbonated products was carried to provide more insights on the nature of the observed carbonate phases (Figure 3). Calculated data from 120 °C experiments fits very well with reference data corresponding to hydromagnesite. The FWHM of the two more intense XRD peaks from the

carbonated products are very similar to reference hydromagnesite, indicating a well-defined structure, in agreement with above observations. Moreover, the minor peak observed at 1094.6 ± 0.1 (Figure 1, 120°C treatments) fits very well with reference magnesite, and its presence is correlated with the emergence of the 328.3 ± 0.1 peak, which is also characteristic of magnesite [79,95,96]. Only traces amounts are observed of this latter mineral, which explains its relative inexistence on the XRD patterns (Figure 2, 120°C treatments). The formation of magnesite could come from the transformation of hydromagnesite or directly from brucite [53,55,97].

The calculated Raman data (Figure 3a) from the 50°C experiments shows that the peak located at 1122.3 ± 0.1 fits well with reference dypingite. Moreover, the identified two more intense XRD peaks (Figure 3b) have very similar positions when compared to reference hydromagnesite XRD peaks but with higher FWHM, indicating a more disordered structure, as previously discussed. The Raman peak located at 1093.3 ± 1.1 has a much higher FWHM than the other identified and reference carbonate phases, as well as higher peak position variability, indicating a possibly highly disordered or amorphous carbonate phase. Some studies have also observed this peak and its presence is related to dypingite [84,98]. The disordered to semi-disordered structure of dypingite is reflected on the difficulties to obtain good quality Raman spectra [98]. The possible coexistence of semi-ordered dypingite-like phases with a possible amorphous phase increases the difficulties to associate Raman spectra to pure dypingite phases. It is not clear if this peak (1093.3 ± 1.1) whether belongs to the semi-ordered dypingite or it is prompted by the vibration of $\nu_{1\text{sym}}$ peaks of coexisting highly to semi-ordered disordered dypingite-like phases with a possible amorphous carbonate phase [84,98]. Therefore, the nature of the hydrated Mg carbonate that generates the 1093.31 ± 1.1 Raman peak is yet unknown. This “unknown Mg-carbonate” (UMC) may be associated with the amorphous component observed with XRD (Figure S3c, S4).

Figure 3. FWHM vs peak position of (a) Raman $\nu_{1\text{sym}}$ peaks and (b) two more intense XRD peaks of the carbonated products reacted at 50 and 120°C, 1-10 bar. M: Magnesite, N: Nesquehonite, H: Hydromagnesite, D: Dypingite. The FWHM and peak position of reference minerals were calculated from Lafuente, et al., 2015 [99].

Microstructural changes occurring upon carbonation have been studied by SEM (Figure 4). The starting material consists of well-defined hexagonal crystals of brucite (< 1 μm ; Figure 4a), similar to those previously studied by Pang et al. (2011). After 16 h at 50°C, only some sub-euhedral brucite grains can be identified and the microstructure is dominated by an irregularly-shaped massive material (Figure 4b) that might be associated with UMC. Energy dispersive spectrometry (EDS) analysis of such material reveals the presence of a carbonate component, different from the carbon-free (brucite) starting material (Figure S5). When temperature reaches 120°C, characteristic hydromagnesite plates of maximum sizes of ~1 μm are observed (Figure 4c), with morphological features similar to those identified by Zhang et al. (2006). Fully developed hydromagnesite plates are observed at 10 bar (Figure 4d), as well as rhombohedral magnesite [103]. This latter constituting a minor phase (Figure 4d, inset).

Figure 4. Representative SEM images of the progressive carbonation stages, from (a) brucite starting material (euhedral hexagonal crystals $\leq 1\mu\text{m}$) to (b) relict subhedral brucite immersed in a massive carbonate matrix (see Figure S5) formed at 50°C , (c) well developed hydromagnesite plates ($\sim 1\mu\text{m}$) appearing at 120°C with some residual brucite and (d) euhedral hydromagnesite plates ($\leq 10\mu\text{m}$) and rhombohedral magnesite ($\leq 1\mu\text{m}$) formed at 120°C and 10 bar. Bru: Brucite, Mg': massive irregularly shaped carbonate, Hmg: Hydromagnesite, Mag: Magnesite.

The reaction products obtained at 120°C are composed of crystalline carbonate phases. At 50°C temperatures, possibly amorphous and semi-ordered phases emerge providing challenges for predicating and controlling the evolution of such minerals for long term-storage since the properties of amorphous Mg-carbonates are not well established [104].

