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Farhang, F.; Oliver, T. K.; Rayson, M.; Brent, G.; Stockenhuber, M. & Kennedy, E.
“Experimental study on the precipitation of magnesite from thermally activated
serpentine for CO₂ sequestration” Published in the *Chemical Engineering Journal*, Vol.
303, pp. 439-449, (2016).

Available from: <http://dx.doi.org/10.1016/j.cej.2016.06.008>

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Experimental study on the precipitation of magnesite from thermally activated serpentine for CO₂ sequestration

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Abstract

Mineral carbonation has the potential to store billions of tonnes of CO₂ safely and permanently. Enhancement of the kinetics of the formation of magnesium carbonate from magnesium-bearing silicate minerals has been the subject of numerous research studies. However, significant progress is yet to be achieved. This is, in part, due to a lack of understanding of the mechanism of the formation of magnesite in the presence of additives and under mineral carbonation conditions. In this work, an in-depth study was performed to investigate the precipitation of magnesium carbonate during single step high pressure, high temperature carbonation of thermally activated serpentine in an aqueous bicarbonate solution. Slurry samples were obtained throughout the duration of the carbonation experiments, enabling analysis of both the aqueous and solid compositions over time, providing insight into the reaction mechanism. Additionally, the effect of operating temperature on the formation of various magnesium carbonate species was examined. TGA-MS, in combination with XRD and SEM, confirmed the formation of hydromagnesite in the absence of carbon dioxide (CO₂) during the reactor heat up period, owing to a reaction with the sodium bicarbonate (NaHCO₃) carrier solution. Hydromagnesite was transformed to magnesite over time, with the rate of this phase transformation highly dependent on the reaction temperature. At 185 °C all hydromagnesite converted to magnesite in a few minutes whereas at 120 °C even after 90 minutes hydromagnesite remained in the reactor.

PHREEQC thermodynamic software was used to assess the observed formation of carbonate species. The model prediction was consistent with the experimental results obtained in this work.

Keywords: Mineral carbonation, CO₂ storage, magnesite, hydromagnesite, precipitation, serpentine

Graphical Abstract

Highlights

- Solid products of the CO₂ mineralization were characterised as a function of time.
- A sampling technique was applied to track changes in the carbonation products.
- The formation of hydromagnesite prior to magnesite was shown experimentally.
- Transformation of hydromagnesite to magnesite strongly depends on reaction T and P.

1. Introduction

With the atmospheric concentration of carbon dioxide (CO₂) steadily increasing, there is a need for an alternative strategy for dealing with carbon emissions arising from energy production [1-3]. One possible solution to capture and store CO₂ is the reaction of ultramafic minerals such as serpentine with CO₂ (Mineral carbonation). This process results in the formation of a thermodynamically stable form of magnesium carbonate [2, 4-6]. However, with the current process the typical yield in the range of 40-50% in 1 hour for < 75 micron particles [7, 8] is still far below industry expectations [9]. Mineral

carbonation researchers have been striving for years to improve the kinetics of the reaction and increase the overall conversion (i.e. extent of reaction) of mineral into carbonate [10-12]. The complexity of the magnesium (Mg)-carbonate system, with numerous forms of hydrated and basic carbonates, has hindered understanding the mechanism for the formation of magnesium carbonates and insight into the reaction pathways [13]. The pathways leading to the formation of these magnesium carbonate species is essential to improve the mineral carbonation process.

Magnesium carbonate exists in various forms including hydrated carbonates. Magnesium has a strong tendency to form a series of metastable hydrous and hydroxy carbonates. These metastable hydrous carbonates include hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, or $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), artinite ($\text{Mg}_2\text{CO}_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), and lansfordite ($\text{MgCO}_3 \cdot 5\text{H}_2\text{O}$) [14, 15]. Depending on the temperature, partial pressure of CO_2 and pH, any form of magnesium carbonate can form in the $\text{MgO}-\text{CO}_2-\text{H}_2\text{O}$ system [16]. Amongst all magnesium carbonates, magnesite (MgCO_3) is the most thermodynamically stable and efficient (with respect to its 1:1 magnesium to CO_2 ratio) carbon storage medium [17]. However, the formation of magnesite at ambient temperature is virtually impossible. In an aqueous solution at room temperature through to 328 K and partial pressure of CO_2 close to ambient pressure or below, nesquehonite is precipitated [18, 19]. With a further increase of the reaction temperature (333–368 K) and pH, hydromagnesite becomes the preferred mineral [18]. Highly saline conditions offer the most favourable circumstances for magnesite crystallization. The transformation of nesquehonite to hydromagnesite and hydromagnesite to magnesite in brine has been reported previously [20-23]. In an effort to understand if the highly hydrated character of Mg^{2+} ion in aqueous solution is responsible for the difficulty in precipitating magnesite, Sayles and Fyfe [24] studied the kinetics of the crystallization of magnesite from hydromagnesite. Their results demonstrated an inhibition of magnesite crystallization by an aqueous species of Mg (possibly a hydrolysis product of Mg^{2+}) and strongly positive catalytic

