CO_2 mineral sequestration: physically activated dissolution of serpentine and pH swing process

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Abstract

The effect of the physical activation on the dissolution of serpentine was investigated and a pH swing scheme was developed to improve the overall conversion of the CO_2 mineral sequestration process. Various methods of the surface agitation such as ultrasound, acoustic, and internal (in-situ) grinding were examined for their effectiveness in removing the diffusion limiting SiO_2 layer in order to promote further dissolution of the inner MgO layer of serpentine. It was found that the fluidization of the serpentine slurry with 2 mm glass beads was most effective in refreshing the surface of the serpentine particles during the dissolution process. Unlike the external attrition grinding, this method could be much less energy intensive. It was also found that the mechanical agitation via the internal grinding alone did not enhance the dissolution of serpentine, while the combination of the internal grinding and Mg leaching solvent resulted in rapid serpentine dissolution. Using the proposed pH swing scheme, the overall conversion of the mineral carbonation radically improved. By controlling the pH of the system, three solid products were generated from the mineral carbonation process: SiO_2-rich solids, iron oxide and $MgCO_3^*3H_2O$. Since the iron oxide and $MgCO_3$ produced were highly pure, these value-added products could eventually reduce the overall cost of the carbon sequestration process.
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1. Introduction

Although the effects of increased CO_2 levels on global climate are uncertain, many scientists believe that a significant change in atmospheric CO_2 concentration could have a variety of serious environmental effects. Since fossil fuels will remain the main source of energy production for the foreseeable future, it is crucial to reduce CO_2 emissions in order to stabilize atmospheric CO_2 levels. Geological sequestration, ocean disposal, and biological fixation have been extensively reported in the literature, while mineral carbonation is a new and less explored method of sequestering CO_2—a disposal option that has great potential in the light of the availability of large quantities of mineral materials.

Mineral carbonation mimics natural chemical transformations of carbon dioxide, such as the weathering of noncarbonate minerals to form geologically and thermodynamically stable mineral carbonates. This sequestration process offers a safe and permanent method of CO_2 disposal, since there is no possibility of an accidental release of CO_2 from the disposal site for centuries as CO_2 is chemically incorporated into the mineral and is immobilized. Furthermore, the reactions that bind CO_2 to the mineral are exothermic in nature and, if integrated efficiently, could result in CO_2 disposal processes that are net energy producers with a very high potential for economic viability (Lackner et al., 1995).

Because of the large amounts of CO_2 requiring disposal, the raw materials for CO_2 sequestration should be abundant in nature and contain a large fraction of reactive components such as Ca and Mg-oxides. A recent report by a team of researchers at Los Alamos National Laboratories and the US Geological Survey identified large amounts of olivine

(Mg_2SiO_4) and serpentine ($Mg_3Si_2O_5(OH)_4$) deposits in the United States and Puerto Rico that have the potential to sequester CO_2 emissions for many decades (Goff et al., 2000). There are also large deposits of these minerals in Canada and parts of Europe.

Currently, there are a few research groups investigating CO_2 mineral sequestration. Some researchers are examining direct dry mineral carbonation, i.e., gas–solid reaction (Zevenhoven et al., 2002), whereas most of the researchers in the United States are studying aqueous carbonation reactions (i.e., gas–solid–liquid reaction). Until now, dry mineral carbonation has not been successful in achieving significant conversion. On the other hand, there has been much progress in the field of aqueous mineral carbonation. 80% stoichiometric conversion to $MgCO_3$ was achieved within 30 min at 185 °C and 150 atm for 30% initial slurry concentration of either heat treated serpentine or attrition ground olivine (O'Connor et al., 2002). The energy requirements, however, for these pretreatment options are extremely high. As a result, the search for more practical treatment methods was desired.

