

# CO<sub>2</sub> Mineral Sequestration: Chemically Enhanced Aqueous Carbonation of Serpentine

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A large amount of anthropogenic carbon dioxide emission into the atmosphere results from the combustion of fossil fuels for the production of energy. Considering the importance of fossil fuels to the health of the global economy, there is an urgent need to develop an effective approach to carbon management. This requires capturing and securely storing carbon emitted from global energy systems – a process known as carbon sequestration. Any viable system for sequestering carbon must be safe, economical, environmentally benign, and acceptable to the public. Given the magnitude of the carbon reductions needed (nearly 1 GtC/year by 2025 and 4 GtC/year by 2050) to stabilize the atmosphere, the capture and sequestration of CO<sub>2</sub> could be a major tool in reducing carbon emissions from fossil fuels (US DOE, 1999). Furthermore, sequestration may be essential for the continued large-scale use of fossil fuels. An enhancement of the understanding of the science and an investigation of the potential impact and economic viability of all carbon management-related processes should be key considerations in achieving the goal of sequestering a significant amount of CO<sub>2</sub>.

Various schemes, such as geological sequestration, ocean disposal, mineral carbonation, and biological fixation have been devised to reduce CO<sub>2</sub> emissions which also allow the continued use of fossil fuels (US DOE, 1999). Mineral carbonation is a new and, consequently, less studied method of sequestration, and it has great potential to sequester substantial amounts of CO<sub>2</sub>. This approach attempts to mimic natural chemical transformations of CO<sub>2</sub>, such as the weathering of rocks to form calcium or magnesium carbonates, and the dissolution of CO<sub>2</sub> in seawater/saline waters to form bicarbonates. This sequestration process offers a safe and permanent method of CO<sub>2</sub> disposal, since there is almost no possibility of an accidental release of CO<sub>2</sub> from the disposal site as CO<sub>2</sub> is chemically incorporated into the mineral and immobilized. Furthermore, the reactions that bind CO<sub>2</sub> to the mineral are exothermic in nature (leading to the formation of thermodynamically stable carbonate forms) and, if integrated efficiently, they could be developed into CO<sub>2</sub> disposal processes that are net energy producers with a very high potential for economic viability (Lackner et al., 1995). In this work, the aqueous reaction of CO<sub>2</sub> with the Mg-bearing mineral (i.e. serpentine) has been investigated in order to design more effective mineral sequestration processes that can convert captured and separated CO<sub>2</sub> to products amenable for long-term, environmentally benign, and unmonitored storage.

As one of the greenhouse gases, it is essential to reduce CO<sub>2</sub> emissions in order to stabilize CO<sub>2</sub> levels in the atmosphere while allowing the continued use of fossil fuels. Abatement of CO<sub>2</sub> by mineral carbonation has been proposed as one of the most promising methods for CO<sub>2</sub> emission control in the flue gas from coal-fired power plants. However, little is known about the fundamental characteristics of CO<sub>2</sub>-mineral reactions. The overall goal of this study was to investigate the mechanisms of the aqueous reactions of CO<sub>2</sub> with Mg-bearing minerals. Specifically, the focus was on the enhancement of the mineral dissolution.

Il est essentiel de réduire les émissions de CO<sub>2</sub>, un gaz à effet de serre, afin de stabiliser les niveaux dans l'atmosphère tout en permettant encore l'utilisation des combustibles fossiles. La réduction de CO<sub>2</sub> par la carbonatation minérale a été proposée comme l'une des méthodes les plus prometteuses pour le contrôle des émissions de CO<sub>2</sub> dans les gaz de carneau venant des centrales électriques au charbon. On sait toutefois peu de choses sur les caractéristiques fondamentales des réactions minéraux-CO<sub>2</sub>. Le but général de cette recherche est d'étudier les mécanismes des réactions aqueuses du CO<sub>2</sub> avec les minéraux porteurs de Mg. L'accent a été mis en particulier sur l'amélioration de la dissolution des minéraux.