effect due to ionic strength and CO₂ partial pressure (P_{CO2}). They hypothesized that hypersaline conditions may accelerate rates in two ways. The effect of ionic strength at relatively low concentrations may be due to changes in the nature of the solution-crystal interfaces. As ionic strength increases, the thickness of the double layer decreases, thereby facilitating access of reactants and removal of soluble products to and from reaction sites. Moreover, saline environments may enhance reaction rates through decreasing the activity of water and thus facilitating the dehydration of the Mg²⁺ ion. Zhang [21] reported transformation times between 2 h at 200 °C in a solution saturated with sodium chloride (NaCl), and over 100 days at 110 °C and lower salinity in a closed system. They proposed two mechanisms for the transformation of hydromagnesite to magnesite in brine. In brines with low magnesium concentration, hydromagnesite dehydration with concomitant formation of brucite and magnesite is favoured. In brines with high magnesium concentration a hydromagnesite dissolution–magnesite precipitation process is favoured.

Wolf, Chizmeshya, Diefenbacher and McKelvy [25] reported direct formation of magnesite without observable intermediate formation at 150 °C and 15 MPa CO₂ in the presence of NaCl (1M) and NaHCO₃ (0.64 M). Hanchen, Prigiobbe, Baciocchi and Mazzotti [26] employed FTIR and Raman spectroscopy to study the precipitation of different forms of magnesium carbonate at various temperatures and CO₂ pressures. They also observed direct formation of magnesite at 120 °C and P_{CO2} of 100 bar. At elevated levels of supersaturation, the co-precipitation of magnesite and hydromagnesite was observed, and the hydromagnesite transformed within a few hours into magnesite.

The aim of the current work is to understand the mechanism of the formation/precipitation of magnesite in the well-known single-step aqueous carbonation process developed by the ARC/NETL group [4]. This work provides deep insight into the reaction mechanism by characterizing the reaction products over the duration of the reaction.

2. Experimental

2.1. Material

The magnesium source material used for these experiments was lizardite serpentine from the Great Serpentine Belt, NSW, Australia. Powder XRD confirmed lizardite $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ as the primary serpentine phase (≈ 95 %wt.) rather than antigorite or chrysotile, with traces of clinochlore $\text{Mg}_{3.75}\text{Fe}^{2+}_{1.25}\text{Si}_3\text{Al}_2\text{O}_{10}(\text{OH})_8$ (≈ 4 %wt.) and magnetite Fe_3O_4 (≈ 1 %wt.) also detected. The elemental composition of the material was determined by X-ray fluorescence (XRF). The sample contains 35.9% magnesium oxide (MgO), 41.04% silicon dioxide (SiO_2) and 2.4% iron (II) oxide (FeO), 2.4% iron (III) oxide (Fe_2O_3) and 2.21% aluminium oxide (Al_2O_3). The loss on ignition (LOI) in Ar was 12.23% which is slightly less than the water content derived from the theoretical formula $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ namely 13.04%. Considering other impurities including magnetite and clinochlore given by chemical analysis, the expected weight loss is in agreement with the observed experimental value. The material was crushed, ground, magnetically separated, wet sieved (using a 75 μm sieve) and oven dried at 110 $^\circ\text{C}$. Mineral particles used in experimentation were smaller than 75 μm in diameter with a d_{80} of 45 μm (80% of particles smaller than 45 μm) measured by laser diffraction method (Malvern, Mastersizer 2000). The sieved and dried material was heat activated in an electrically heated rotary kiln (RSR 80/500/11, Nabertherm, Germany) at 630 $^\circ\text{C}$, for 4 h.

The CO_2 and N_2 gas used in this work was provided by Coregas, Australia and sodium hydrogen carbonate (NaHCO_3) by Fisher Scientific UK (purity 99.9%).

2.2. Equipment

The experimental setup consisted of a stirred high-pressure batch reactor equipped with a sampling unit. The schematic diagram of the experimental apparatus used to perform the experiments is shown in Figure 1. The reactor consisted of a stainless steel vessel with a pressure rating of 200 bar having an

80 mm inner diameter and a 300 mL volume. The reactor included a magnetically coupled stirrer with down-pumping six bladed turbine impeller. The reactor was also equipped with a heating jacket, pressure gauge, thermocouple, gas release valve, and rupture disc.

A pressure booster pump (MAXIMATOR GmbH) delivered high pressure CO₂ to the reactor, enabling the reactor to be pressurized to a maximum pressure of 160 barg.

A sample collection vessel was installed on the reactor to allow for the withdrawal of slurry samples at elevated temperatures and pressures during the reaction. This vessel had a volume of 10 mL and was equipped with isolation, vent and drain valves. The isolation valve was used to seal the vessel once the sample was transferred. The vent valve was used to release any residual pressure in the line between the sample valve and the sample vessel. Slurry samples were finally removed by opening the drain valve. To remove any residue from the previous sampling, the sampling vessel and lines were washed 3 times by distilled deionized water between sampling.