3.1.1. Evolution of carbonate phases at 50°C

In order to provide more insights on the identification of the carbonate phases, a systematic characterization of the reaction products of experiments carried at 50°C, 10 bar from 7 minutes to 120 hours (Figure 5) was carried out. Figure S6 summarizes the variation of Raman peak intensity of the reaction products for each experiments plotted against reaction time. Dypingite was already identified after 7-minute reaction (Figure 5a, S7) together with a minor Raman peak associated with UMC. From 15 minutes to 2 hours, another Raman peak emerges with position 1101.1 cm^{-1} (Figure 5a) as well as new XRD peaks (Figure 5b, S7) characteristic of nesquehonite [81,105]. UMC and dypingite are also identified (Figure 5, S8). Analogous comparison of the XRD analysis baselines as performed in section 3.1 (Figure S3 and S4) show the appearance of previously observed plateau (Fig S7b, c), suggesting the possible presence of an amorphous component.

Figure 5. (a) Raman and (b) XRD analysis of the carbonated product of reactions from 7 minutes to 120 hours. B: Brucite, D/H: Dypingite/Hydromagnesite phase, N: Nesquehonite.

Nesquehonite is no longer identified at 4 hours of reaction and UMC and dypingite are the only identified carbonate phases (Figure 5a, S7). It is known that at temperatures 50°C and below, nesquehonite and dypingite are commonly formed under carbonation reaction. Nesquehonite often acts as a precursor for hydromagnesite and hydromagnesite like-phases, such as dypingite [84,86]. Such transformation might undergo the presence of an amorphous precursor [106]. It remains unknown if nesquehonite formed directly from brucite or if it underwent intermediate precursors. However, our results show that nesquehonite acted as a precursor of dypingite and/or UMC.

Brucite is no longer identified after 48 h. However, dypingite is still forming as the UMC Raman peaks and XRD baseline plateau are diminishing. The Dypingite/UMC ratio of $\nu_{1\text{sym}}$ Raman peak intensity (Figure S6b) shows that UMC is forming at a similar rate to dypingite at reaction times of 24 hours or shorter. However, at longer reaction times (48 and 120 hours), dypingite formation is increased relative to UMC, suggesting that UMC nourished dypingite growth (Figure S6a). This differential behavior might suggest that dypingite and UMC related peak behave like two different carbonate phases, being UMC the most disordered or possibly amorphous.

The carbonation reaction probably proceeds through an amorphous precursor that is converted into a structurally semi-ordered phase (dypingite) that over time slowly becomes more organized, following the Ostwald step rule, where the transformation of phases often evolves to a structurally similar phase rather than a thermodynamically more stable phase [107].

FWHM vs Peak position of the reaction products shows that the nesquehonite Raman and XRD peaks fit very well with the reference mineral. Dypingite peaks are continuously approaching the calculated hydromagnesite reference over longer reaction times (7 minutes to 120 hours), indicating a more organized structure and possibly with less molecular water per unit. UMC calculated data remained on the same region as identified on Figure 3a (1093 ± 2.05).

Previous studies have identified the presence of an AMC after 0.4 minutes of reaction a peak emerged with position 1082 cm^{-1} and FWHM 8 cm^{-1} which was associated with AMC [97]. It should be noted that there are several disordered precursors and unnamed Mg-carbonate phases that could possibly have played

a role during our carbonation experiments [84]. However, the AMC Raman peak identified by Montes-Hernandez, et al., 2016 [97] has a very low FWHM which is often associated with ordered materials [93] and its peak position different from any known Mg-carbonate and very close to calcium carbonates, which are characterized by a lower $\nu_{1\text{sym}}$ peak position than Mg carbonates [79].

Figure 6. FWHM vs peak position of (a) Raman $\nu_{1\text{sym}}$ peaks and (b) two more intense XRD peaks of the carbonated products reacted at 50 °C, 10 bar from 7 minutes to 120 hours. N: Nesquehonite, H: Hydromagnesite, D: Dypingite. The FWHM and peak position of reference minerals were calculated from Lafuente, et al., 2015 [99]. Dashed line represents the evolution of different phases over time.

The SEM study (Figure 7) reveals that reaction products obtained from 30 minutes treatments consist of platy dypingite crystals ($\leq 1\mu\text{m}$) [89,108], organized in agglomerates with brucite hexagonal crystals (Figure 7a). Nesquehonite rod crystals of about $10\mu\text{m}$ in length is observed after 1 hour of reaction, showing etch pits and overgrowths of platy dypingite crystals, producing a “house of cards” texture [84,109] (Figure 7b). Almost complete covered nesquehonite rod by etch pits and overgrowths of dypingite, exhibiting a well-developed “house of cards” texture is observed at 2 hours of reaction (Figure 7c). Moreover, a massive carbonate layer has been observed to partially cover residual pristine nesquehonite (Figure 7c inset). The edges between this massive layer and nesquehonite are irregular. This layer is similar to the one observed

for an amorphous hydrated Mg carbonate identified in Zhang, et al., 2018 [58], suggesting that it may be amorphous and may be associated with the presence of UMC. The “house of cards” texture is often interpreted as resulting from a dissolution-recrystallization self-assembly growth mechanism. The overgrowth of dypingite crystals act as nucleation points, analogous to the transformation of nesquehonite into hydromagnesite [84,109]. It is likely that such transformation involves multiple semi/ordered crystalline and/or amorphous precursors [84]. Such behavior is a good example of the Ostwald step rule [107]. A former nesquehonite rod-like structure is observed replaced by platy dypingite crystals which is partially covered by a massive carbonate layer (Figure 4d). Well-developed dypingite plates are observed after 120 hours of reaction (Figure S9).

