COMPARISON OF PHYSICAL AND CHEMICAL ACTIVATION OF SERPENTINE FOR ENHANCED CO_2 SEQUESTRATION

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Introduction

In response to rising atmospheric concentrations of carbon dioxide (CO_2) and concerns over possible global climate change, focus has been placed on carbon sequestration. Mineral carbonation, the reaction of magnesium-rich minerals with CO_2 to form stable mineral carbonates, is a novel and promising approach to carbon sequestration. Suitable feedstocks include olivine (Mg_2SiO_4) and serpentine ($Mg_3Si_2O_5(OH)_4$) minerals, although serpentine exists in far greater quantities. The reaction of serpentine with CO_2 to form magnesite ($MgCO_3$), silica (SiO_2) and water is shown in Equation 1.

$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O \qquad (1)$$

The mineral carbonation approach offers several inherent advantages: the long term stability of benign mineral carbonates; the vast capacity of natural resources; and the overall process being exothermic, and therefore potentially economically viable. However, the reaction kinetics are a substantial drawback. Previous studies have required extensive communition of the raw minerals (<37 µm), heat treatment (600-650°C), high temperatures (>155°C), high partial pressures (>125 atm), and long reaction times (>6 hours) to overcome the kinetics barriers.

The objective of this research was to investigate the effectiveness of various pretreatment methods aimed to promote and accelerate carbonation reaction rates and efficiencies through surface activation and moisture removal. Previous studies have shown that mineral dissolution rates are surface controlled, and the carbonation reaction stops when the magnesium at the mineral's surface becomes depleted and/or blocked by mass transfer resistance.[1,2] It has also been demonstrated that the inherent water content of serpentine is detrimental to the carbonation process.[1-3] Therefore, it was envisioned that an increase in surface area and decrease in moisture would result in higher reaction rates and efficiencies. This would allow the integration of various synergistic features for the development of a cost-effective sequestration technology, including accelerating the carbonation efficiency without extensive mineral particle communition or heat treatment and lowering the temperature and pressure conditions of the carbonation reactions.

A series of activation experiments were performed on a serpentine mineral to promote its carbonation reactivity. Physical activation was performed with steam, and chemical activations utilized a suite of acids. Several studies were designed to increase the surface area of the mineral and reduce its inherent moisture content, while additional investigations involved the extraction of magnesium from the serpentine to form magnesium-rich solutions and solid magnesium hydroxide ($Mg(OH)_2$). Carbonation studies were then performed with the activated serpentines and solutions.

Experimental

Sample Overview. The serpentine sample was provided by the Department of Energy - Albany Research Center and originally obtained from the Cedar Hills Quarry, which lies along the border between Pennsylvania and Maryland. It was ground to minus 75µm, and a major portion of the iron was removed through a magnetic separation process.

Physical Activation. Physical activation was performed with steam at 650°C in a horizontal tube furnace for 3 hours. Water was supplied by a HPLC pump at 0.5 mL/min and carried by N_2 at 300 mL/min.

Chemical Activation. Chemical activations were performed with a suite of acids: HCl, H_2SO_4, H_3PO_4, and CH_3COOH. Initial activations using HCl, H_2SO_4, and H_3PO_4 were conducted at ambient temperature for 24 hours. Around 200 g of serpentine were reacted with 200 mL of acid in a 2 L beaker and continuously mixed with a magnetic stir bar. Three magnesium extractions were performed at 50°C for 8 hours – two with H_2SO_4 to form $MgSO_4$ solutions and one with CH_3COOH to form a $Mg(CH_3COO)_2$ solution. The extractions were carried out by reacting 50 g of serpentine with 340 mL of distilled water and either 92 g of H_2SO_4 or 57.5 g of CH_3COOH. $Mg(OH)_2$ was precipitated from the leachate of one of the H_2SO_4 extractions by adding NaOH.

Thermogravimetric Analysis (TGA). TGA analyses were performed using a Perkin Elmer TGA 7. The studies were conducted in a non-oxidizing atmosphere of nitrogen (N_2) at atmospheric pressure. Analyses were conducted over a temperature range of 25°C to 900°C, with a constant heating rate of 10°C/minute.