Figure 1 Schematic diagram of the experimental set-up

2.3. Procedure

2.3.1. Carbonation reaction: The process studied in this work is similar to that of the single stage process developed by ARC/NETL [4] with the following variations: In the ARC process the reactor is heated under 10 bar CO₂ whereas in this work the reactor is heated under atmospheric pressure after being purged with CO₂ gas. In this work the use of NaCl in the buffer solution is avoided as chlorides have the potential to induce unpredictable and catastrophic stress corrosion cracking of austenitic stainless steels under high temperature and pressure regimes [27].

A mixture of 26.0 g of heat treated serpentine, 7.0 g NaHCO₃ and 140 ml of distilled water was freshly prepared and charged into the reactor. Once the slurry was loaded into the cell, the lid of the reactor was lowered onto the cell and tightened to ensure a proper seal before pressurizing. The stirrer was operated at 500 rpm to ensure the slurry remained suspended to promote transfer of CO₂ into the aqueous phase. The remaining volume of the reactor and all the loading lines were purged with CO₂ by increasing the pressure to 5 barg and then venting the reactor completely. To avoid air contamination in the system, this cycle was repeated three times. After purging, the reactor was heated to the desired temperature. Experiments were performed at 3 different temperatures; 120, 150 and 185 °C, and named CA1, CA2 and CA3, respectively. When the temperature stabilized, the reactor was pressurized to 140 barg CO₂ using the booster pump. The reactor was then isolated from the CO₂ storage cylinder by closing the gas inlet valve. The pressure was maintained at 140 barg during the reaction.

The time when the pressure in the reactor reached 140 barg was denoted as time zero (t_0). The reaction time was 90 min, after which the reactor was cooled down to 45 °C (taking between 7 to 9 min to reach 45 °C) and then depressurized. During the reaction samples were taken at t_0 , t_5 , t_{15} , t_{30} , t_{60} with the subscripts denoting elapsed time in minutes after t_0 .

2.3.2. Heat up: The aim of this experiment was to study the changes in the slurry during heating and before introducing CO₂ to the reactor. For this experiment slurry was prepared in the same manner as

that employed for the carbonation experiments. The reactor was purged and pressurized to 15 barg using N₂ to provide a sufficient driving force for sample removal. Then the slurry was heated to 150 °C with samples taken at 120, 140 and 150 °C during heating.

2.3.3. Sample analysis and characterization: Solid and liquid phases of each slurry sample were separated using a laboratory centrifuge (SIGMA 6-15). The supernatant was decanted, filtered, diluted and analyzed by ICP-OES (Varian 715-ES). The solid was washed 3 times with distilled deionized water to remove any NaHCO₃ residue and then dried in a vacuum oven at 70 °C for 48 h. After drying, the sample transformed into a relatively hard, thick layered solid that required grinding using a small mortar and pestle for TGA sample preparation. The thermal behaviour of powder samples was analyzed using a TGA (Mettler Toledo Star e System –TGA/DSC1) coupled to a mass spectrometer (ThermostarTM, GSD 301 T3). The samples were heated with the heating rate of 5°C/min in an open alumina crucible in a flowing Ar atmosphere (flowrate of 20 ml/min). The gas exiting the TGA cell was then analyzed by the mass spectrometer. The surface morphology of the precipitated solids was examined using a Scanning Electron Microscope SEM (Zeiss Sigma VP FESEM). Prior to any SEM imaging, the powder samples were routinely coated by a thin layer of gold at 10 mA. The samples were imaged at 15 kV and 10-15 mm working distance.

XRD patterns were recorded by Philips X'Pert MPD using graphite monochromated Cu-K_α radiation operating at 40 kV and 40 mA. Scans were performed at 0.013° (2θ) over the 2θ range 5-90° for 3h.

3. Thermodynamic modelling

PHREEQC thermodynamic software [28] was used to assess the observed formation of hydromagnesite during the reactor heat up period. The assessment included modelling the predicted aqueous speciation through the process of reactor heat up, and potential solid phase formation during this period using the “WATEQ4F” thermodynamic database. In order to model the dissolution of the thermally activated serpentine, proxy mineral data was used equivalent to a generic serpentine with the

solubility product adjusted to ensure the observed degree of magnesium extraction during reactor heat up was realized in the model.

For aqueous calculations PHREEQC uses ion-association and Debye Hückel expressions including the use of an ionic-strength term (in the Debye Hückel expressions) to account for the non-ideality of aqueous solutions. These ionic-strength terms have been fitted for the major ions using chloride mean-salt activity-coefficient data [29]. The wateq4f.dat database used in modelling within PHREEQC is consistent with the aqueous model of WATEQ4F Ball and Nordstrom [30]. Equilibrium between a multicomponent gas phase and the aqueous phase is modelled with heterogeneous mass-action equations, and for the fixed-pressure gas phase, an equation for total pressure. PHREEQC assumes all gas components to behave ideally with one gas phase allowed to exist in equilibrium with the aqueous phase, but this gas phase may contain multiple components.