Figure 7. Representative SEM images of the progressive carbonation stages performed at 50°C and 10 bar. (a) brucite euhedral hexagonal crystals ($\leq 1\mu\text{m}$) and dypingite characteristic plates (30 min); (b) nesquehonite rod crystal ($\sim 10\mu\text{m}$) showing etch pits and overgrowths of platy dypingite crystals $\sim 10\mu\text{m}$, producing a “house of cards” texture (1h); (c) well developed “house of card texture”, inlet shows a naked dypingite (Dyp) crystal; (d) former nesquehonite (Former Nsq) rod crystal with overgrowths of dypingite (Dyp) and Mg' crystals.

section of nesquehonite being covered by a massive and irregularly shaped carbonate (Mg'; 2h); (d) former nesquehonite rod that has been replaced with dypingite plates, which itself is covered by a massive carbonate matrix (4h). Bru: brucite, Nsq: nesquehonite, Dyp: dypingite and Mg': massive irregularly shaped carbonate.

The $\text{CO}_2\text{:H}_2\text{O}$ ratio of the carbonation products was estimated with the aid of TGA (Figure S10-S14). Figure 8 shows the $\text{CO}_2\text{:H}_2\text{O}$ ratio of the reaction products from section 3.1 (Figure 8a) and 3.1.1 (Figure 8b). At 120°C the reaction products have a hydration level consistent with stoichiometric hydromagnesite (Figure 8a). At 50°C, the hydration level of the carbonated products is more like that of stoichiometric dypingite and, in some experiments, it reached the level of stoichiometric nesquehonite.

Experiments carried at 50°C, 10 bar from 7 minutes to 120 hours (Figure 8b) show that initially the carbonate product has a hydration level very close to stoichiometric nesquehonite but, over longer reaction times, it starts to dehydrate, reaching a hydration level below that of stoichiometric hydromagnesite (48 and 120 hours). Such partial dehydration is related with a more structurally ordered dypingite (Figure 6), suggesting a cell shrinkage with less waters of crystallization.

Figure 8. $\text{CO}_2\text{:H}_2\text{O}$ (wt.%) ratios as estimated with TGA of the solid product of reaction at (a) 50 – 120 °C, 1 - 10 bar from 4 to 16 hours and at (b) 50°C, 10 bar, 7 minutes to 120 hours. Error bars were estimated

on the average of three different experiments. Dashed line represents the evolution of the $\text{CO}_2\cdot\text{H}_2\text{O}$ (wt.%) ratio from reaction performed at 7 minutes until 120 hours.

Figure S14 shows the TGA patterns of the reaction products of experiments carried at 50°C, 10 bar from 7 minutes to 120 hours. Dehydration temperature ranges of dypingite starts at room temperature (rT) and continues steadily up to 380°C. However, many differences are observed among different studies [110–112]. Such discrepancies may be related with the possible coexistence of highly to semi-ordered dypingite-like phases with a possible amorphous phase. The mass loss from rT to 180°C is diminishing as the mass loss from 180°C to 380°C is increasing upon longer reaction times. Comparison of Raman, XRD and TGA shows that there is a strong correlation between the initial mass loss (up to 180°C) with the UMC peak and the possible amorphous component. Such dehydration temperature ranges are also characteristic of nesquehonite [113]. Therefore, UMC might have similar composition and thermal dehydration temperature ranges to that of nesquehonite. Zhang et al., 2018 [58] have identified a hydrated AMC which have thermal dehydration behavior similar to nesquehonite [59, 60]. Moreover, White, et al., 2014 [70] identified a hydrated AMC with very similar molecular water per unit as nesquehonite.

