Recent developments in the carbonation of serpentinite derived Mg(OH)$_2$ using a pressurized fluidized bed

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Abstract

By using a pressurized fluidized bed (PFB) reactor for the carbonation of serpentinite derived Mg(OH)$_2$, we want to utilize, for the purpose of minimizing process energy requirements, the exothermic reaction that leads to the binding of CO$_2$ in a stable and environmentally benign form, MgCO$_3$. Recent results show that most of the carbonation takes place only minutes into the experiment, suggesting that a carbonate layer forms on top of the Mg(OH)$_2$ core and inhibits further carbonation. However, this problem might be eliminated/reduced by increasing the fluidization velocity. On the other hand, the suddenly lowered reactivity might also be the result of MgO formation, which is much less reactive than the initial Mg(OH)$_2$. These and other aspects of gas/solid carbonation using a PFB being investigated include CO$_2$ pressure, temperature, particle size, particle amount (or bed size) and water injection. The influence of temperature and pressure on the carbonation of Mg(OH)$_2$ is evident, but the other factors are less clear. For instance, water has been shown by others to catalyze magnesium carbonation, but our results obtained so far using small amounts (0.1-2 % vol-H$_2$O/vol-CO$_2$) of H$_2$O injected into the CO$_2$ stream have not confirmed this. This does not mean that H$_2$O injection could not be beneficial, but implies that its effect has hitherto been clouded by other factors. Most of the experiments have been performed using commercially produced (Dead Sea Periclase Ltd.) Mg(OH)$_2$, but progress in our Mg extraction process for magnesium silicate rock has resulted in sufficient amounts of Mg(OH)$_2$ for use in our PFB reactor as well. Preliminary tests have been promising resulting in around 50% magnesium carbonation conversion in less than 10 minutes for Mg(OH)$_2$ particles of 250-425 µm at 500°C and 20 bar. In comparison, the Dead Sea Mg(OH)$_2$ particles of same size fraction resulted in only 27% conversion in otherwise similar conditions. This is apparently a result of much lower porosity (0.024 vs. 0.24 cm$^3$/g) and specific surface area (5.4 vs 46.9 m$^2$/g) for the Dead Sea Periclase sample.

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1. Introduction

Carbon dioxide sequestration via mineral carbonation is considered a marginal carbon dioxide capture and storage (CCS) method despite its significant CO$_2$ mitigating potential. Mineral carbonation was introduced briefly in
1991 when Seifritz noted that “it would be advantageous if there were an abundant mineral to which the CO₂ could be bound chemically via an exothermic reaction to form a stable, permanent substance” [1]. Following this statement, several abundant CO₂ trapping mineral types have been reported and possibly the best description of these minerals abundance was recently given by Keleman and Matter [2]. They calculated that carbonating all of the peridotite (a silicate rock type rich in magnesium) located in one place only, i.e. Oman (eastern edge of the Arabian Peninsula), would consume 77 trillion tons of CO₂. This is around 24 times more than the total amount of CO₂ in the atmosphere.

Besides this, and perhaps more importantly, the reaction of CO₂ with a magnesium (or calcium) containing mineral such as peridotite or serpentinite is exothermic. This means that CO₂ may be converted into a stable carbonate without additional energy input in a properly optimized process. This fact is the foundation of our mineral (specifically serpentinite) carbonation research at Åbo Akademi University (ÅA) and our goal is to develop a CCS method suitable for locations where underground storage capacity do not exist (e.g. Finland).

Although the overall reaction between serpentinite and CO₂ is exothermic, direct carbonation of serpentinite is extremely slow in most (temperature, pressure) conditions. Therefore, we have developed a process of first extracting the magnesium from the mineral at hand [3,4]. This requires energy, but keeping in mind that the carbonation step is exothermic, the overall process could still be rendered energy neutral (or even negative). Here, the focus will be on the carbonation step for which recent developments will be presented in detail.