4. Results

4.1. Thermal and mass spectroscopy analysis

Figure 2 shows the TGA-DTGA-MS patterns of the solid samples that were obtained from slurry samples at various times during the carbonation reaction at 150 °C and 140 barg (CA2). The thermal behaviour of the carbonated products differs depending on the time of sampling. The TGA patterns of samples CA2-t₀ to CA2-t₃₀ shows that thermal decomposition occurs at six temperatures namely 235, 387, 453, 586, 700 and 779 °C (see Figure 2 a-d). However, samples CA2-t₆₀ and CA2-t₉₀ decomposed at four temperatures these being 507, 586, 700 and 779 °C (see Figure 2 e and f). According to the MS spectrum, for the first three temperatures the mass loss was due to the release of both water and CO₂, whereas, the last three mass loss events were only due to the loss of water. The intensity of the first two peaks, at 235 and 387 °C, increased for the first 15 minutes of the reaction, and subsequently decreased, whereas the intensity of the third peak, initially at 453 °C, increased progressively whilst

also shifting to higher temperatures. The three different CO₂ peaks present in the first 30 minutes of the reaction indicate the presence of different carbonated species in the solid products. As mentioned previously, magnesium has a strong tendency to form any number of a series of metastable hydrous carbonates. Among different hydrous carbonates, the decomposition behaviour of hydromagnesite, which is a low temperature hydrothermally formed mineral, is similar to a number of the samples analyzed in this work. Hydromagnesite has been reported to decompose in five steps; two dehydration steps at lower temperature ranges (25-121 °C and 121-181 °C), one dehydroxylation at 181-274 °C, one de-carbonation at 274-394 °C and one oxygen loss at 394-508 °C [14]. Although the oxygen spectra are not shown in Figure 2 oxygen peaks ($m/z = 32$ amu) were also observed over this temperature range. Comparison between the TGA mass loss traces of hydromagnesite [14, 31] and those of samples CA2-t₀ to CA2-t₃₀ showed that the first two mass loss peaks are reasonably similar to the dehydroxylation and de-carbonation of hydromagnesite. However, the third peak at 453 °C that shifts to higher temperature over time is related to the decomposition of magnesite [32]. These results show that under carbonation conditions both hydromagnesite and magnesite are formed in the reactor. This finding was subsequently confirmed by XRD and SEM analysis.

It is also informative to compare the mass spectra ion current signal of CO₂ of all carbonated samples. Figure 3 clearly shows that in the first 15 minutes of the reaction CA2 (conducted at 150 °C) the intensity of the CO₂ peaks at 387 °C and 453 °C increased, and the peak position shifted to higher temperatures. This demonstrates that both hydromagnesite and magnesite were formed at the initial stage of the reaction, however, hydromagnesite appears to be the dominant phase compared to magnesite. At t₃₀ the intensity of the peak that corresponds to hydromagnesite has decreased and magnesite increased significantly. After one hour at 150 °C the hydromagnesite peak completely

disappeared and the magnesite peak grew to its maximum height. An insignificant increase in magnesite yield was observed upon increasing the reaction time from 60 to 90 min.

Figure 2 TGA-DTGA-MS graphs of solid samples taken throughout the carbonation reaction CA2 at 150 °C and 140 barg (a) t_0 , (b) t_5 , (c) t_{15} , (d) t_{30} , (e) t_{60} and (f) t_{90}

Figure 3 MS analysis of the CO₂ released from carbonated samples of test CA2. Comparison of the CO₂ spectra shows simultaneous formation of magnesite and hydromagnesite at the beginning of the reaction. After 60 min the first CO₂ peak had disappeared indicating that all hydromagnesite transformed into magnesite.

4.2. Microscopic analysis

SEM analysis assisted in elucidating the general morphology and structural changes of the precipitated solids over the duration of the reaction. To investigate the changes in the structure of the solid material under carbonation conditions, six solid samples collected throughout the duration of the reaction CA2 and were then imaged. The solids exhibited different morphologies. Figure 4 shows SEM micrographs of the samples taken during the reaction. At the beginning of the reaction, the morphology of the precipitates can be described as thin plates (Figure 4 a-b). Hydromagnesite crystals typically display sheet/plate morphology [33] and as the reaction progressed more plate-like crystals were observed (Figure 4 c). Rhombohedral crystals of magnesite were observed, mostly at the end of the reaction period. However, at various extent of reaction, rhombuses of magnesite were found next to or on the surface of hydromagnesite, indicating gradual phase transformation of hydromagnesite to magnesite. After one hour of reaction, hydromagnesite was no longer detected in the carbonated products and only magnesite was observed (Figure 4 e-f). The SEM images clearly show the structural evolution of the

solid carbonated products as a function of reaction time. SEM also confirmed simultaneous precipitation of magnesite and hydromagnesite at the early stages of the reaction. At the initial stages of the reaction, the majority of the precipitates were hydromagnesite rather than magnesite. This implies that although magnesite is the more thermodynamically favoured species, the kinetics of hydromagnesite crystallization are faster than for magnesite. As the reaction proceeds, hydromagnesite disappeared and only magnesite was found in the sample indicating that over time hydromagnesite transformed to magnesite under reaction conditions. This is also in agreement with the previously reported Raman spectroscopy study by Hanchen, Prigiobbe, Baciocchi and Mazzotti [26].