X-ray Diffraction (XRD). XRD analyses were carried out on a Scintag Pad V unit with a vertical theta/2-theta goniometer. The unit utilized a Cu-Kα X-ray source and was operated at a voltage of 35 kV and a current of 30 mA. A quartz zero background holder was used to mount the powder samples during XRD analyses. The samples were analyzed over a 2-theta range of 5.0° to 90.0°, with a step-scan rate of 0.1°/minute. Peaks were identified using the ICDD Powder Diffraction Files.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). ICP-AES analyses were performed with a Leeman Labs PS3000UV inductively coupled plasma spectrophotometer. Both solutions and solid samples were analyzed, with the solid samples being dissolved by a lithium metaborate fusion technique before analysis. The loss on ignition (LOI) values were calculated by measuring the weight loss of the samples upon heating to 750°C in a muffle furnace for approximately 12 hours, followed by cooling in a dessicator.

Brunauer, Emmett, and Teller Surface Area Analysis (BET). BET surface area analyses were carried out using a Quantachrome Autosorb-1 Model ASIT adsorption apparatus. Adsorption isotherms were obtained under N_2 at a temperature of 77K. The BET surface areas were calculated using the adsorption points at the relative pressures (P/P_o) 0.05 - 0.25.

Scanning Electron Microscopy (SEM). A HITACHI S-3500N was used to conduct the SEM analyses. Experiments were performed using secondary electrons under high vacuum and an accelerating voltage of 20 kV. Images were taken at magnification levels up to 10,000 times, with a working distance of 7-9 mm. The powder samples were mounted on a holder using carbon tape. In addition, the samples were spattered with a thin layer of gold to provide an electrically conductive surface.

Carbonation Experiments. All carbonation experiments were performed at the National Energy Technology Lab (NETL) in Pittsburgh, PA. High temperature and pressure analyses were carried out in a 1 L Hastelloy C-2000 continuous-stirred-tank-reactor (CSTR) unit, while low temperature and pressure carbonation reactions were performed in a 500 mL Hastelloy C-276 CSTR vessel. In a representative high temperature and pressure experiment, 30 g of serpentine and 360 g of buffer solution were charged into the 1 L CSTR, and it was sealed and purged with gaseous CO_2. Liquid CO_2 was injected through a side port until a pressure of 126 atm was

reached. A gas booster pump was used to maintain a relatively constant CO_2 pressure. The unit was heated to 155°C and the carbonation reaction was allowed to proceed for 1 hour. In a representative low temperature and pressure experiment, 180 mL of sample, including buffer, were charged into the 500 mL CSTR, and it was sealed and purged with gaseous CO_2. Liquid CO_2 was injected through a side port until a pressure of 45 atm was reached, and the unit was kept at 20°C. The reaction was allowed to proceed until the CO_2 pressure stabilized. At the end of all carbonation tests, the remaining CO_2 was vented, and the carbonated slurry was flushed from the CSTR and filtered to separate the solids. The solids were washed and dried overnight at 105°C. Carbonation efficiency calculations were based on the concentration of MgO in the starting serpentine solids and the weight gain due to carbonate formation. For the aqueous samples, the conversion was determined by the amount of magnesium that was recovered as magnesium carbonate in the precipitate that formed after carbonation.

Results and Discussion

Characterization of parent and activated serpentine samples XRD results indicated that the primary phase present in the serpentine feed sample was antigorite, $(Mg,Fe^{2++})_3Si_2O_5(OH)_4$. The serpentine was determined to be approximately 39% MgO by weight, with moisture accounting for nearly 14% of the remaining weight. BET surface area analysis reported a surface area of only $8m^2/g$.

After activation, forsterite (Mg_2SiO_4) was the primary phase present in the mineral, along with smaller amounts of antigorite. As expected, physical activation with steam removed much of the moisture from the sample, and the activated serpentine was determined to be 2.6% moisture by weight. An additional 43% of the sample was MgO by weight. The effect on the surface area was minimal (15.8 m^2/g).

The HCl, H_2SO_4, and H_3PO_4 activated serpentines became slightly amorphous after activation, and antigorite was identified as the primary mineral phase present within the samples. The chemical activations did not effectively reduce the moisture content of the minerals, with moisture accounting for approximately 11% of each sample by weight. Surface areas were increased by up to two orders of magnitude, ranging between 80 m^2/g for the HCl activated serpentine and 330 m^2/g for the H_2SO_4 activated serpentine. However, chemical treatments resulted in a net loss of MgO from the serpentine, with the MgO content being reduced to as low as 12% by weight for the H_2SO_4 activated serpentine. Thus, although the chemical treatments of serpentine were effective in raising the surface area of the mineral, they essentially decreased the mineral MgO content, and therefore decreased the amount of CO_2 that could potentially be sequestered by the treated serpentine.

The characterization results from the acid treated solids indicated the possibility of extracting the magnesium into solution as Mg^{2+} ions. In particular, over 70% of the magnesium was removed during treatment with H_2SO_4. Consequently, three additional chemical treatments were performed to produce solutions with high Mg^{2+} ion concentrations.