In the aqueous mineral sequestration process, the dissolution of the mineral was generally considered to be the rate-limiting step. Since it was observed that the acidity produced by CO_2 dissolved in water was not sufficient to dissolve the mineral (O'Connor et al., 2002), various physical and chemical enhancement schemes were proposed to aid in this process. The authors' earlier work showed that a mixture of weak acids and chemical additives enhanced the dissolution of ground serpentine at low-energy costs while preventing the precipitation of Fe(III) on the surface of the Mg-bearing mineral particles (Park et al., 2003). Thus, the present work mainly focused on a continued effort of enhancing serpentine dissolution and developing a pH swing process in order to develop an advanced energy efficient CO_2 mineral sequestration process. Particularly, physical activation using the internal grinding unit was preferred because when a fluidized bed reactor is used, this method could provide physical agitation without significant energy requirements. The bombardments between the larger and harder (may not be particularly denser) grinding media and fine serpentine particles in the slurry would chip away the layer of SiO_2 that inhibits further dissolution.

2. Experimental

Serpentine mined from Pennsylvania was used throughout the experiments, and it contains approximately 27, 20, and 4.3 wt% of Mg, Si, and Fe, respectively. Serpentine was first ground and sieved to less than 75 μm (average particle size of 37 μm). In this work, fine serpentine powder was used for the purpose of studying the reaction kinetics, but when a suitable grinding medium is selected, a larger average particle size could be used. Depending on the effectiveness of the internal grinding system and the economics of

the overall process, the initial particle size of the serpentine will be optimized. Surface and pore properties of serpentine samples were determined using a low temperature N_2 adsorption BET apparatus (NOVA 2200). The specific surface area and total pore volume of serpentine were 4.6 m^2/g and 0.013 mL/g, respectively. The measured density of serpentine was 2.55 g/mL. Most physical activation experiments were carried out in a 5 cm diameter fluidized bed reactor, which was constructed of Plexiglas, while a glass batch reactor was used for the serpentine dissolution step at high temperature.

2.1. Removal of SiO_2 layers from the surface of the serpentine particles

From our earlier work, it was found that removing the diffusion limiting SiO_2 layer to expose the inner Mg layer is important to promote the further dissolution of the mineral (Park et al., 2003). Several methods were proposed including internal grinding, ultrasound, acoustic, and microwave. First, the ground serpentine was dissolved in 1 M HCl for 5 h at 70 °C and ambient pressure. Approximately 40% of Mg was leached out from the serpentine slurry. Since the purpose of this dissolution step was to prepare the solid samples with a high concentration of SiO_2 on the surface, the dissolution process was not carried out to the full conversion at this point. The solids were then collected via vacuum filtration and washed with distilled water three times before air-drying. As desired, these solids had thick layers of the SiO_2 skeleton that remained on the surface. Six sets of the slurries were prepared using these SiO_2-rich solids with dissolved surfaces. The slurry concentration was 2.5 g/80 mL, which is ideal for particle size analysis using the SediGraph5100 manufactured by Micromeritics.

Table 1 describes each method in detail. When using microwave, the slurry temperature exceeded its boiling temperature during its operation; thus, the results were not compared with other methods, because the temperature increase may have promoted the dissolution of serpentine. Although the digestion of the mineral is desired for the overall process, the effect of temperature had to be minimized in order to determine the isolated effects of various surface renewing methods. All other methods were tested under ambient temperature and pressure. In addition, there were no chemical additives (i.e., acids) added to the system. The four other cases were compared for their effectiveness in removing the SiO_2 layer. Fig. 1 illustrates how the internal (in-situ) grinding system was applied.

2.2. Effect of internal (in situ) grinding unit on serpentine dissolution

From various proposed methods of physical activation, an internal (in-situ) attrition grinding system was chosen to investigate its effect on serpentine dissolution with and with-