**Keywords:** CO<sub>2</sub> mineral sequestration, serpentine, chelating agent, fluidized bed reactor.

## Background

In the aqueous mineral sequestration process, the dissolution of the mineral has generally been speculated as the rate-limiting step. When CO<sub>2</sub> comes in contact with water, it dissolves slightly and forms hydrated oxide or CO<sub>2</sub>(aq). After this dissolution, a small proportion of the CO<sub>2</sub> reacts with water to form carbonic acid, H<sub>2</sub>CO<sub>3</sub>. This acid dissociates into carbonate and bicarbonate ions. Thus, when CO<sub>2</sub> is dissolved in water, equilibrium is established between protons [H<sup>+</sup>], carbonate [CO<sub>3</sub><sup>2-</sup>] and bicarbonate [HCO<sub>3</sub><sup>-</sup>] ions (Lower, 1999). Because of the presence of the protons, the solution becomes acidic and its pH

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decreases. The solubility of CO<sub>2</sub> will increase with pressure, and the pH of the saturated solution of CO<sub>2</sub> varies from 3.7 at 101 kPa to 3.2 at 2.37 MPa (Pierantozzi, 1991). Therefore, at high CO<sub>2</sub> pressures the lowered pH would enhance the dissolution of the minerals. Once the active species are released into the water, the carbonation would proceed via ionic reactions. However, it has been observed that the acidity produced by CO<sub>2</sub> dissolution in water is not sufficient to dissolve the mineral, and various enhancement schemes were proposed therefore to aid in this process.

Attempts that have been made to increase the mineral dissolution include heat treatment, dry or wet attrition grinding, and the use of chemical additives such as NaHCO<sub>3</sub>/NaCl (Fauth et al., 2000; O'Connor et al., 2002). As NaHCO<sub>3</sub> is dissolved into the aqueous phase, the bicarbonate ion hydrolyzes olivine (Mg-bearing mineral) and the carbonate, hydroxide ions, and free silica are formed by the following reaction (O'Connor et al., 2000).



The hydroxide ions then react rapidly with CO<sub>2</sub>(aq) to reform the bicarbonate, and the dissolution of CO<sub>2</sub> in the aqueous phase is promoted (O'Connor et al., 2000). Thus, the solubility of the mineral increases with increasing NaHCO<sub>3</sub> concentration, as well as with the solid concentration and the reaction temperature. However, in spite of recent research in this area, there is still considerable work to be done in order to address the unanswered questions and discrepancies that remain for the reaction kinetics and mechanisms. Moreover, these pretreatment options are highly energy intensive and may not be suitable and economical for a large-scale CO<sub>2</sub> sequestration. Hence, the search for a more practical activation method is necessary. The goal is to achieve a mineral dissolution at low-energy costs (by using chemical additives/catalysts).

## Experimental Procurement and Characterization of Suitable Minerals

Minerals with high contents of Mg oxides from different regions were procured and characterized. Samples of the minerals were ground and sieved to obtain particles with a size of less than 75 μm. An optimization of the particle size will be necessary considering the grinding cost, but for the purpose of investigating reaction rates, this fine size has been used. Exact initial chemical compositions of the procured minerals were measured using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and an X-ray Diffractometer (XRD). The results are summarized in Table 1. Surface and pore properties, thermal characteristics, and surface morphology of the procured minerals were determined using a low temperature N<sub>2</sub> adsorption B.E.T apparatus, a Thermal Gravimetric Analyzer (TGA), and a Scanning Electron Microscopy (SEM), respectively.