Two $MgSO_4$ solutions were produced by reacting serpentine with H_2SO_4, and one of the solutions was used to produce solid $Mg(OH)_2$. The $MgSO_4$ solution that was directly carbonated had a magnesium concentration of 13,000 ppm by volume. The precipitated $Mg(OH)_2$ was determined to be approximately 35% MgO by weight. Na_2SO_4, which formed during precipitation with NaOH, and moisture accounted for much of the remaining sample weight. XRD results indicated that the sample consisted primarily of $Mg(OH)_2$ and Na_2SO_4. The magnesium concentration of the $Mg(CH_3COO)_2$ solution was found to be 5,250 ppm by volume. As the ICP-AES results indicate, both H_2SO_4 and CH_3COOH were effective in creating a solution with Mg^{2+} ions being the dominant species, although treatment with H_2SO_4 resulted in a much higher Mg^{2++} dissolution.

Carbonation studies Table 1 contains a summary of the carbonation reaction conditions and conversions for the untreated and activated serpentines and solutions. The chemically activated serpentines (HCl, H_2SO_4, and H_3PO_4) did not sequester any CO_2. In fact, the amount of sample that was recovered at the end of the carbonation experiments was less than that which was originally placed in the reactor. This small weight loss was accredited to the removal of moisture during the experiments. Similarly, the carbonation of the $Mg(CH_3COO)_2$ solution did not result in the formation of a carbonate. The amount of precipitate that formed in the solution was negligible. A sizeable amount of precipitate formed in the carbonated $MgSO_4$ solution. However, XRD analysis of this precipitate identified limited amounts of magnesium carbonate minerals. The primary constituent was determined to be Na_2SO_4. Further investigation into the roles of each chemical species present within the carbonation solutions is necessary to determine why the Mg^{2+} ions in the $MgSO_4$ and $Mg(CH_3COO)_2$ solutions did not react with CO_2 to form carbonates.

On the other hand, the untreated parent serpentine, the physically activated serpentine, and the $Mg(OH)_2$ solution underwent varying degrees of carbonation. The untreated parent sample underwent a 7% conversion at 155°C and 126 atm in 1 hour. Under identical conditions, the steam activated serpentine underwent a 60% conversion, illustrating the benefit of removing moisture from the serpentine. However, high temperature treatment is very energy intensive. CO_2 was also sequestered during the carbonation of the $Mg(OH)_2$ solution. Based on the amount of magnesium recovered in the precipitate after the 3.5 hour reaction, the carbonation efficiency was estimated to be at least 53%.

Carbonation products varied for the reactions and included magnesite ($MgCO_3$) and several hydrated magnesium carbonate minerals. The high temperature and pressure reactions with the untreated parent sample and the physically activated serpentine resulted in the formation of $MgCO_3$. The rhombohedral-shaped $MgCO_3$ crystals that formed during the carbonation of the physically activated serpentine are shown in Figure 1.

Table 1. Summary of Carbonation Experiments with Physically and Chemically Activated Serpentine

Sample	Temperature (˚C)	Pressure (atm)	Time (hr)	Buffer Composition	Conversion
Untreated Parent Serpentine	155	126	1	0.6 M $NaHCO_3$; 1.0 M NaCl	7
Steam Activated Serpentine	155	126	1	0.6 M $NaHCO_3$; 1.0 M NaCl	59
HCl Activated Serpentine	155	126	1	0.6 M $NaHCO_3$; 1.0 M NaCl	---
H_2SO_4 Activated Serpentine	155	126	1	0.6 M $NaHCO_3$; 1.0 M NaCl	---
H_3PO_4 Activated Serpentine	155	126	1	0.6 M $NaHCO_3$; 1.0 M NaCl	---
$Mg(CH_3COO)_2$ Solution	20	45	4	1.34 g NaOH	---
$MgSO_4$ Solution	20	36	6	8.11 g NaOH	---
$Mg(OH)_2$ Solution	20	45	3.5	Reverse Osmosis Water	53