Table 1
Various methods of removing of SiO_2 layer

| Method	Description
Internal grinding (Glass beads)	Fluidization with 20 vol% of 2 mm glass beads for 15 min (fluidizing gas = air, superficial gas velocity = 20 cm/s)
Internal grinding (Zirconia balls)	Fluidization with 20 vol% of 5 mm zirconia balls for 15 min (fluidizing gas = air, superficial gas velocity = 7 cm/s)
Ultrasonic	Ultrasonic liquid, Sonicator 3000, 5 min agitation time (Power setting 7)—slight increase in temperature but minimal
Acoustic	Made by Adv. Sonic Processing Systems, Sample was placed in a cold water bath to maintain temperature, 5 min agitation time (20 kHz, 400 W)
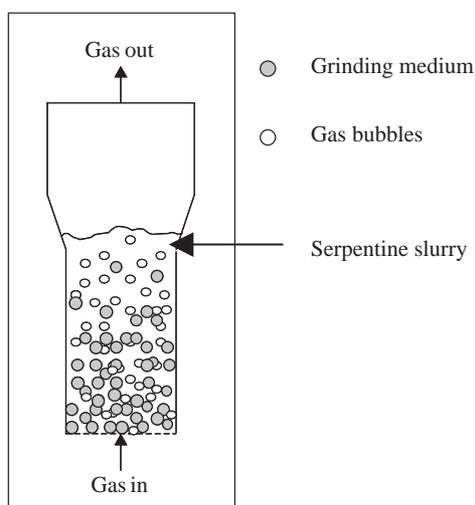
Fig. 1. Schematic diagram of the internal grinding system.

out adding any chemical additives. 20 vol% of both glass beads (2 mm diameter) and zirconia balls (5 mm diameter) were used as the grinding media. Air was used as the fluidizing gas to study the effect of internal grinding on serpentine dissolution independently from the mineral dissolution and the carbonation caused by dissolved CO_2.

2.3. pH swing process

Based on the findings in the dissolution studies, aqueous carbonation of serpentine was investigated using ground serpentine and the prepared solvent. The overall reaction for serpentine can be given as:

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 + 2H_2O \rightarrow 3MgCO_3 + 2Si(OH)_4 \text{ or } 3MgCO_3 + 2SiO_2 + 4H_2O. \quad (1)$$
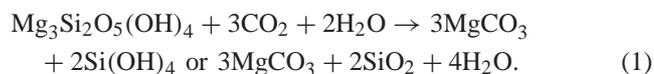
First, at 70 °C ground serpentine ($< 75\,\mu m$) was dissolved in acidic solvents ((a) a mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic acid and 0.1 wt% EDTA that was earlier used by the authors (Park et al., 2003), (b) 1.4 M ammonium bisulfate), while being fluidized with internal grinding media (20 vol% of 2 mm glass beads at Ug = 20 cm/s). At this stage, the reactor was not pressurized since the rate of surface dissolution was not a function of the operating

pressure when acids and internal grinding system were used to leach out Mg.

After the dissolution stage, the slurry was filtered and the undissolved solids were collected as Product 1, which should be high in SiO_2 content. Next, the Mg- and Fe-rich solution was cooled to ambient temperature and the pH of the solution was increased to pH ~ 8.6 by adding NH_4OH where iron oxide was expected to precipitate. It was important to increase the pH slowly to minimize the gelation. Product 2 was separated out from the Mg-rich solution. Finally, pure CO_2 was bubbled through the ambient temperature Mg-rich solution for 10 min. Once the solution was saturated with dissolved CO_2, the pH of the solution was further increased to ~ 9.5 by adding additional NH_4OH. After 5 min, the slurry was collected and filtered. The white precipitates (Product 3) were dried in a low-temperature oven. All three solid products were analyzed using an X-ray diffractometer (XRD) and thermal gravimetric analyzer (TGA).

3. Results and discussions

3.1. Removal of SiO_2 layers from the surface of the serpentine particles

Serpentine is a sheet silicate mineral with a 1:1 structure due to the alternation of tetrahedral silica-type and octahedral brucite-type layer. The silica-type layer in a sheet silicate mineral is called a "siloxane surface" (Stumm, 1992). It is expected that the dissolution at the brucite-type surface be more rapid at low pH conditions. In fact, the dissolution at the edge surface would be the fastest. Natural minerals are not homogeneous in their compositions, and thus, Fe may occasionally replace Mg in the serpentine structure. As a result, serpentine as a mineral usually contains a small amount of Fe (~ 4.3 wt%). The dissolution mechanism of the FeO containing layer is expected to be similar to that of the MgO layer.