### Solubility Tests

Many studies in the literature suggest that mineral dissolution in the aqueous phase can be increased in the presence of anions, protons, organic ligands, and weak acids. In this work, solubility studies were carried out to determine the effects of chemical surface activation on the dissolution/leaching of the active

**Table 1.** Results of chemical and physical characteristic analyses of serpentine

Mg [wt%]	27.1
Si [wt%]	20.1
Fe [wt%]	4.3
Specific Surface Area [m <sup>2</sup> /g]	4.6
Total Pore Volume [mL/g]	0.013
Density [g/mL]	2.55

species (i.e., Mg) in the aqueous phase. The chemical activation includes adding various catalysts/chemicals such as ascorbic acid, calcium chloride, and potassium dihydrogen phosphate (Wogelius and Walther, 1991; Bonifacio et al., 2001). It has been reported in the literature that the addition of organic ligands improves olivine dissolution rates in acidic and near neutral pH conditions (Wogelius and Walther, 1991). Nine sets of the proposed weak acids and/or chemical additives were used to dissolve 3 g of ground serpentine in a 200 ml solution at ambient temperature and pressure. The slurry was constantly stirred at 750 rpm during the experiments. Slurry samples were collected periodically and the filtrates were analyzed for Mg in a flame atomic absorption spectrometer (flame-AAS).

### Aqueous Carbonation Studies

Aqueous carbonation studies were performed in a high pressure, high temperature three-phase fluidized bed reactor, shown in Figure 1. The maximum operating pressure and temperature of this system are 210 atm and 250°C, respectively. The reactor is 102 mm (4 in) diameter and 1.37 m height, and three pairs of quartz windows were installed on the front and rear sides of the column for visualization purposes. A T-type thermocouple was inserted directly into the reactor to monitor the reaction temperature, and a backpressure regulator was used at the downstream of the reactor to control the internal pressure. The high pressure CO<sub>2</sub> gas was then introduced into the reactor from the bottom through a distributor, and the vigorous movement of CO<sub>2</sub> bubbles provided a mixing to the slurry.

### Results and Discussion

Serpentine was chosen as the potential reactant for CO<sub>2</sub> mineral sequestration and was procured from D.M. Stoltzfus & Son, Inc. Serpentine is readily available in the United States and samples used in this work were obtained from the Talmage Quarry in Pennsylvania. The average contents of Mg and Si for the serpentine samples were measured using the flame-AAS and were approximately 27.1 and 20.1 wt %, respectively. A measurable amount of Fe was also found from the tests (~ 4.3 wt %). These Fe atoms exist in the mineral as iron silicate. From XRD scans, serpentine was identified as Mg<sub>3</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (magnesium silicate hydroxide/antigorite).

### Dissolution of Fine Serpentine Slurry

The dissolution of the mineral is a multi-step surface chemical reaction process, and the reaction was reported to be pseudo-first order overall for less than 30% conversion with respect to the magnesia in serpentine ore (Fouda et al., 1996). Serpentine consists of layers of octahedral Mg(OH)<sub>2</sub> situated between the layers of sheet silicate tetrahedrons. Therefore, Si dissolution or

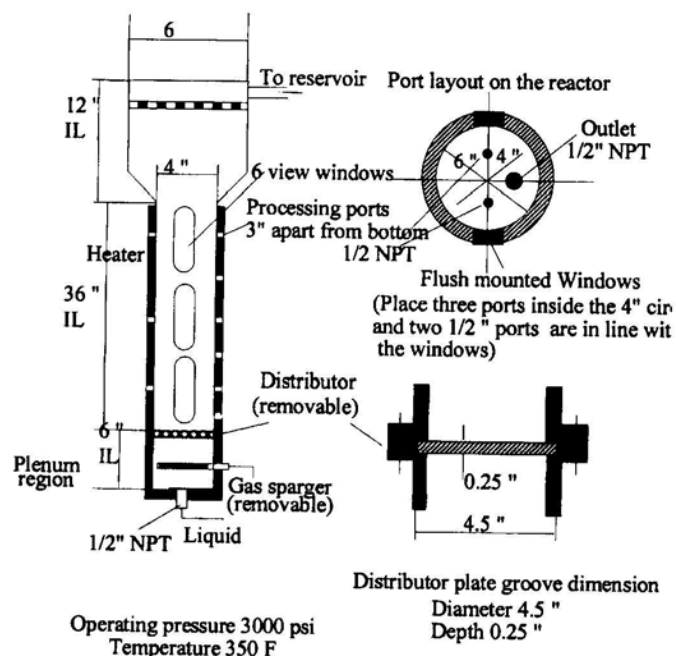


Figure 1. Detailed schematic of high pressure, high temperature three-phase fluidized bed reactor.