The possible coexistence of a highly disordered and/or possibly amorphous component with semi-ordered dypingite-like phases together with the TGA, Raman, XRD and SEM observations may indicate that the wide $\nu_{1\text{sym}}$ Raman peak is associated to this amorphous component. It is unclear whether early dypingite was formed from UMC or directly from brucite, however, it was observed the UMC nourishes the late formation of dypingite. Analogous behavior was also previously reported from the transformation of AMC to a hydromagnesite-like phases [65,69]. The possible AMC was observed to play an important role during the formation of highly-disordered dypingite-like phases. White et al., 2014 [70] proposed that the atomic structure of AMC is heterogeneous, where regions rich in Mg^{2+} and CO_3^{2-} are interspersed with small “pores” of water molecules. Regions rich in H_2O might be less tightly bound in the disordered matrix. As discussed by the authors, such heterogeneity might play an important role on the dehydration mechanisms responsible for the transition of hydrated AMC to anhydrous AMC. Such heterogeneity might also play an important role on its transition to a highly disordered dypingite-like phase, since the regions

rich in Mg^{2+} and CO_3^{2-} might tend to be more organized (under carbonation conditions) crystallizing into a highly-disordered and less-hydrated dypingite-like phase. Only partial dehydration will occur on such process, which might be explained by the slow dehydration of Mg^{2+} [69]. Over time, shrinkage of dypingite structure occurs, caused by the loss of molecular water, producing a more organized structure. On the other hand, the early formation of nesquehonite remains also unclear. However, nesquehonite was observed to nourish UMC and/or dypingite growth, following the Ostwald rule. The proposed reaction pathway is shown in Figure 9.

Research on brucite carbonation in the presence of moisture have speculated on the formation of an hydrous AMC coexisting with crystalline carbonate phases [17,19,55]. However, the difficulties associated to the characterization of coexistent amorphous phases with poorly to well-organized crystalline phases makes difficult the differentiation of such intermediate phases. Our results suggest that a hydrous precursor AMC was probably formed upon carbonation. Moreover, it also provides new insights on the role that plays the possible AMC and/or highly disordered Mg-carbonate phases on the phase evolution of carbonate phases during accelerated carbonation of brucite under moderately low temperature and pressure conditions.

Amorphous carbonate phases play a key role on the nucleation of different hydrated crystalline phases, as they possibly control the level of hydration of the crystalline carbonates. An example being the formation of monohydrocalcite, $\text{CaCO}_3 \cdot \text{H}_2\text{O}$ (MHC), which requires simultaneous formation of MHC and a $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$ phase, which was previously associated to nesquehonite [114]. However, more recent research has suggested that this $\text{MgCO}_3 \cdot n\text{H}_2\text{O}$ phase might correspond to an amorphous hydrous Mg carbonate instead of nesquehonite [65,66,115]. Fukushi et al., 2017 [65] suggested that AMC coats MHC surface, inhibiting the ability of MHC to form spherical morphology, and possibly passivating the MHC transformation to a more stable calcium carbonate. Recent research has emphasized the importance of an amorphous precursor in order to produce crystalline calcium carbonates [93]. Understanding the processes that take place during accelerated carbonation is of paramount importance for accelerating such reactions and the nucleation of preferential carbonate phases

Figure 9. Scheme of the carbonate phases evolution during carbonation reactions performed at 50°C, 10 bar during 7 minutes to 120 hours. Bru: Brucite, Dyp', Dyp* and Dyp represent the evolution of dypingite-like phases from early highly disordered to late semi-ordered, Nsq: nesquehonite, UMC: possible amorphous Mg carbonate that might have played an important role on the nucleation and/or partial crystallization of semi-ordered dypingite.

3.2. Flue gas experiments

The solid products of the reaction carried at 120°C using simulated flue gas (SFG) at 1 and 10 bar experiments yield to products with similar carbonate mineralogy to that found when using concentrated CO₂ (CC) at 120°C. Calculated FWHM vs peak position data of both XRD and Raman peaks correlates well with reference hydromagnesite (Figure 10, S15). Brucite remained detectable after each experiment. Only traces of hydromagnesite were identified with Raman from experiments at atmospheric pressure (Figure 10a); this low abundance probably explains the apparent lack of this phase in the XRD patterns

(Figure 10b). Increasing the pressure enhances significantly the carbonation of brucite, as evidenced by the formation of hydromagnesite. This latter phase constitutes the most abundant mineral in each experiment carried from 4 to 10 bar.

The $\text{CO}_2\text{:H}_2\text{O}$ ratio, calculated from TGA data (Figure S16-18), shows that the SFG reaction products are less hydrated than those obtained with CC and reference hydromagnesite (Figure S19).

Figure 10. (a) Raman and (b) XRD analysis of phase evolution treatments at 120°C, 1 and 10 bar using SFG. H: hydromagnesite, B: Brucite

3.3. Time-resolved carbonation efficiency

The extent of carbonation (expressed as $\text{g CO}_2 / 100 \text{ g}$ of sample) and the estimated carbonate content achieved after CC and SFG experiments are summarized in Figure 11. During experiments at 120°C it was possible to sequester more CO_2 than at 50°C when using CC (Figure 11a), and was always favored by pressure especially in the range of 1 to 4 bar. On the other hand, experiments carried using SFG yielded a similar amount of CO_2 sequestered to the experiments at 50°C, using CC. Carbonation at atmospheric pressure with SFG was nearly negligible. However, when using CC, a total of 11.5 to 22.1 $\text{g CO}_2 / 100 \text{ g}$ sample (depending on temperature and reaction time) was successfully sequestered by carbonate minerals.