Figure 4 SEM micrographs (secondary electron (SE) imaging) of synthetic magnesium carbonates formed at 140 barg CO_2 and 150 °C. Images of the precipitated solids show structural changes over time under carbonation reaction conditions.

4.3. X-Ray Diffraction Patterns

XRD diffraction patterns for precipitated solids are shown in Figure 5. Phase identification of the carbonated samples confirmed that the solids are comprised of hydromagnesite and magnesite as well

as parent minerals (i.e. lizardite, clinocllore, forsterite, magnetite and hematite). In Figure 5 arrows show the main peaks of hydromagnesite at $15.2^{\circ}2\theta$ ($d = 5.80403 \text{ \AA}$) and magnesite at $32.5^{\circ}2\theta$ ($d = 2.7515 \text{ \AA}$). The intensity of a diffraction peak is generally proportional to the concentration of the corresponding chemical compound or phase [34]. Therefore, by comparing the intensity of the magnesite peak over the period of the reaction it is evident that the concentration of magnesite increased significantly. The concentration of hydromagnesite was reduced after 15 minutes, and after 60 minutes of the reaction the peaks of hydromagnesite had disappeared completely. These results are in agreement with the TGA-MS and SEM results reported in previous sections.

Figure 5 X-Ray diffraction patterns of solid carbonated samples taken at 150°C and 140 barg CO_2 . HM= hydromagnesite, M=magnesite

4.4. Conversion calculations

The fraction of magnesium extracted from the heat activated solid mineral, either dissolved in aqueous phase or precipitated as any form of magnesium carbonates, were calculated from TGA-MS and ICP-OES data. Previous XRF analysis showed that raw material used in this study contains 35.9% wt. MgO which corresponds to 24 %wt. magnesium in the heat treated material considering that almost 10% of mass is lost after heat activation (dehydroxylation). As discussed in Sec 4.1 for the solid samples

containing multiple carbonate phases, CO₂ spectra of each sample were examined to distinguish between the two solid carbonate phases, hydromagnesite and magnesite. The mass fraction of each phase was calculated from the mass loss due to the release of CO₂. The chemical formulas of hydromagnesite and magnesite (i.e. 4MgCO₃·Mg(OH)₂·4H₂O and MgCO₃, respectively) were used to calculate the fraction of magnesium present in each phase. It was possible to relate the mass loss for a specific decomposition event to mass percent of that phase in the total solids, based on the stoichiometry of these phases. For example based on the TGA curve of t₁₅ the mass loss due to the decarbonation of hydromagnesite and magnesite was 3.78 and 2.86 %, respectively. These quantities correspond to 10.45 %wt. hydromagnesite and 5.64 %wt. magnesite in the solid sample. The total amount of magnesium extracted from the parent mineral was obtained by adding the magnesium contained in the reaction liquor (determined using ICP) to the amount of magnesium in carbonated phases, determined by TGA-MS analysis. Figure 6 shows the percentage of magnesium extracted from the heat activated mineral in test CA2. As seen in this figure, the maximum percentage of magnesium extracted and precipitated as magnesite after 60 minutes was 40% and this figure increased by only 2% after 90 minutes. This implies that after the expiration of a certain period of time, as yet unidentified factors act to inhibit the reaction. Currently these factors are not well-known, however, the formation of amorphous silica-rich passivation layers on the surface of Mg-bearing silicates during carbonation is recognized as a possible factor inhibiting the reaction [35].

Figure 6 The amount of magnesium dissolved in supernatant or precipitated as any form of magnesium carbonate. Experiments were performed at 150 °C and 140 barg CO₂

4.5. The effect of temperature on the precipitation of magnesium carbonate

Two reactions similar to CA2 were performed at 120 and 185 °C to investigate the effect of operating temperature on the precipitation of different magnesium carbonate phases. Figure 7 and Figure 8 summarize the results. Simultaneous precipitation of hydromagnesite and magnesite at the beginning of both reactions is shown in these figures. It was found that the rate of formation of these phases largely depends on temperature. Figure 7 indicates that at the beginning of the reaction at 120 °C, the hydromagnesite yield was as high as 10% and remained more or less the same until the end of the reaction. On the other hand the rate of formation of magnesite is relatively slow, unlike that observed at higher temperatures. The final magnesite yield at 120 °C is 20%, which is significantly lower than the 42% yield obtained at 150 °C and 185 °C. It appears that a reaction time of 90 min was too short to transform all hydromagnesite produced to magnesite. As shown in Figure 8 at high temperatures (185 °C) hydromagnesite converts to magnesite rapidly as hydromagnesite was only present in the system for less than 15 min. At this temperature, magnesite formation started immediately after pressurising the reactor and grew throughout the reaction. The magnesite yield in the initial stage of the reaction at 185 °C is considerably higher (7%) than the magnesite yield at 120 °C (1.9%). The magnesium