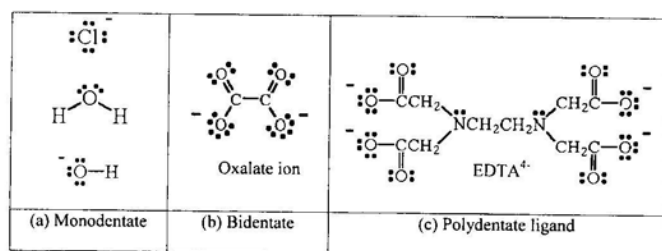


Figure 2. Structure of various complexing agents.

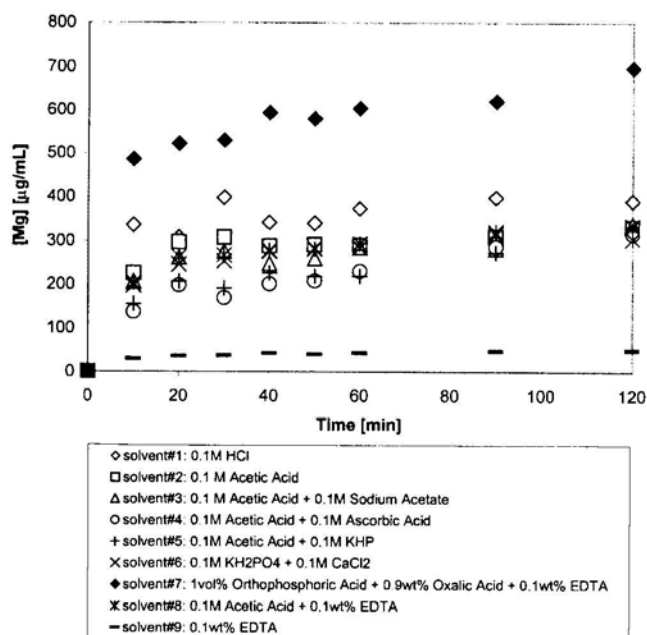
physical removal is also essential in order to expose the underlying Mg-rich layers. In the aqueous solutions, negatively charged organic ligands react with exposed Mg on the mineral surface and form organo-metallic surface complexes. Figure 2 shows examples of the structures of the ligands used in this work. These complexes polarize and the weakening of Mg-O or Mg-OH bonds results. As Mg-ligand complexes disengage the surface, the underlying layers are exposed to further interaction with the solvent (Swaddle, 1997). The complex ions are soluble in the aqueous phase, and, therefore, the solubility of an insoluble salt is increased as a complex forms. Specifically, polydentate ligands are used to dissolve deposits of metal oxides, hydroxides, sulfides, and carbonates (Swaddle, 1997). For example, the parent acid  $\text{H}_4(\text{EDTA})$  is dissolved in water which results in a negatively charged EDTA with the successive  $\text{pK}_a$  values of 2.0, 2.7, 6.2, and 10.3 at room temperature (Swaddle, 1997). The negatively charged EDTA ions displace solubility equilibria to the formation of complex ions by reducing free metal ion concentration to very low levels (Swaddle, 1997). As  $\text{CO}_2$  is introduced into the aqueous phase containing Mg-ligand complexes, magnesium carbonate will be formed. Since these chelating effects occur near neutral pH, there is no need to use costly acids to lower the solution's pH.