The increase of pressure plays a significant role on the acceleration of the carbonation reaction during SFG experiments.

The comparison between CO₂ sequestered/100g sample normalized by the CO₂ partial pressure is shown in Figure S20. Carbonation using CC at pressures of 4 bar and higher have significantly lower CO₂ fixation capacity per unit of pressure when compared to experiments at 1bar. Therefore, the carbonation process is very efficient (defined as the capacity to fix CO₂) at atmospheric pressure and this efficiency is greatly decreased with increasing pressure (from 4 to 10 bar). CC experiments exhibit higher amounts of CO₂ sequestered than SFG experiments. However, SFG experiments results shows high CO₂ fixation capacity per unit of pressure when compared to the CC experiments at 4 to 10 bar. On the other hand, it was observed a successful carbonation of brucite using SFG at pressures 4 bar and higher. Our results highlight the importance of the CO₂ partial pressure during brucite accelerated carbonation at moderately low temperature and pressures, providing insights on the utilization of industrial flue gas as an alternative to implement accelerated carbonation as in integrated capture and storage processes.

The reaction proceeded similarly for either CC or SFG experiments (section 3.2), in agreement with previous research [74,75]. However, it was observed faster reaction kinetics during CC experiments, especially for the low-pressure experiments (1 and 4 bar). Research on brucite carbonation in the presence of moisture has suggested that such reaction is favored when working near 100% RH, by allowing the formation of hydrated intermediates [19]. The lower carbonation kinetics when using SFG when compared to CC might be explained by the lower RH during SFG experiments. Moreover, a more recent research has also identified different CO₂ uptakes when using different CO₂ partial pressures during carbonation of heat activated serpentine [72]. It was also suggested that there is an optimal CO₂ partial pressure for carbonation of heat activated serpentine.

Figure 11. (a) CO₂ sequestered (gCO₂/100g sample) of experiments carried using concentrated CO₂ (50, 120°C) and simulated flue gas (120°C) from 1 to 10 bar at 4, 8 and 16 hours. Error bars estimate the average between three analogous experiments (b) calculated carbonate content based on the sequestered CO₂. Error bars represent the estimated carbonate content based on the different carbonate mineralogy (Figure S13).

Carbonate contents were calculated on the basis of CO₂ sequestered/100g sample for different carbonate phases (Figure 11b). Experiments using CC at 120°C, 10 bar and 16 hours of reaction yield to almost complete carbonation of brucite (*ca.* 98%). For SFG, the final carbonate contents reached values of 53-70 %, depending on pressure conditions. Such carbonate contents are similar to those obtained at 50°C treatments using CC. The high-purity of the products obtained when using CC could have an important sale value, thus, it will contribute to overcome the carbonation processing cost, which is already reduced by the low temperature and pressure conditions [72]. Further brucite carbonation acceleration is required when using SFG in order to obtain high-purity carbonate products. Highfield et al., 2016 [19] reported similar extents of brucite carbonation under moderately low temperature and pressures ($\leq 120^{\circ}\text{C}$, ≤ 10 bar) in the presence of water vapor to those obtained in this research.

Typical temperatures of flue gas from coal-fired power plants range from 160 to 180°C [116], therefore no additional heating and/or prior CO₂ capture processes would be needed to consider the reactions discussed

in this work for CO₂ sequestration. Moreover, results from experiments at atmospheric pressure show a higher carbonation potential when using SFG; however, further carbonation acceleration is needed. Results from this work are reported on reactions that have occurred below the typical temperatures of flue gas, therefore, an increase in the amount of water vapor and/or temperature may probably play a significant role on enhancing the carbonation reaction using SFG at atmospheric pressure [16,21,22].

Magnesite is the preferred Mg-carbonate for mineral carbonation processes, since it has the highest CO₂ sequestration capacity (Mg/C=1), is the most stable, least soluble and lighter Mg carbonate phase, therefore, leading to lower transportation and processing costs [18]. At pressure and temperature conditions near to those of flue gas emission, its formation is kinetically inhibited by the formation of hydrated carbonates [19,117]. It is also worth considering that the hydrated carbonates formed during SFG experiments do not require the addition of any water since typical flue gas may contain up to 8 mol % of water vapor [77]. In this study only traces of magnesite were identified. Therefore, further research is needed to accelerate the either direct or indirect formation of magnesite at conditions near to those of flue gas emissions. Swanson et al., 2014 [117] demonstrated that the nucleation of magnesite can be accelerated by seeding the reactive material with magnesite particles.

Reaction maintained at 50°C from 7 minutes to 120h using CC shows a continuous increment of the CO₂ sequestered/100 g sample over time until it reaches 48h (Figure S21). At this time a complete carbonation of brucite to hydrated carbonate phases is observed.