2. Methodology and process description

The product of the magnesium extraction step [4,5] is Mg(OH)₂ and it is the reactant of the following carbonation step. In order to utilize the heat released during carbonation the reaction has to be fast enough. Increasing the reaction rate is therefore our highest priority. Naturally most reactions can be accelerated by increasing the temperature as molecular movement increases and collisions become more frequent. However, the stability of MgCO₃ limits the temperature to around 370°C at ambient conditions, but increasing the CO₂ partial pressure also increases the magnesium carbonate stability allowing for higher temperatures. Of course, a high temperature and pressure requirement for fast reactions sounds energy intensive, and it would be, unless the carbonation reaction was exothermic, which it is. Thus, a fast enough reaction will provide the heat necessary to maintain the elevated reactor conditions as long as a steady stream of reactants (CO₂ and Mg(OH)₂) is introduced to the system. For this purpose we have built a laboratory scale pressurized fluidized bed (PFB) reactor.

![Diagram of PFB mineral carbonation setup](image-url)

The height of the reactor part is 40 cm and the inner diameter is 1.4 cm, other details of the PFB setup are described elsewhere [5,6], but the basic layout is depicted in Figure 1 together with a schematic picture of the overall process. As can be seen from Figure 1, the idea of the mineral carbonation process under investigation is to extract the reactive component, magnesium, from an abundant source rock (such as serpentinite) and then carbonate...
3. Results and discussion

A significant amount of carbonation experiments using a small pressurized fluidized bed setup situated at ÅA have been performed since the GHGT-9 event two years ago [6]. Previously, it has not been possible to exceed pressures over 30 bar in the PFB, but that limitation has been removed. It is now possible to explore the effects of supercritical CO₂ (>73.9 bar) although when it comes to reaction kinetics lower pressures might suffice. A number of experiments with Mg(OH)₂, using both commercial and serpentine-derived material, have shown that carbonation up to around 50 %-wt is fast (within minutes), but for reasons discussed below, higher conversion degrees have not yet been obtained.

3.1. Temperature and pressure effects

In our previous studies it was noted that the carbonation rate and degree might increase exponentially with time as long as a high enough CO₂ pressure could be maintained [7], meaning that the CO₂ pressure exceeds the minimum pressure of stable MgCO₃. As such, this is not a new observation [8,9], but we have not been able to exceed some 50 %-wt carbonation conversion. However, this may be due to the fact that, so far, not many experiments have been performed above a 50 bar CO₂ pressure.

The increasing trend of higher carbonate contents as a function of bed temperature can be seen from a number of experiments. In fact, plotting all of the experiments in a single graph, Figure 2, regardless of other variables (time, H₂O content, fluidization velocity, feed type/mass and particle size fraction), shows a rough trend towards higher conversion degrees as a function of temperature (and pressure). The results obtained with Mg(OH)₂ produced from Finnish serpentine rock are included in the Figure.

![Figure 2](image_url)

Figure 2. Carbonation degree as a function of temperature (left) and pressure (right) for commercial Mg(OH)₂. The experiments that have been circled represent serpentine-derived Mg(OH)₂ experiments. The dashed line in the right graph shows the pressure beyond which CO₂ is supercritical (SCO₂).

The data points in Figure 2 represent different experiments and a number of different experimental parameters, which will be discussed below. The scatter in the results clearly indicates the importance of other variables besides pressure and temperature alone. As mentioned, temperature and pressure are linked by the stability of the product, MgCO₃, at a certain temperature, which is the reason for the similar trends in both graphs in Figure 2. If the temperature is too high, MgO formation is favored over MgCO₃ and carbonation is inhibited. Thus, increasing the pressure allows for operating at higher temperatures and it can be seen that an increased temperature results in higher carbonate levels. Carbon dioxide is supercritical above 73.9 bar (and 31 °C) and preliminary experiments (not visible in Figure 2) above this critical point did not reveal any additional benefits when it comes to accelerating
conversion rate or increasing the final carbonation degree. However, future experiments will provide more information about carbonation at higher and supercritical pressures.