According to the literature, serpentine can dissolve congruently as indicated in the following reaction equation (Stumm, 1992):

$$Mg_3Si_2O_5(OH)_4 + 6H^+ \rightarrow 3Mg^{2+} + 2Si(OH)_4 + H_2O. \quad (2)$$
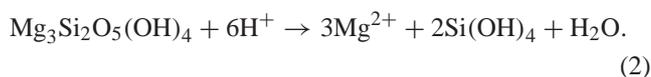
Congruent solution occurs when a mineral is totally dissolved in the ground water while incongruent solution occurs when the mineral and water react but leave a new solid along with parts of the old mineral in solution. However, during the initial stage of the serpentine dissolution, the mineral dissolves in a noncongruent pattern as a result of an initial exchange of surface Mg^{2+} ions with H^+ on the brucite-type surface (Stumm, 1992). Under acidic conditions, it is reported that $> Mg\text{-}OH$ and $> Mg\text{-}OH_2^+$ are predominant surface species (Bales and Morgan, 1985). Due to this difference in the initial dissolution rates, it was expected that any undissolved siloxane layer would act as the diffusion limiting layer that inhibits the dissolution of the inner Mg layers. This was confirmed in the authors' earlier work (Park et al., 2003). From the equilibrium calculation, it was also found that the dissolved Si-oxide layer of serpentine would form $SiO_2(s)$ and $H_4SiO_4(aq)$ during the mineral carbonation process.

Various methods were tested for their effectiveness in removing the diffusion limiting layer on the particle surface during serpentine dissolution. In the case of internal grinding with 20 vol% of 2 mm glass beads, the densities of the serpentine particles and the glass beads were very similar so that both the serpentine particles and the glass beads were easily fluidized even at a low gas flow rate. By increasing the gas velocity (up to 20 cm/s), the bombardment action between the glass beads, which refreshed the surface of the serpentine particles, was increased.

When a much denser material, zirconia balls, was used, a lower gas velocity (Ug = 7 cm/s) was applied. Even at a high gas velocity (Ug > 20 cm/s), the zirconia balls were not fluidized. Instead, they were acting as a fixed layer on top of the gas distributor, and the gap between the zirconia balls was filled with high velocity gas rather than the slurry, which eliminated the physical interaction between the grinding media and the mineral particles. Thus, a lower gas velocity was used to maintain the slurry circulation around the fixed zirconia ball layer during fluidization. At Ug = 7 cm/s, the slurry at the bottom of the column was agitated by the air bubbles rising through the network of the zirconia balls.

After processing five sets of slurries with the proposed physical activation methods, the samples were analyzed for their particle size distributions (PSD), and the results are shown in Fig. 2. The PSD of the unprocessed original SiO_2-rich serpentine particles followed the normal distribution quite closely. The average particle size was 29 μm. This value was smaller than the initial average particle size of 37 μm due to dissolution. When various methods of removing the SiO_2 layer were employed, the overall PSD shifted to the smaller particle size, and there was an increase in the amount of particles smaller than 5 μm. The generation of extremely fine particles was expected due to broken pieces of SiO_2 in the slurry. Particularly, the fluidization with 2 mm glass beads was found to be very successful at removing the diffusion limiting SiO_2 layer. In this case, the average particle size was decreased to 17 μm. The ultrasonic method
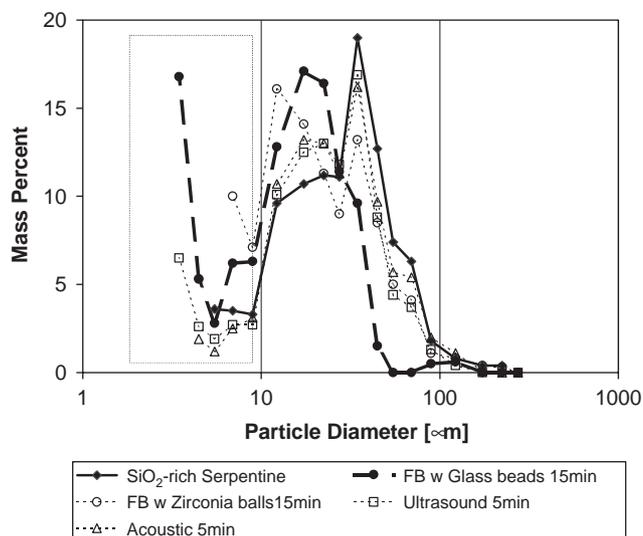