4. Conclusions

The carbonation of brucite been studied experimentally in the temperature and pressure ranges of 50-120°C and 1-10 bar using concentrated CO₂ (CC) and simulated flue gas (SFG). At 120°C hydromagnesite was identified with trace amounts of magnesite. At 50°C, coexistent nesquehonite, highly to semi-ordered dypingite-like phases with possibly an amorphous carbonate phase were observed. A Raman peak located at 1093 ± 2.05 with high FWHM, that doubles any crystalline reference Mg-carbonate, might be associated

with the possible amorphous component, which has similar composition and dehydration temperature ranges to those of nesquehonite. It is unclear whether early dypingite was formed from the crystallization of the possible amorphous phase or directly from brucite. However, our results suggest that this possible amorphous phase nourishes the late formation of dypingite, following the Ostwald rule. It also remains unclear whether nesquehonite forms directly from brucite or if underwent an amorphous precursor. However, nesquehonite is observed to be precursor of dypingite and/or possibly the amorphous phase. This latter phase nourishes the late-formation of dypingite, which over longer reaction times losses molecular water and becomes structurally more ordered.

Concentrated CO₂ (CC) experiments results gave higher amounts of CO₂ sequestered (CO₂/100g sample) compared to the experiments carried using simulated flue gas (SFG). A maximum of *ca.* 37wt%. of CO₂ was successfully sequestered at 120°C, 10 bar during 16 hours using CC, reaching an almost complete brucite carbonation (>98%). However, SFG experiments were able to utilize more efficiently the CO₂ partial pressure, especially at 4 to 10 bar. For both SFG and CC experiments carried at 120°C, only crystalline hydrated carbonate phases were observed. Ongoing research is focused on the further enhancement of the carbonate reactions at atmospheric pressure using SFG. Results from this work may provide additional insights on the CO₂ utilization from flue gas and concentrated CO₂ streams, through the formation of Mg-carbonates, in the optimization of carbon sequestration technologies focused on the carbonation of brucite.

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Supplementary information for:

Phase evolution during accelerated CO₂ mineralization of brucite under concentrated CO₂ and simulated flue gas

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This document includes: Figure S1 to S21 and tables S1 and S2.

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Figure S1. Schematic of steam pressurized continuous flow reactor setup. Modified after [1].

P _T \ T	Concentrated CO ₂ (Relative Humidity > 90%)		Simulated Flue Gas
	50°C	120°C	120°C
1 bar	4, 8, 16h*	4, 8, 16h*	4, 8, 16h*
4 bar	4, 8, 16h*	4, 8, 16h*	4, 8, 16h*
7 bar	4, 8, 16h*	4, 8, 16h*	4, 8, 16h*
10 bar	0.125, 0.25, 0.5, 1, 2, 4, 8, 16, 24, 48, 120h*,♦	4, 8, 16h*	4, 8, 16h*

Table S1. Summary of the carried experiments. P_T and T stands for total pressure and reaction temperature, respectively. Results are presented and discussed in section 3.1 (*), 3.1.1(♦) and 3.2 (*).

	Concentrated CO ₂ (Relative Humidity > 90%)		Simulated Flue Gas
$P_{T(m)}$ \ T	50°C	120°C	120°C
1 bar	P_{CO_2} : 0.89 $P_{H_2O(g)}$: 0.11	P_{CO_2} : 0.36* $P_{H_2O(g)}$: 0.64*	P_{CO_2} : 0.14 $P_{H_2O(g)}$: 0.01 P_{N_2} : 0.85
4 bar	P_{CO_2} : 3.97 $P_{H_2O(g)}$: 0.028	P_{CO_2} : 3.54 $P_{H_2O(g)}$: 0.45	P_{CO_2} : 0.58 $P_{H_2O(g)}$: 0.04 P_{N_2} : 3.38
7 bar	P_{CO_2} : 6.98 $P_{H_2O(g)}$: 0.016	P_{CO_2} : 6.74 $P_{H_2O(g)}$: 0.26	P_{CO_2} : 1.01 $P_{H_2O(g)}$: 0.07 P_{N_2} : 5.91
10 bar	P_{CO_2} : 9.98 $P_{H_2O(g)}$: 0.011	P_{CO_2} : 9.81 $P_{H_2O(g)}$: 0.18	P_{CO_2} : 1.45 $P_{H_2O(g)}$: 0.1 P_{N_2} : 8.45

Table S2. Estimated CO₂ (P_{CO_2}), H₂O_(g) ($P_{H_2O(g)}$), N₂ (P_{N_2}) partial pressure of the carried experiments (Table S1). CO₂ dilution with water vapor (relative humidity > 90% and 5% for concentrated CO₂ and simulated flue gas experiments, respectively) was estimated following the saturated water vapor pressure Antoine equation and Raoult's law. $P_{T(m)}$ refers to the total pressure measured during the experiments. * shows the estimated P_{CO_2} and $P_{H_2O(g)}$ of experiments carried at 120°C and 1 bar taking into account the proportion between calculated P_{CO_2} and $P_{H_2O(g)}$ and the measured total pressure, since the carbonation system consists on a pressurized continuous flux reactor that does not allow the increase of pressure above the set-pressure.