Various complexing agents were selected and nine different sets of solvents were prepared. There were no detailed data available for the dissolution of serpentine, but there were some results available for olivine dissolution. First, sodium acetate and EDTA were chosen since they have been tested for their effectiveness in dissolving olivine (Grandstaff, 1978; Davie and Durrani, 1978). EDTA, which is a polydentate ligand, is known to have very high binding constants with most metals. Ascorbic acid and potassium acid phthalate (KHP) are buffering agents that are chemically similar to various organic molecules present in the natural environment, and they have also been used to dissolve olivine (Furrer and Stumm, 1986). In addition, phosphate ions were reported to take a part in the ligand exchange buffering mechanism during the dissolution of serpentine in the presence of  $\text{Cl}^-$  ions (Bonifacio et al., 2001). In this work, potassium hydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) was used as the source of the phosphate ions. Solvent #7 was prepared by simulating the recipe of the etchant for olivine crystals used by Davie and Durrani (1978). However, in this case the concentration of each of the components were modified and NaOH was not added to adjust pH, since the lower pH is favorable for mineral dissolution. Solvents #2-5 and solvent #8 contained weak acid, 0.1 M acetic acid, in order to eliminate the delay in lowering pH by dissolving  $\text{CO}_2$ . Since strong acids such as HCl have been commonly used to extract Mg from serpentine, the dissolution rate of 0.1 M HCl solution was first examined as the reference case. Figure 3 lists the detailed compositions of the solvents.

As Figure 3 shows, higher initial solubility was observed in all cases. This might be due to the disordering of crystal surfaces during grinding. The total amounts of Mg leached out into the aqueous phase were up to 15% after 20 min and 20% after 2 h. Acetic acid (0.1 M) was not as effective as hydrochloric acid, or orthophosphoric acid and oxalic acid at removing Mg from the mineral surface structure. The addition of sodium acetate (solvent #3), ascorbic acid (solvent #4), and KHP (solvent #5) to acetic acid solution did not significantly affect the dissolution rate of serpentine. It was found that solvent containing phosphate ions and  $\text{CaCl}_2$  (solvent #6) digested mineral as much as 0.1 M acetic acid. These dissolution rates were much higher than that in the case without any chemical additives, but the dissolution rate in 0.1 M HCl (solvent #1) was still approximately 1.3 to 2 times greater than in these solvents (solvents #2 to 6).

When solvent #7 was used, the amount of Mg that was dissolved was about 1.5 times higher than that with 0.1 M HCl. Again, it was a very fast process and more than 80% of total dissolved Mg was leached out within the first 10 min. Considering that the dissolution was performed at ambient temperature and pressure, these results are very promising. Then, solvents #8 and 9 were tested to confirm the effectiveness of EDTA<sup>4-</sup>. In the acetic acid solution, the role of EDTA was not significant in aiding the dissolution rate. EDTA is also a weak acid, but when EDTA alone was added to the distilled water, the dissolution rate was found to be the lowest. Once Fe and Mg ions were extracted from the mineral and formed complex ions with the chelating agent (i.e., EDTA and oxalate ion), further dissolution of serpentine was promoted.

Although in all solvent cases the dissolution rate is considered to be surface reaction controlled, early leveling off of the Mg concentration in the filtrates shown in Figure 3 suggests a diffusion limitation on the dissolution at the later part of the process. In fact, from preliminary experiments, it was suspected



**Figure 3.** Dissolution of serpentine: Time versus Mg concentrations in filtrates for various compositions of solvents at ambient temperature and pressure (15 mg/mL initial solid concentration).