3.2. The influence of other variables

Due to the nature of the experiments, high pressure and temperature, visual inspection of the fluidized bed during operation is not possible and this inevitably leads to some uncertainty whether or not the experiment is progressing in accordance to expectations. There is always a risk of channeling of the gas flow through the bed, meaning no fluidization, particularly for the smallest size fractions as has been observed in several experiments. This may also be a reason for the large scatter in the data, as further analyzed below.

3.2.1. Time

One of the more interesting results is that the reaction time does not influence the final carbonation degree to the extent anticipated. It seems that the reaction is very fast to a certain carbonation degree, determined by other factors, after which no further conversion takes place. By plotting the carbonation degree as a function of time for otherwise similar reaction conditions a clear trend can be observed. Still it is uncertain, what the exact reason for inhibition is as scanning electron microscopy (SEM) images [10] have not been able to reveal any clear layered structure on the surface of the hydroxide particles. It could be argued that the layering – if present – is too thin to be detectable by SEM as noted by Béarat et al. [9], but this seems unlikely as carbonation degrees of around 50 %‑wt have been achieved.

Figure 3. Carbonation degree as a function of reaction time for experiments performed using a PFB reactor (crosses) and a static bed system [11].

From Figure 3 it can be seen that for the PFB case a certain maximum level of carbonation is reached around 10 minutes into the experiment after which no significant further carbonation takes place. This trend was observed for various experimental conditions, but the observed “maximum” carbonation degree seems to increase as a function of temperature and pressure. In comparison, experiments performed using a static bed system (i.e. a pressurized thermogravimetric analyzer) are inhibited by carbonate layer build-up only to some extent, but not completely, as can be seen from the 360 minute data in Figure 3. The reason for this behavior is not fully understood, but it was noted by Butt et al. [8] that the best Mg(OH)₂ carbonation results were obtained using slowly flowing CO₂ rather than high flow rates (or no flow at all).

3.2.2. H₂O content

Previously it has been noted that water vapor can influence the carbonation of Mg(OH)₂ [12,13], but we have not been able to confirm this, at least for low levels of water vapor up to 2 %‑vol. Increasing the amount further remains an option to be explored and evaluated from a scale-up point of view.
Table 1. Selected experimental data to demonstrate the influence of water vapor. The last column (%CO2) gives the achieved magnesium carbonation degree, $v_{FB}$ is the flow velocity over the bed, $v_{FB}/v_{MF}$ is the ratio of the flow velocity over the minimum fluidization velocity and $V_{H_2O}/V_{CO_2}$ is the volume ratio of water to CO2.

<table>
<thead>
<tr>
<th>Mass (g)</th>
<th>Time (min)</th>
<th>Pressure (bar)</th>
<th>Temp. (°C)</th>
<th>$v_{FB}$ (cm/s), $v_{FB}/v_{MF}$</th>
<th>$V_{H_2O}/V_{CO_2}$</th>
<th>%CO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>29</td>
<td>20</td>
<td>485</td>
<td>7.9 (1.7)</td>
<td>0.1 %</td>
<td>28 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>489</td>
<td>7.8 (1.7)</td>
<td>1.6 %</td>
<td>26 %</td>
</tr>
<tr>
<td>4.0</td>
<td>10</td>
<td>35</td>
<td>517</td>
<td>6.2 (1.4)</td>
<td>-</td>
<td>44 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>531</td>
<td>6.4 (1.4)</td>
<td>1.0 %</td>
<td>38 %</td>
</tr>
<tr>
<td>20.0</td>
<td>15</td>
<td>30</td>
<td>478</td>
<td>5.2 (1.1)</td>
<td>1.0 %</td>
<td>18 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>476</td>
<td>5.8 (1.2)</td>
<td>-</td>
<td>24 %</td>
</tr>
<tr>
<td>4.0*</td>
<td>10</td>
<td>45</td>
<td>511</td>
<td>5.2 (1.0)</td>
<td>1.3 %</td>
<td>24 %</td>
</tr>
</tbody>
</table>

* No SiO2 (other experiments 1:3 mass ratio Mg(OH)$_2$ to SiO$_2$) used as fluidization material.