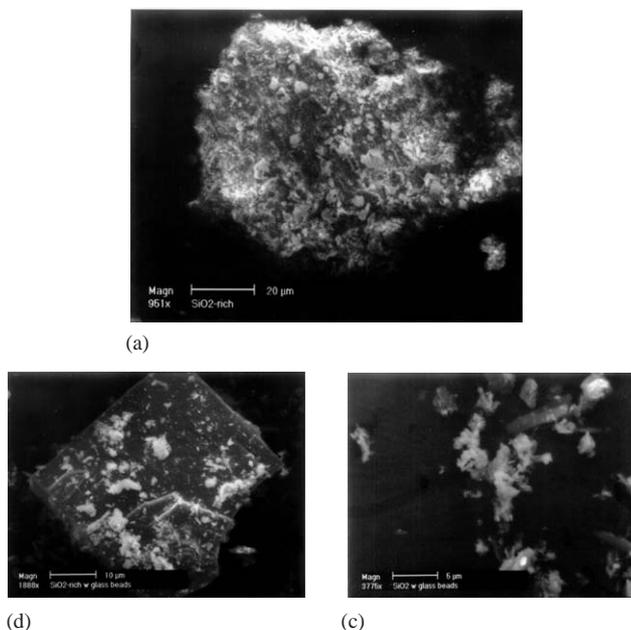Fig. 2. Particle size distribution for various internal grinding methods.

Fig. 3. SEM photos of particles before and after fluidization with 2 mm glass beads for 15 min. (a) SiO_2-rich serpentine particle, (b) serpentine particle with refreshed surface, (c) small pieces of SiO_2 and serpentine particles removed from the SiO_2-rich serpentine particles.

also showed promising results in removing the SiO_2 layer, but the extra energy consumption was a concern.

To confirm the physical removal of the SiO_2 layer using 2 mm glass beads, SEM photos were obtained after collecting solid samples. Fig. 3a shows the very porous and complex surface of a large serpentine particle after dissolution in 1 M HCl solution. This surface morphology can be compared to those shown in Fig. 3b and c. The surface of the large particle shown in Fig. 3b is similar to that before dissolution. Clearly, the removal of the SiO_2 layer was successful and
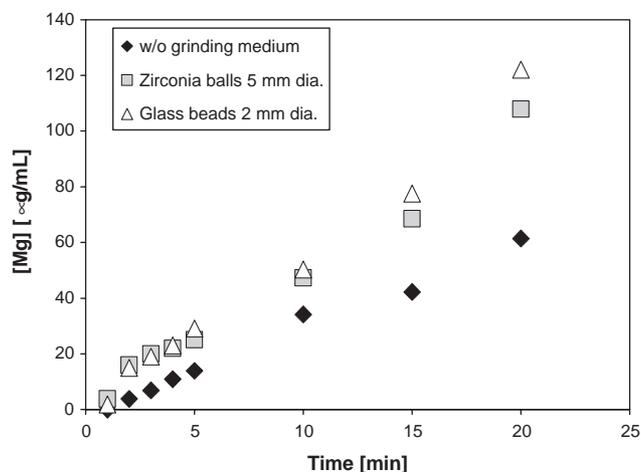
Fig. 4. Effect of internal grinding on serpentine dissolution without any chemical additives under neutral pH condition.

Fig. 5. Effect of internal grinding on serpentine dissolution with chemical additives under acidic condition.

the inner layer of serpentine was exposed for further dissolution. Only a small amount of the SiO_2 skeleton remained on the mineral surface. Fig. 3c shows clusters of the broken pieces of SiO_2, which were much smaller in size and showed a similar morphology as the surface shown in Fig. 3a. Based on Moh's hardness scale, serpentine (hardness ~ 3) is softer than glass (hardness ~ 5.5), and therefore, the smaller particles in Fig. 3c not only contained broken SiO_2, but also small pieces of serpentine.