**Figure 4.** SEM of surfaces of serpentine particle before and after dissolution in solvent #7 at 20°C. (a) After 10 min grinding. (b) After 2 h of dissolution.

that the remaining skeleton of  $\text{SiO}_2$  or precipitation of iron oxide on the surface of serpentine particles hinders the further dissolution of Mg and other components. Both speculations assume that  $\text{MgCO}_3$  does not precipitate on the surface of the mineral particles. Figure 4 illustrates the change in surface characteristics of ground serpentine after dissolution with solvent #7. Figure 4a shows the disordered crystal surfaces after 10 min of grinding in a mixer/mill. It is clear from Figure 4b that the surface of serpentine particle becomes more complex during dissolution in acidic condition. This could be due to either a remaining skeleton of silica or precipitated silica. Jonckbloedt (1998) has reported a layer of precipitated silica during dissolution of olivine with acids at elevated temperatures. He suggested that the reaction slurry must be mixed vigorously to prevent the precipitation of silica on the dissolving olivine particles.

In fact, the initial colour of the slurry was dark grey, and, in all cases, the colour of the slurry became lighter as the dissolution proceeded. The final colours of the filtrates of solvents #7 and 8 were yellow/green due to free iron ions in the solution, while, that of solvents #2, 3 and 5 were red/brown which corresponds to the colour of iron precipitates. The colours of the filtrates of

solvents #1, 4, 6, and 9 were clear. In other words, when no effective chelating agents exist in the solution, the leached out iron ions will form precipitates and change the colour of the slurry to red/brown. Subsequently, the precipitated layer of iron-bearing phase impedes the further surface dissolution reaction of serpentine. However, if strong chelating agents such as EDTA and oxalate ion were added to the solution, ferrous ions would form complex ions with these organic ligands, which are soluble in water. This complexation process would reduce the activity of the ferrous ion in the solution and thus also reduce the precipitation of an iron-bearing phase on the serpentine surface (Mast and Drever, 1987).

### Dissolution of Serpentine Shards

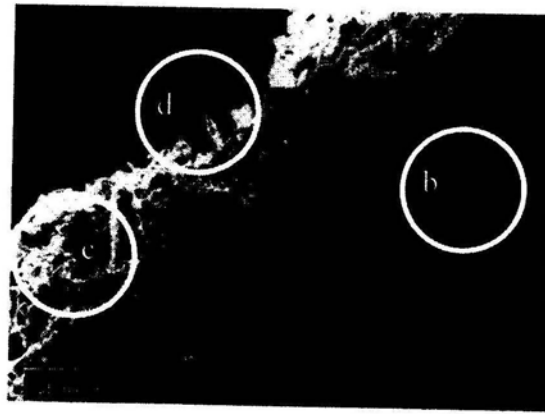
In order to confirm the hindrance of the dissolution process due to limited diffusion, controlled dissolution and carbonation experiments were performed. Two serpentine shards, about 1 cm in diameter, were placed into each flask containing 0.1 M HCl, 0.1 M acetic acid or solvent #7. These shards were relatively nonporous and there were no deep cracks on the surface, since they were used as shipped from the quarries. The solution was constantly stirred to ensure homogeneity of the aqueous phase, while the shards remained stationary at the bottom of the flask to prevent destruction of the surface. The temperature was kept at 90°C to promote faster dissolution. The color changes of the shard surfaces were observed visually, and SEM photos were taken to examine the changes in the surface structures.

As expected, after two hours of the dissolution process, the colour of the serpentine shards in acetic acid solution changed to reddish brown, indicating the precipitation of iron ions. On the other hand, the surface of the shards in both HCl solution and solvent #7 turned white due to higher silica content on the surface. These results are comparable with the observation made during dissolution experiments performed using serpentine slurries.  $\text{CO}_2$  was then bubbled through these flasks containing shards in order to proceed with carbonation at 90°C. After two hours of carbonation, a white surface layer that is the same color as  $\text{MgCO}_3$  was observed on the surface of the shards in HCl solution and solvent #7. No significant evidence of carbonation was observed in the acetic acid case. This was expected because the dissolution rate of serpentine was slower in acetic acid. The shards were then fractured to show the cross-sectional view.