concentration in supernatant for the experiment performed at 120 °C remained almost constant around 7%, whereas for the sample formed at 185 °C the concentration of magnesium in supernatant dropped essentially to 0 after 15 minutes. The final magnesite yield at t_{90} is 42% which is identical to the experiment performed at 150 °C. It is possible that blockage of surface reaction sites by a product of the reaction or by precipitation of silica inhibits complete reaction.

Figure 7 (a) the amount of magnesium dissolved in supernatant or precipitated as any form of magnesium carbonate (b) CO₂ MS spectra. Experiment was performed at 120 °C

Figure 8 (a) the amount of magnesium dissolved in supernatant or precipitated as any form of magnesium carbonate (b) CO₂ MS spectra. Experiment was performed at 185 °C

4.6. The formation of hydromagnesite during heat-up

The effect of heating on the precipitation of magnesium carbonate hydrates was investigated before introducing high pressure CO₂ to the system. In this experiment, a slurry of 15%wt. serpentine/water and 0.58 M NaHCO₃ was loaded into the reactor and the reactor and then purged three consecutive

times with N_2 . This process involved the flow of N_2 through the reactor head space followed by a brief stoppage prior to the next period of purge. Following purging, the reactor was pressurized to 15 barg with N_2 . The total duration of purging was less than 5 min and during this time the stirrer was continuously operated at 500 rpm.

In order to track the formation of hydromagnesite in the reactor, samples were taken during the heat up process at 120, 140 and 150 °C. These temperatures corresponded to sampling times of 17, 19 and 30 min respectively from commencement of heating (after the reactor had been charged to 15 barg under N_2). Samples were routinely separated to solid and liquid parts using the centrifuge as previously described. The liquid samples were analyzed by ICP-OES to determine the amount of magnesium extracted. The solid was washed, dried and then analyzed by TGA-MS. The results are summarized in Figure 9.

Figure 9 (a) the amount of magnesium dissolved in supernatant or precipitated as hydromagnesite (b) CO_2 MS spectra.

The results show that the formation of hydromagnesite commences during reactor heat up prior to the introduction of CO_2 to the system. During this period, carbonate species formed through the dissolution of $NaHCO_3$ react with magnesium ions produced from partial dissolution of the activated serpentine leading to the formation of hydromagnesite. The intensity of the CO_2 peak that corresponds to hydromagnesite was found to increase as the reactor temperature was raised from 120 to 150 °C. This

feature of the results can be explained by the fact that crystal growth of hydromagnesite is preferred at higher temperature [36]. Both flaky [37] and plate-like [38] shapes of hydromagnesite were observed by SEM as shown in Figure 10.

(a) Scale= 1 μm Mag= 15 kX

(b) Scale= 1 μm Mag= 25 kX

Figure 10 SEM images of solid samples heated to 150 °C in the presence of aqueous NaHCO_3 and N_2 .

5. Discussion

The formation of hydromagnesite prior to magnesite is undesirable for the mineral carbonation process. Magnesite is the preferred form of magnesium carbonate product due to it having the highest sequestration efficiency (magnesium to carbon stoichiometric ratio of 1), lowest process water requirement (no structural water), and increased chemical stability for long-term storage. The formation of hydromagnesite at elevated temperature in the system containing an aqueous mixture of activated serpentine and NaHCO_3 has been demonstrated in this work. Moreover, hydromagnesite was shown to form during the reactor heat up period in the absence of added CO_2 .

The formation of hydromagnesite prior to pressurizing the reactor with CO_2 , can be described as the reaction of NaHCO_3 and the thermally activated serpentine mineral as shown by eq. 1.

In eq. 1 reactants and products listed in molecular form and denoted as solids may exist as aqueous species.

Hydromagnesite dissolution and precipitation in aqueous solution can be described by eq. 2.

The solubility product for hydromagnesite is defined as the equilibrium constant of eq. 2, and this is shown in eq. 3.

$$K_{\text{sp-HM}} = [\text{Mg}^{2+}]^5 \cdot [\text{CO}_3^{2-}]^4 \cdot [\text{OH}^-]^2 \quad (\text{eq. 3})$$

where bracketed terms denote species activities at equilibrium.

The degree of mineral saturation (S) for solid phases is given by eq. 4.

$$S = \frac{\text{IAP}}{K_{\text{sp}}} \quad (\text{eq. 4})$$

where IAP is the ion activity product, and K_{sp} is the solubility product for the precipitation reaction as previously defined (for hydromagnesite, see eq. 3). The IAP for hydromagnesite can be expressed by eq. 5.

$$\text{IAP}_{\text{HM}} = [\text{Mg}^{2+}]^5 \cdot [\text{CO}_3^{2-}]^4 \cdot [\text{OH}^-]^2 \quad (\text{eq. 5})$$

where bracketed terms denote actual species activities.