3.2. Effect of internal (in-situ) grinding unit on serpentine dissolution

The effect of an internal (in-situ) attrition grinding system was further studied. This system was proposed to provide physical activation without additional energy requirements. Glass beads and zirconia balls (both 20 vol%) were used as the grinding media in order to minimize the potential impurities, and they were about 2 and 5 mm in diameter, respectively. A denser bed was formed by these grinding media at the bottom of the reactor, and this region acted as the internal attrition grinder. During the experiments, air was used to fluidize the slurry instead of CO_2 gas to ensure that there was no carbonation occurring during the dissolution process.

As shown in Fig. 4, the physical activation by internal grinding alone did not significantly enhance the dissolution of serpentine. Since the concentration of the grinding media (20 vol%) was much lower than that of an external attrition grinder (up to 50 vol%), less interaction was occurring between grinding media. Thus, this method of grinding was not as effective as external attrition grinding used by the group at the Albany Research Center (final average particle size $\sim 2 \mu m$) (Penner et al., 2003). However, since the main goal of the internal grinding was not particle size reduction, the internal grinding method would be sufficient
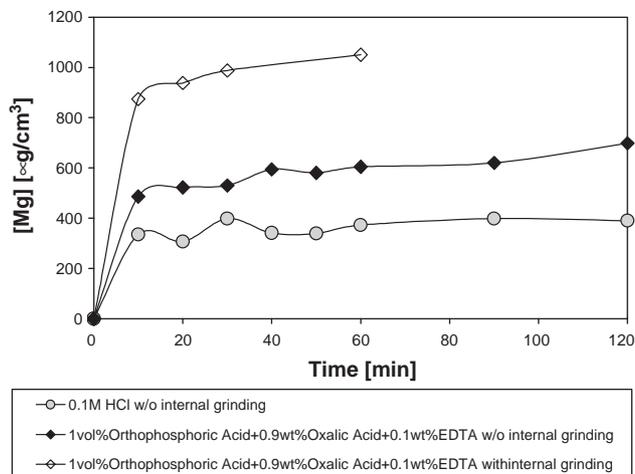
to refresh only the surface of the particles with less energy requirements. As shown in Fig. 5, the presence of grinding media in the slurry during the dissolution aided the access of leaching acid to the inner portion of the serpentine particles and resulted in a higher overall conversion. Therefore, the key to the fast serpentine dissolution process will be to find a suitable combination of solvents and internal grinding. Compared to the energy requirement of an external attrition grinder, this internal (in-situ) grinding unit would be much more energy efficient and easy to incorporate into the overall CO_2 mineral sequestration scheme.

3.3. pH swing process

From our earlier work, it was found that when the aqueous phase was fairly acidic, the overall conversion was limited by the extent of carbonic acids dissociation into bicarbonate or carbonate ions (Park et al., 2003). From a thermodynamic equilibrium calculation, it was confirmed that even at high partial pressures of CO_2, actual concentration of CO_3^{2-} was much smaller than the concentration of Mg^{2+}. Consequently, the overall conversion of the aqueous carbonation of serpentine was limited at low pH conditions. Thus, it was important to raise the pH of the solution to increase the degree of aqueous carbonation. The optimum pH for the aqueous carbonation is around 10, while the dissolution of serpentine is preferred at low pH conditions.

Based on these findings, a pH swing was proposed to achieve a higher overall conversion for the CO_2 aqueous mineral sequestration process. First, at $70\,°C$ the ground serpentine was dissolved in prepared solvents ((a) a mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic acid and 0.1 wt% EDTA that was earlier used by the authors (Park et al., 2003), (b) 1.4 M ammonium bisulfate) with aid of an internal grinding system (20 vol% of 2 mm glass beads at $Ug = 20\,cm/s$). The reactor was operated at ambient pres-

sure which would allow for a lower capital cost for the future dissolution unit. After 1 h of the dissolution process, the first solid product was separated via vacuum filtration. SiO_2 should be the only solid component left in the reactor if the dissolution was fully completed, but according to the flame-AAS analysis on the liquid samples, the amounts of Mg leached out within 1 h were approximately 65% in solvent (a) and 42% in solvent (b).