From Table 1 it can be noticed that the low levels of water vapor used in the experiments performed so far have not resulted in any significant changes to the process, i.e. the carbonation degree. From the three similar experiments, using a mixture of 2.5 g Mg(OH)$_2$ and 7.5 g SiO$_2$, it can be seen that the different levels of vapor in the fluidization gas do not significantly influence the resulting carbonation degree, whereas the following three comparative experiments actually indicate a negative influence of water vapor on carbonation. However, in case of the 35 bar experiments, the drop in carbonation degree for the water vapor experiment is presumably due to a too high temperature (531 °C).

The main objective for the use of water vapor has been to minimize dehydroxylation and thus enhance the reaction kinetics in accordance to previous studies [3]. It has been noted that Mg(OH)$_2$ is much more reactive towards carbonation than MgO, but unfortunately Mg(OH)$_2$ becomes unstable at high temperatures and low water vapor pressures. Therefore, a fast (and complete) carbonation reaction requires that, of the two competing reactions (carbonation and dehydroxylation), carbonation is preferred.

![Sample composition of carbonation experiments arranged from left to right according to rising MgCO$_3$ content.](image)

In order to study the extent to which the carbonation experiments had also dehydroxylated, the experiment products (of known carbonate degree) were heated to 750 °C and the resulting (carbonate and H$_2$O free) sample was weighed. The difference between the sample weight before heating and after heating is equal to the combined amount of H$_2$O and CO$_2$ released from the sample. The results of a few such experiments (not all have been...
analyzed yet) are given in Figure 4 and although no experimental data is given in the graph, the temperature increases linearly from left to right.

The trend in Figure 4 shows that two competing reactions are simultaneously taking place inside the PFB reactor. On one hand Mg(OH)₂ converts to MgCO₃ and on the other hand it converts to MgO. In PFB experiments performed with calcined Mg(OH)₂, i.e. MgO, the obtained carbonation degree was minimal. Thus, in order to increase the carbonation degree, MgO formation has to be avoided or at least minimized as previously suggested [3]. However, this might be more complicated than the simple addition of a small amount of water vapor to the CO₂ stream, while the carbonation reaction itself reduces the CO₂ pressure. As evident in both Table 1 and Figure 4, our results with H₂O + CO₂ mixtures have not revealed any significant influence on the carbonation reaction. The white arrows in Figure 4 indicate the location of the MgO to Mg(OH)₂ border for experiments done using water injection, but they do not stand out from the rest of the experiments. If the small amount of water had influenced the reaction, the arrows would point to locations not following the general trend. It seems that the Mg(OH)₂ content decreases as a function of increased MgCO₃ (and MgO) content to a certain level after which the MgO content suddenly drops. This drop, although unexplained as of yet, is promising regarding the possibility to achieve still higher carbonation degrees and will be a point of further research.

3.2.3. Fluidization velocity

One of the most important reasons for using a PFB for mineral carbonation is the fact that the particles are in constant motion inside the reactor. This implies that the particles are continuously colliding with each other and the reactor walls causing attrition, abrasion and possibly also fragmentation of the particles. Thus, new unreacted material becomes available for reaction at the surface of the particles, while the chipped of material is carried away from the reactor by the passing CO₂ stream. Continuous operation of the mineral carbonation plant would be possible by maintaining a constant stream of fresh Mg(OH)₂ into the reactor.

The key parameter that controls the motion of the bed is the fluidization velocity, i.e. the velocity of the passing CO₂ stream through the bed. The velocity has to be faster than the minimum fluidization velocity (v_MF), determined by the bed attributes and fluid properties, but slower than the terminal velocity of the feed material as to prevent the particles from being carried away too quickly (i.e too soon) from the reactor. We have assumed that good bubbling bed behavior is obtained for around four times the minimum fluidization velocity, but due to an error in earlier estimates for bed voidage (porosity), most of the experiments have actually been performed with lower fluid velocities than what was the objective. The importance of achieving good fluidization can be seen from Figure 5 by plotting the carbonation result as a function of the fluid velocity over the bed.