Figure. S2. FTIR-ATR of the starting and carbonated materials at 50 and 120°C and 1 to 10 bar, maintained for 16h (RH = 100%). B: Brucite.

Figure S3. (a) XRD data showing the low intensity and broad peaks of the reaction products from treatments at 50 and 120°C and 1 to 10 bar, maintained for 16h (RH > 90%). D/H: Dypingite/Hydromagnesite phase, H: Hydromagnesite, B: Brucite. (b) XRD data baseline comparison between the starting materials and the reaction products obtained at 120°C and 10 bar. (c) XRD data baseline comparison between the reaction products obtained at 50 and 120°C, 10 bar. “Amorphous component” refers to the observed plateau between 24 to 54 2θ° and with center near 31 2θ°.

Figure S4. XRD data showing the low intensity and broad peaks of the reaction products from treatments at 50 from 1 to 10 bar, maintained for 16h (RH > 90%) and their XRD baseline comparison with treatments performed at 120°C and 10 bar. “Amorphous component” refers to the observed plateau between 24 to 54 2θ° and with center near 31 2θ°.

Figure S5. SEM images (left) of the progressive carbonation stages from the solid products of the experiments at 4 bar (RH > 90%), maintained for 16h with varying temperature (50 and 120°C). Qualitative EDS analysis (right) of single points shown on the SEM images (a) Brucite hexagonal crystals ($\leq 1\mu\text{m}$); (b) Residual brucite surrounded by a poorly crystalline material with no associated shape (50°C); (c) Hydromagnesite plates and residual brucite ($\sim 1\mu\text{m}$; 120°C).

Figure S6. (a) Raman semi-quantitative intensities of the Raman characteristic peaks of different phases (b) Raman semi-quantitative ratio intensities of the characteristic Raman peaks of Dypingite/UMC. Bru: Brucite, Nsq: nesquehonite, Dyp: dypingite, UMC: “Unknown Mg carbonate”, Avg(Dyp/UMC) shows the average Dypingite/UMC Raman ν_{sym} peak intensity ratio of the experiments carried from 7 minutes to 24 hours, E⁺ and E⁻ represent the estimated error of the Dypingite/UMC Raman ν_{sym} peak intensity ratio considering both highest and lowest ratio value within the 7 minutes to 24 hour treatments, respectively.

Figure S7. (a) XRD data showing the low intensity and broad peaks of the reaction products from treatments at 50 and 10 bar, maintained from 7 minutes to 120 hours ($RH > 90\%$). D/H: Dypingite/Hydromagnesite phase, H: Hydromagnesite, B: Brucite; XRD data baseline comparison between the reaction products from (b) 4 to 120 hour treatments and (c) 7 minutes to 2 hour treatments with reaction products obtained at 120°C and 10 bar. “Amorphous component” refers to the observed plateau between 24 to 54 $2\theta^\circ$ and with center near 31 $2\theta^\circ$.

Figure S8. Deconvoluted Raman $\nu_{1\text{sym}}$ peak comparison between the reaction products obtained from treatments at 50°C, 10 bar for (left) 2 and (right) 4 hours. Inlet shows the overlapping and differentiating features among both analyses. N: nesquehonite, D: dypingite, UMC: “Unknown Mg Carbonate”.

Figure S9. SEM image showing well developed platy dypingite crystals ($\sim 1\mu\text{m}$) as the reaction products of treatments performed at 50°C and 10 bar over 120 hours.

Thermogravimetric Analysis (TGA)

The total carbonate contents after reaction were assessed by TGA. In this work, differential thermogravimetric (dTG) data are used for representing mass changes during thermal decomposition of the solid reaction products (16h, Figure 10; 8h, Figure S11; 4h, Figure S12).

Dehydration of brucite starts at 275 °C and is completed at 420 °C, with a total mass loss of 31 wt.%, corresponding to the amount of stoichiometric water [2,3]. On the other hand, dehydration and decarbonation of hydromagnesite formed at 120 °C were observed to occur in the temperature ranges of 165-340°C and 350-550°C, respectively, in agreement with previous studies [4–6].

The initial mass losses between 25-150°C observed in the products of experiments carried out at 50°C may be interpreted as the dehydration of nesquehonite [7] and/or Dypingite-like phases [8–10] and possibly a carbonate amorphous phases with the same dehydration temperature ranges, as observed by [11]. The mass losses between 165-270 °C are associated with the dehydration of hydromagnesite and dypingite-like phases.