Figure 5 shows the surface characteristics of serpentine at the various stages of the process. As shown in Figure 5b, the inner surface, which is the unreacted portion of serpentine shard, is quite smooth and shows nonporous characteristics. Figure 5c was taken near the surface of the shard, and at the same magnification, etch-pits, cracks and precipitated silica are visually discernible due to dissolution. These SEM photos illustrate how the specific surface area of the serpentine was increased due to the etching out of cleavage surfaces and the creation of higher relief (Grandstaff, 1978). This was not because of the formation of authigenic phases that have high specific surface areas as others have claimed. Figure 5d shows a growth of  $\text{MgCO}_3$  crystal on the very surface of the serpentine shard. This precipitated carbonate resembles the crystal formed during the carbonation of  $\text{Mg}(\text{OH})_2$  solution shown in Figure 7.

The dissolution rate would be further improved if the reaction temperature were increased, although the increased temperature would slow down the dissolution rate of  $\text{CO}_2$ . Figure 6 shows

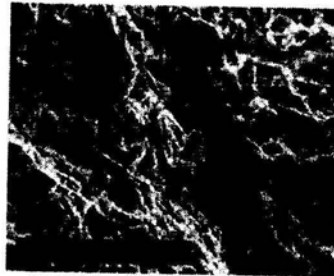




(a)



(b)

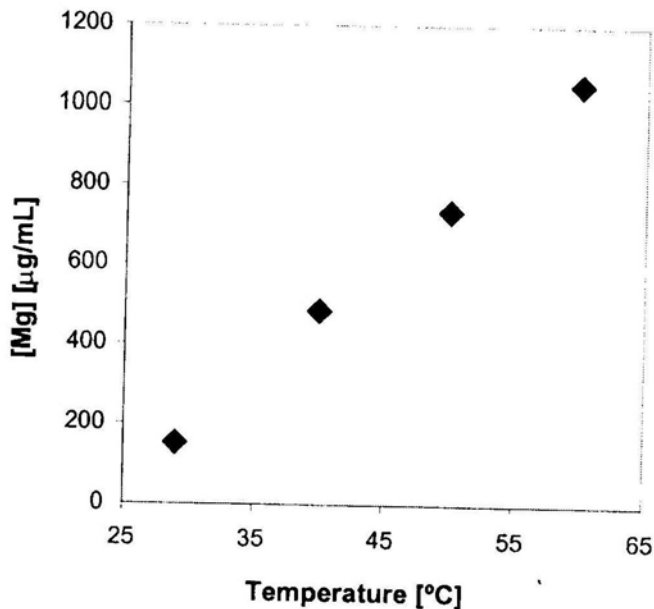


(c)

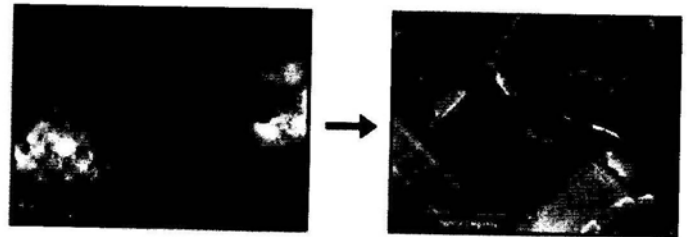


(d)

**Figure 5.** SEM of cross-sectional view of serpentine shard dissolved and carbonated in solvent #7. (a) Overall view of cross-sectional area. (b) Inner surface. (c) Dissolved outer surface. (d)  $\text{MgCO}_3$  crystal



**Figure 6.** Effect of temperature on the dissolution of serpentine (initial solid concentration = 25 mg/mL, total dissolution time = 20 min; concentration of  $\text{NaHCO}_3$  = 0.4 M).



**Figure 7.** SEM photos of pure  $\text{Mg}(\text{OH})_2$  (left) and reaction product  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  (right)

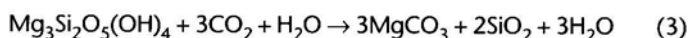
the preliminary experimental results for the dissolution of serpentine with  $\text{NaHCO}_3$  at the various temperatures. The dissolution of serpentine increased up to seven times as the temperature was raised by 30°C.