![Figure 5. Carbonation degree as a function of fluid velocity over the bed in a PFB reactor.](image)

As can be seen from Figure 5, the benefits of having a fluidized bed over a static bed are clear. The sudden jump in the carbonation degree at around 9 cm/s superficial velocity indicates the sudden change going from a non-moving bed to a fluidized bed. The results of the experimental results given in Figure 5 were all obtained at 25 bar and between 495 and 512 °C for particles between 212-250 µm. The reaction time was varied between 10 and 60
minutes, giving yet another indication of a maximum carbonation degree being achieved within 10 minutes. We have speculated already earlier that the reason for the sudden inhibition of carbonation, as shown by the lack of time dependence, could be due to too slow fluid velocities [5]. Changing from a bubbling fluidized bed to a circulating fluidized bed would allow for much higher velocities and stronger attrition and abrasion effects.

3.2.4. Feed type/mass

The feed types used include different magnesium hydroxides and quartz (i.e. sand). The magnesium hydroxide samples can be divided into a commercial type (Dead Sea Periclase Ltd.) and serpentinite-derived, which has been produced according to a method developed at ÅA [4,14,15]. (This method involves heating the rock material as mixed with ammonium sulphate powder, followed by stepwise precipitation of iron oxides and magnesium hydroxide from an aqueous solution. For the latter, ammonia vapor released from the first step is used; the ammonium sulphate is recovered for re-use). The difference between these two Mg(OH)₂ materials is significant when it comes to reactivity: the serpentinite derived Mg(OH)₂ is nearly twice as reactive as the commercial one as can be seen from Figure 2. The difference has been attributed to the much larger surface area and pore volume size of the serpentinite-derived material [16]. In addition to Mg(OH)₂, some of the experiments have been performed using a mixture of quartz and Mg(OH)₂ to support fluidization, but its effect on the carbonation degree cannot yet be established.

3.2.5. Particle size fraction

A surprising feature of the carbonation experiments performed has been the small importance of particle size as can be seen from Figure 6. The figure shows that for particle mean sizes between 125-250 and 250-425 µm there appears to be little difference in reactivity. Still, the importance of this parameter on the overall carbonation process (see Figure 1) is minimal as the Mg(OH)₂ materials used were both precipitated from a solution rather than e.g. crushed and grindied from a rock.

![Figure 6. Carbonation degree as a function of temperature (°C), pressure (bar), and mean particle size (µm).](image-url)

4. Conclusions

A significant amount of gas/solid Mg(OH)₂ carbonation data has been collected since GHGT-9, showing also the good characteristics of Mg(OH)₂ produced from magnesium silicate-containing rock. While the reaction between CO₂ and Mg(OH)₂ is fast at elevated temperatures and pressures inside the pressurized fluidized bed (PFB) reactor, the resulting carbonation levels leave room for improvement. Carbonation degrees of just under 50 %-wt is achieved in less than 10 minutes, but increasing the time to 20 minutes or more does not result in additional carbonation. Here we have attributed this to two features, being mainly the hardness of the formed carbonate layer besides the competition between Mg(OH)₂ dehydroxylation and carbonation reactions. A small but positive effect on the
carbonation degree of increased fluidization velocities suggests that carbonate layer build-up could be an inhibiting factor. On the other hand the correlation between a high degree of MgO and MgCO₃ in the sample suggests that the reason for a considerable reduction in carbonation is dehydroxylation. Achieving at least 90% conversion would be required before scale-up can be considered and future experiments will continue to prioritize increasing the carbonation degree. In addition, future experiments will also study in detail each of the parameters discussed here and hopefully result in a better understanding of their influence on carbonation and eventually result in a successful descriptive model of the system.

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