Then, decarbonation of the different carbonate phases occurs between 350 and 550 °C [4–11]. Remnant brucite is identified in the reaction products of both 50 and 120°C experiments.

Figure S10. Differential thermogravimetric analysis (dTGA) of mass change upon thermal decomposition of carbonation products at 50 (left) and 120 (right) °C, from 1 to 10 bar carried during 16 hours using concentrated CO₂. Solid and dotted curves represent, respectively, the differential change (mass % per degree) and the mass variation upon thermal decomposition. Thermal decomposition temperature ranges of brucite (bru), nesquehonite (Nsq), hydromagnesite (Hmg), dypingite (Dyp) and possibly “Unknown Mg-carbonate” (UMC) are indicated with double-ended arrows. The dehydration of such phases occurs from room temperature to 270 °C) and decarbonation (350-550 °C).

Figure S11. Differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products at 50 (left) and 120 (right) °C, from 1 to 10 bar carried during 8 hours using concentrated CO₂.

Figure S12. Differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products at 50 (left) and 120 (right) °C, from 1 to 10 bar carried during 4 hours using concentrated CO₂.

Estimation of CO₂ sequestered and carbonate content

CO₂ released upon thermal decomposition of carbonates was estimated after dTG peak deconvolution of the region 350-550°C, since the identified hydrated carbonates phases decarbonates within this temperature range. However, brucite dehydrates within the temperature range 275 °C - 420 °C, overlapping with the decarbonation temperature range of identified hydrated carbonates. Therefore, estimation of the CO₂ released upon thermal decomposition of the carbonate phases was carried out by subtracting the mass loss corresponding to brucite dehydration, when this latter mineral was identified.

Carbonate contents were calculated on the basis of stoichiometric compositions of nesquehonite and/or hydromagnesite, considering that those phases represent the maximum and minimum hydrated states of the reaction products. The ranges of the estimated carbonate contents at 50°C have been calculated on the basis of considering either all nesquehonite (lower value) or all hydromagnesite (higher value), as the relative proportions of the carbonate mineral phases is unknown.

Figure S13. Peak deconvolution of differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products at 50 °C and 4 bar, maintained for 16h using

concentrated CO₂ (RH > 90%). Solid and dashed curves represent the differential mass change (% / deg) and cumulative peak fitting curve, respectively. Thermal decomposition temperature ranges of Bru: brucite (filled area), nesquehonite (Nsq), hydromagnesite (Hmg), dypingite (Dyp) and possibly “Unknown Mg-carbonate” (UMC) are indicated with double-ended arrows. The dehydration of such phases occurs from room temperature to 270 °C) and decarbonation (350-550 °C).

Figure S14. Differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products obtained at 50°C, 10 bar during 7 minutes to 120 hours using concentrated CO₂. Thermal decomposition temperature ranges of brucite (bru), nesquehonite

(Nsq), hydromagnesite (Hmg), dypingite (Dyp) and possibly “Unknown Mg-carbonate” (UMC) are indicated with double-ended arrows. The dehydration of such phases occurs from room temperature to 270 °C) and decarbonation (350-550 °C).

Figure S15. FWHM vs peak position of (a) Raman $\nu_{1\text{sym}}$ peaks and (b) two more intense XRD peaks of the carbonated products reacted at 120°C, 10 bar from 4 to 16 hours using simulated flue gas. H: Hydromagnesite. The FWHM and peak position of reference minerals were calculated from Lafuente, et al., 2015 [12].

Figure S16. Differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products at 120°C, from 1 to 10 bar carried during 16 hours using simulated flue gas. Thermal decomposition temperature ranges of brucite (bru) and hydromagnesite (Hmg) are indicated with double-ended arrows.

Figure S17. Differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products at 120°C, from 1 to 10 bar carried during 8 hours using simulated flue gas.

Figure S18. Differential thermogravimetric analysis (dTG) of mass change upon thermal decomposition of carbonation products at 120°C, from 1 to 10 bar carried during 4 hours using simulated flue gas.

Figure 19. CO₂:H₂O (wt.%) ratios as estimated with TGA of the solid product of reaction at 120 °C, 1 - 10 bar from 4 to 16 hours using simulated flue gas. Error bars were estimated on the average of three different experiments.

Figure S20. CO₂ sequestered (gCO₂/100g sample) normalized by the partial pressure (bar; Table S1) of experiments carried using concentrated CO₂ (50, 120°C) and simulated flue gas (120°C) from 1 to 10 bar at 4, 8 and 16 hours. Error bars estimate the average between three analogous experiments

Figure S21. (a) CO₂ sequestered (gCO₂/100g sample) of experiments carried using concentrated CO₂ at 50°C, from 1 to 10 bar from 15 minutes to 120 hours. (b) calculated carbonate content based on the sequestered CO₂. Error bars represent the estimated carbonate content based on the different carbonate mineralogy.

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