#### Carbonation Studies

First, a 10 wt% slurry of  $\text{Mg}(\text{OH})_2$ , which has a higher solubility in water than serpentine, was prepared. Using the reactor shown in Figure 1, carbonation reaction was carried out by bubbling  $\text{CO}_2$  through this solution. It was found that at 15 atm the conversions were 32% and 90% for 160°C and 20°C, respectively. The conversion at the lower operating temperature was higher, as both  $\text{CO}_2$  and  $\text{Mg}(\text{OH})_2$  are more soluble at a lower temperature. Through the viewing windows of the reactor it was observed that  $\text{Mg}(\text{OH})_2$  was completely dissolved and the total reaction time was approximately 1 h, which is still

not sufficiently fast for an economical application. As expected, the rate of carbonation/precipitation was relatively fast in this case. From the solid product characterization using TGA and XRD, it was found that when  $\text{Mg}(\text{OH})_2$  was used,  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  was the final form of the product. Generally, magnesium carbonates associate with 1, 3 or 5 molecules of water during crystallization (Durrant and Durrant, 1970).

Based on the findings in the dissolution studies, carbonation studies were carried out using ground serpentine ( $< 75 \mu\text{m}$ ) and solvent #7 at 7 MPa and  $80^\circ\text{C}$ . The superficial gas velocity (99.999%  $\text{CO}_2$ ) was maintained at 5 cm/s. The slurry was mixed by the vigorous movement of  $\text{CO}_2$  gas bubbles. The overall reaction for serpentine can be given as:



After 30 min of reaction time, the slurry was collected and filtered. The extent of carbonation was determined by calcining the final product at  $500^\circ\text{C}$  using a TGA since the weight change during calcination corresponds to the amount of  $\text{CO}_2$  captured by carbonation. Note that TGA experiments could be complicated by dehydroxylation reactions of  $\text{MgCO}_3 \cdot x\text{H}_2\text{O}$  ( $x = 1, 3$  or  $5$ ). The solid product was found to contain approximately 25% carbonated material from the TGA analysis. It was noticed that the filtrate of the slurry was still green in colour, indicating high concentration of free Fe(II) in the solution. When it was tested for Mg ion concentration, it was found that large amounts of Mg ions (~22% of total Mg content) were not carbonated and remained in the aqueous phase. In other words, when the solvent was acidic, the overall reaction rate was limited by the rate of carbonation, which was limited by dissolution of  $\text{CO}_2$  and dissociation of carbonic acids. A lower reaction temperature would increase the dissolution of  $\text{CO}_2$  and thus could increase the overall conversion. In addition, since bicarbonate and carbonate ions are predominant in concentration at high pHs, a pH swing might be required to achieve a higher conversion for the  $\text{CO}_2$  mineral carbonation process. Further studies are underway to look into the feasibility of such pH swing for mineral carbonation.

## Conclusions

Preliminary screening of mineral samples for their application in the  $\text{CO}_2$  mineral sequestration scheme identified serpentine to be the viable candidates. The procured Mg-rich serpentine samples contained approximately 27.1 wt% of Mg. According to the experimental results, the chemically enhanced aqueous carbonation of serpentine showed promising results. From the investigation of serpentine dissolution in various solvents, it was found that a mixture of 1 vol% orthophosphoric acid, 0.9 wt% of oxalic acid and 0.1 wt% EDTA greatly enhanced the Mg leaching process of ground serpentine while preventing the precipitation of Fe(III) on the surface of the mineral particles. When this acidic solvent was used for the aqueous mineral carbonation, the overall process was limited by the rates of dissolution of  $\text{CO}_2$  and dissociation of carbonic acid, rather than the dissolution rate of the mineral. The solid products were examined using a TGA, XRD and SEM in order to quantify the degree of carbonation and identify the reaction mechanisms.

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