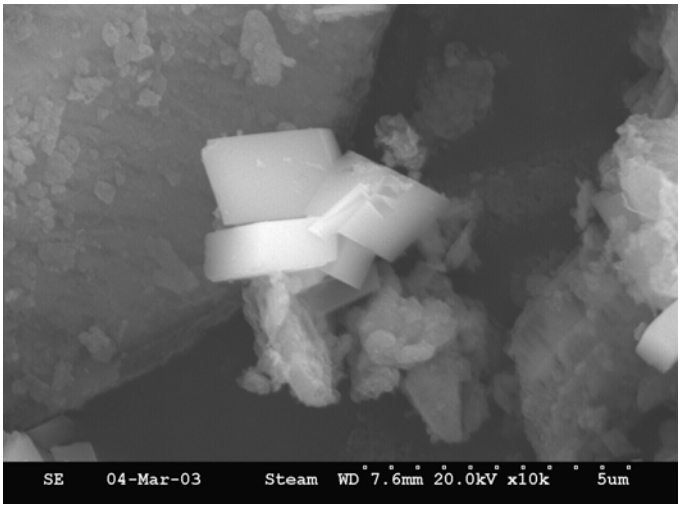

Figure 1. SEM image of magnesite crystals ($MgCO_3$) that formed during the carbonation of the physically activated serpentine (10,000X).

At lower temperatures and pressures, the carbonation of the $Mg(OH)_2$ solution resulted in the formation of various hydrated magnesium carbonates, primarily nesquehonite ($MgCO_3 \cdot 3H_2O$). Figure 2 shows an SEM image of the CO_2 that was sequestered in the carbonated $Mg(OH)_2$ solution and precipitated as nesquehonite.

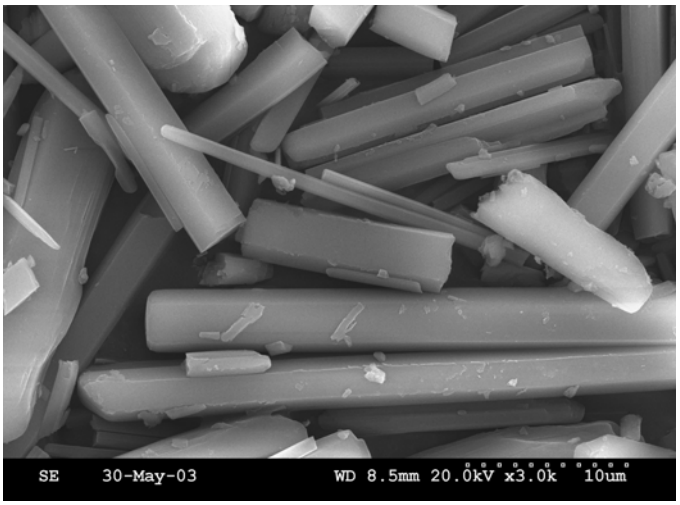

Figure 2. SEM image of nesquehonite crystals ($MgCO_3 \cdot 3H_2O$) that formed in the carbonated $Mg(OH)_2$ solution (3,000X).

The formation of hydrated magnesium carbonates, as opposed to magnesite, is due to the carbonation reaction conditions. During crystallization in aqueous processes, magnesite often associates with 1, 3, or 5 water molecules.[4] This is especially true in reactions conducted at low temperatures and CO_2 pressures, where hydrated forms of magnesite may form more readily than anhydrous magnesite.[5,6]

Conclusions

Mineral carbonation has been studied as a promising approach to carbon sequestration. However, unfavorable reaction conditions have forced previous studies to require energy-intensive operating conditions, including high temperatures and pressures, heat treatment, and extensive particle communition. Thus, the objective of the research presented within this paper was to promote and accelerate carbonation reaction rates and efficiencies through surface activation to the extent that such rigorous reaction conditions were not required. Additional studies were aimed at extracting the magnesium from the minerals for subsequent carbonation under milder reaction conditions.

Experimental results indicate that the surface area of the raw serpentine, which is approximately 8 m^2/g, can be increased through physical and chemical activation methods to over 330 m^2/g. The chemical activations were more effective at increasing the surface area, while the physical activation was more effective at reducing the moisture content of the serpentine. H_2SO_4 was the most effective acid used during the chemical activations, resulting in a mineral surface area greater than 330 m^2/g and the extraction of over two-thirds of the magnesium present within the serpentine.

The most promising results came from the carbonation of the $Mg(OH)_2$ solution. A carbonation efficiency of nearly 53% was observed, comparable to the physically activated serpentine that showed a 60% conversion at 155°C under 126 atm of CO_2 pressure. However, the $Mg(OH)_2$ carbonation reaction was conducted at ambient temperature, 20°C, and low pressure, 45 atm. These reaction conditions are indeed a significant improvement over previous studies that have required temperatures over 155°C and pressures of at least 125 atm. Furthermore, high-temperature heat treatment was avoided and a coarser particle size, 75 µm, was used in this work, compared to <37µm in previous studies. Finally, a provisional patent has been submitted based on this work.

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