Precipitation occurs away from the equilibrium as a consequence of kinetic barriers to precipitation. Therefore values of S in excess of unity realized in solution imply supersaturation and the existence of a kinetic barrier to precipitation. Increased supersaturation, in effect, represents an increase in the driving force for nucleation of the solid phase. The base ten log of the mineral saturation is commonly known as the Langelier Saturation Index (SI).

A limited degree of dissolution of the activated serpentine is achieved during reactor heat up, consuming bicarbonate ions, and increasing the Mg^{2+} and CO_3^{2-} concentrations in accordance with eq. 3. In the absence of CO_2 , consumption of H^+ ions (from bicarbonate) results in a corresponding increase in solution pH. From a thermodynamic point of view, the absence of added CO_2 and greater OH^- concentration favours hydromagnesite precipitation. In this process the initial high pH aids in nucleating hydromagnesite by increasing mineral supersaturation for this phase. As a result the induction time of carbonate nuclei was reduced and the crystal growth was promoted.

Table 1 summarizes results of thermodynamic calculations to determine the saturation indices of three magnesium carbonate species; Magnesite, Hydromagnesite and Nesquehonite, in the supernatant liquid, for various reactor heat up scenarios. The saturation index calculation requires knowledge of the concentration of CO_3^{2-} and pH of the solution. As these were not measured experimentally, an initial simulation was performed to compute these values. Dissolution of the activated serpentine increases the alkalinity of the solution via the accumulation of carbonate and bicarbonate ions. The extent of alkalinity derived from the dissolving mineral is related to the total amount of magnesium extracted in the proportion of 2 to 1 (in accordance with Equation 1). The formation of the solid carbonate (in this instance, hydromagnesite) reduces the amount of magnesium and the carbonate alkalinity for the solution by an amount defined by the amount of solid carbonate formed. The tendency of the solution remaining (i.e. supernatant) for further precipitation can then be estimated knowing the magnesium

source (magnesium silicate), the total amount of magnesium (in solid and liquid form), and the amount of magnesium in the form of hydromagnesite.

In each modelling case, the reactor head space at a fixed pressure of specified composition (either N₂ or CO₂) is equilibrated with the solution comprised of NaHCO₃ and a known amount of the surrogate mineral. The amount of mineral used is that amount defined by the total amount of magnesium (in solid and aqueous form) measured in the system. Hydromagnesite precipitation was achieved by increasing the target SI for the pure solid phase (hydromagnesite) in the aqueous phase. The solution remaining, following the precipitation of the fixed amount of hydromagnesite, is then characterized in terms of its pH and dissolved inorganic carbon (DIC). The remaining solution (supernatant) is then subjected to various reactor heat up scenarios to demonstrate the effect of solution state and the likelihood of precipitation of solid carbonate phases. The DIC content and calculated pH derived from the dissolution of the activated mineral are listed in Table 1. Also listed is the thermodynamic tendency for precipitation of selected magnesium carbonate phases for the scenarios considered as given by saturation indices (SI).

Case 1 is representative of the heat up process used in this study to examine the formation of hydromagnesite in the absence of added CO₂, and cases 2 and 3 the increased pressurization of the reactor with CO₂ using the equivalent level of magnesium extraction for case 1. In order to demonstrate the effect of reactor pressurization at lower temperature, calculations at a temperature of 25 °C have also been included. For these calculations, magnesium extraction data for 120 °C has been used.

Table 1 Saturation indices of principal magnesium carbonate phases in supernatant solutions under varying reactor heat up scenarios in the presence and absence of CO₂ (SI) (molal basis)

Case description	Temp. (°C)	Conc. of dissolved Mg. (m)	Conc. of HM precipitate (m)	Calculated DIC concentration of supernatant (m)	Calculated pH of supernatant	Calculated SI nesquehonite	Calculated SI hydromagnesi te	Calculated SI magnesite
Case 1: Prepared solution under 15 barg N ₂	25	4.019×10 ⁻²	2.130×10 ⁻²	0.4537	9.068	+0.58	+3.76	+3.01
	120	4.019×10 ⁻²	2.130×10 ⁻²	0.4540	7.757	+0.35	+5.36	+2.85
	140	5.220×10 ⁻²	2.876×10 ⁻²	0.4193	7.824	+0.28	+5.91	+2.79
	150	5.581×10 ⁻²	3.172×10 ⁻²	0.4011	7.857	+0.08	+5.36	+2.59
Case 2: Prepared solution under 15 barg CO ₂	25	4.019×10 ⁻²	2.130×10 ⁻²	0.9637	6.332	-1.66	-10.46	+0.78
	120	4.019×10 ⁻²	2.130×10 ⁻²	0.6761	6.920	-0.36	+0.074	+2.14
	140	5.220×10 ⁻²	2.876×10 ⁻²	0.6183	7.097	-0.31	+1.96	+2.20
	150	5.581×10 ⁻²	3.172×10 ⁻²	0.5792	7.197	-0.44	+1.83	+2.08
Case 3: Prepared solution under 140 barg CO ₂	25	4.019×10 ⁻²	2.130×10 ⁻²	4.789	5.287	-2.80	-16.90	-0.26
	120	4.019×10 ⁻²	2.130×10 ⁻²	1.742	5.984	-1.30	-4.85	+1.23
	140	5.220×10 ⁻²	2.876×10 ⁻²	1.641	6.149	-1.25	-3.70	+1.29
	150	5.581×10 ⁻²	3.172×10 ⁻²	1.600	6.229	-1.38	-3.95	+1.16