The color of the dried solid sample (Product 1), which resembled white SiO_2 powder, was much whiter than the ground serpentine. Some unreacted serpentine was also detected in the first solid product. Although pure SiO_2 will have a higher economical value, it would be rather energy intensive to separate pure SiO_2 as the first solid product from serpentine. Low quality SiO_2 might be able to be reused as the seed material for the carbonation process. Unlike in US Patent 3,338,667 (Pundsack, 1967), the dissolution took much less time due to the successful application of both chemical and physical activation of serpentine.

Next, the second product, iron oxide, was precipitated from the cooled Mg- and Fe-rich solution by raising the pH of the solution to pH $\sim$ 8.6 with NH_4OH. Product 2 was quite pure since the precipitation was carried out in a controlled pH condition. NH_4OH was added dropwise to ensure isolated precipitation of iron oxide without formation of $Mg(OH)_2$. Based on the XRD findings, the iron oxide powder (Product 2) was found to be amorphous.

Finally, while bubbling pure CO_2, Mg^{2+} was carbonated and $MgCO_3$ (Product 3) was precipitated at ambient temperature. Due to the higher partial pressure of CO_2 in the system and low operating temperature, the dissolution of gaseous CO_2 into the aqueous phase was rapid. As the pH of the solution was increased to $\sim$ 9.5 with additional NH_4OH, the dissociation of carbonic acids quickly took place and carbonation occurred spontaneously. From XRD analysis, it was found that the final product was relatively pure $MgCO_3^*3H_2O$ (Product 3). Although pure CO_2 at 1 atm was used during this study due to the physical limitation of the pH probe, in the future a much higher pressure of CO_2, which is captured from power plants and transported to the sequestration site, could be used to carbonate the Mg-rich solution. The higher partial pressure of CO_2 will result in a larger amount of dissolved CO_2. Both precipitation of iron oxide and magnesium carbonate were almost instantaneous once the desired pH condition was reached. Thus, the overall conversion to $MgCO_3$ was $\sim$ 65% for solvent (a) and $\sim$ 42% for solvent (b) and the dissolution process was again the rate-limiting step. Considering that these results were obtained at a much lower temperature and pressure (70 °C and 1 atm) than the operating conditions used by others, i.e., 185 °C and 150 atm (O'Connor et al., 2002), it is expected that the operating cost for this proposed process will be much lower. In addition, the overall capital cost is also lower for this process, since only the carbonation unit may require a high pressure reactor.

Using the proposed pH swing process, CO_2 was sequestered by mineral carbonation. Three solid products were generated: SiO_2-rich powder, iron oxide and $MgCO_3^*3H_2O$. Using TGA, it was confirmed that the final product, $MgCO_3^*3H_2O$, is thermally stable up to 320 °C. This makes the proposed process a permanent solution to carbon sequestration. Innovative heat integration between the dissolution unit and the precipitation units and recycling of the chemicals will be essential for the further reduction of the operating cost. These issues are currently being investigated.

4. Conclusions

The effect of the physical activation on the dissolution of serpentine was investigated and a pH swing scheme was developed in order to better-design mineral sequestration processes that can convert separated and captured CO_2 to products appropriate for long-term, environmentally benign, and unmonitored storage. Various physical agitation methods were used to remove the SiO_2 layer on the surface of the serpentine particles that created a diffusion problem for further dissolution of the inner Mg layer. It was found that although the physical activation caused by the interaction with the grinding media alone did not significantly dissolve serpentine, the use of the grinding media in the acidic solvent resulted in a radical improvement in the serpentine dissolution rate. A pH swing process was then proposed to achieve a higher overall conversion. Since the bicarbonate and carbonate ions are predominant at high pHs, by carefully controlling the pH, three solid products were generated from the mineral carbonation process: SiO_2-rich solids, iron oxide and magnesium carbonate.

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