These results indicate that during reactor heat up under the experimental conditions (case 1) all three principal solid magnesium carbonate phases (nesquehonite, hydromagnesite, and magnesite) are supersaturated but that hydromagnesite formation is most favoured. This is consistent with the experimental results shown in Figure 9 which shows hydromagnesite precipitated, and is consistent with previous studies which demonstrated a preference for hydromagnesite at low temperatures (<150 °C) and high levels of supersaturation [26]. The high reactivity of the activated serpentinite enables a high degree of supersaturation with respect to hydromagnesite during the heat up period. High levels of supersaturation favour hydromagnesite [26].

The results of Case 3 show that upon pressurizing the reactor with 140 bar CO₂ the system is no longer saturated with respect to hydromagnesite, while magnesite remains supersaturated. This is consistent with the experimental results that showed that the concentration of hydromagnesite decreased after pressurising the reactor with CO₂. This engenders hydromagnesite dissolution and for the liberated magnesium to precipitate as magnesite (see Figure 6 to 8). The formation of magnesium carbonates is complicated and path dependent and SI does not necessarily dictate which phase is formed ⁵. Nevertheless it is clear from the results presented in Table 1 that reactor heat up under increasing CO₂ pressure progressively favours the precipitation of magnesite rather than hydromagnesite. Pressurization at lower temperature is also advantageous to magnesite precipitation. Therefore a possible strategy to limit the early formation of hydromagnesite in preference to magnesite would be to pressurize the reactor (to near operating pressure) at lower temperature under a CO₂ atmosphere. However charging the reactor under pressurized CO₂ would also result in a greater extent of dissolution of the reactive amorphous phase increasing SIs.

Transformation of hydromagnesite to magnesite has been reported to be a slow process requiring high temperature and pressure. For example, Montes-Hernandez, Renard, Chiriac, Findling and Toche [39]

previously showed that the duration of this phase transformation at moderate pressure and temperatures below 150 °C is in the order of days. Di Lorenzo, Rodriguez-Galan and Prieto [40] has also reported phase transformation at considerably lower pressure although temperature was demonstrated to be a key variable with times of transformation also extending to many days at temperature of 120 °C [40]. In contrast, in the present work at high CO₂ pressure (140 barg) the transformation is in the order of hours. According to the thermodynamic calculations the presence of CO₂ reduces the solution pH to a level where HM is no longer saturated, providing a strong driving force for HM dissolution, whereas, in the absence of CO₂ or at low concentrations of CO₂, pH remains high, providing little driving force for the transformation. Increased temperature to 185 °C shortened the phase transformation period to a few minutes and enhanced the rate of crystallization of magnesite.

These findings confirm that the formation of hydromagnesite is preferential to magnesite during reactor preheating and that the heating operation under CO₂ atmosphere is favoured in order to form magnesite.

6. Conclusion

The magnesium carbonate system is a complex system due to the possibility of the formation of various types of magnesium carbonates. Depending on the temperature and partial pressure of CO₂ the system behaves differently. In this work we specifically studied the mechanism for the formation of anhydrous magnesium carbonate, i.e. magnesite, under reaction conditions used in the single stage mineral carbonation process developed by ARC/NETL. It was found that at 140 barg of CO₂ and temperature ranging from 120 to 185°C the hydrated form of magnesium carbonate, i.e. hydromagnesite, nucleates faster than magnesite. Then over the period of the reaction this intermediate phase transforms to magnesite. The phase transformation process is affected significantly by operating

temperature. The formation of the metastable hydrated magnesium carbonate phase, hydromagnesite, interferes with the production of magnesite because magnesite crystals are slower to both nucleate and grow compared to hydromagnesite. These conclusions were supported by thermodynamic modelling using PHREEQC. To better promote the formation of magnesite during single stage mineral carbonation, the process must be designed to avoid the nucleation of hydromagnesite.

Acknowledgements

The authors would like to thank Dr Glenn Bryant for his technical assistance with ICP analysis. We gratefully acknowledge the facilities, and the scientific and technical assistance, of the Electron Microscope and X-ray unit (EMX) at the University of Newcastle. Mineral Carbonation international (MCI) is thanked for funding this work and for providing permission to publish.

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