Optimization of Mineral Activation for CO_2 sequestration

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Abstract

Mineral carbonation, the reaction of CO_2 with non-carbonate minerals to form stable mineral carbonates, has proved to be a promising concept for permanent CO_2 sequestration. However, there are some drawbacks of this technology: the reaction kinetics that require pulverization of the raw materials, long reaction times and high partial pressures. In the previous studies conducted at the Energy Institute of Penn State University, a novel active carbonation concept, which utilized surface activation to accelerate the reaction rates and efficiencies for forming carbonates from minerals, was developed. This research project took a step forward to further optimize the active carbonation process. A parametric study was conducted in order to increase the efficiency of mineral activation process for subsequent CO_2 sequestration.

Introduction

Fossil fuels are formed in the earth from the plant or animal remains; include natural gas, petroleum, and coal. They account for nearly 85% of the world's energy supply (DOE, 1999). In the past 60 years, the amount of anthropogenic carbon dioxide (CO_2) emitted to the atmosphere, primarily because of expanding use of fossil fuels for energy, has risen from pre-industrial levels of 280 parts per million (ppm) to present levels of over 365 ppm (Keeling and Whorf 1998). Prediction of global energy use in the next century suggests a continued increase in carbon emissions and rising concentrations of CO_2 in the atmosphere. Although the effects of CO_2 levels on global climate are uncertain, there is scientific consensus that a doubling of atmospheric CO_2 concentrations could have a variety of serious environmental consequences in the next century (DOE, 1999).

There are three main approaches to carbon management: (1) to increase the efficiency of primary energy conversion; (2) to substitute lower-carbon or carbon-free energy sources; and (3) to capture and sequester CO_2 emission. It is generally accepted that the first two alternatives will only provide incremental improvements, and therefore, carbon sequestration technologies must be developed to achieve zero emissions (DOE, 1999).

Carbon sequestration refers to the removal and long-term storage of carbon dioxide from the atmosphere or emission source. It is essential for the continued large-scale use of fossil fuels. Some other benefits for carbon sequestration includes: manufacture of commercial products; improved agricultural practice that could reduce

soil erosion, conserve water, and increase the sustainability of food production; the restoration of wetlands, which would help preserve wildlife and protect estuaries; increased biodiversity; enhanced recovery oil and methane; and the development of exportable technologies to help the U.S. economy (DOE, 1999).

Mineral carbonation, which involves the reaction of CO_2 with non-carbonate minerals to form stable mineral carbonates, has proved to be a promising CO_2 sequestration technology. There are several advantages, including a vast natural abundance of the raw minerals, the permanent and benign storage of CO_2 in solid form, and the overall reaction being exothermic, and therefore potentially economically viable (Goff et al., 2000; Herzog, 1997). The theorized reaction equation, where magnesium-rich or calcium-rich minerals, such as olivine (Mg_2SiO_4) and serpentine ($Mg_2Si_2O_5(OH)_4$) react with CO_2 to form geologically stable mineral carbonates, such as $MgCO_3$, is shown below:

$$(Mg, Ca)_x Si_yO_{x+2y} + xCO_2 \ x(Mg, Ca) CO_3 + ySiO_2$$
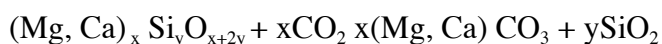
However, there is a primary drawback to mineral carbonation: reaction kinetics. Aging rocks is an example of direct mineral carbonation but the processes are extremely slow of the order of a hundred of thousand years (Herzog, 2002). The processes where the minerals are firstly dissolved before reacting with CO_2 are preferred for faster kinetics (Herzog, 2002). Previous studies have focused on crushing magnesium-rich minerals to very fine particle size $<37\mu m$ to promote surface reactions that are known to control most mineral dissolution reactions (O'Connor et al., 2000). Therefore, higher surface areas will facilitate the magnesium dissolution. In addition to the extensive communion of the raw minerals ($<37\mu m$), these mineral carbonation studies also require high partial pressures ($>1950psig$), and long reactions times (>6 hours) (Maroto-Valer et al., 2003). However, all these operations are very energy intensive and consequently mineral carbonation will only become a viable cost-effective sequestration technology through innovative development of fast reaction routes under milder regimes in a continuous integrated process (Maroto-Valer et al., 2001).

The research group led by Dr. Maroto-Valer from the Energy Institute at Penn State University has developed a novel active carbonation concept (referred here as Phase I), which utilized surface activation to accelerate significantly the reaction rates and efficiencies for forming carbonates from minerals. This concept allows the integration of various synergistic features for the development of a cost-effective sequestration technology, including acceleration of carbonation efficiency without extensive mineral particle communion and without heat treatment. The concept increased the surface area of the serpentine and reacted it with CO_2 at low temperature and pressure (Maroto-Valer et al., 2001). However, the experimental conditions used in Phase I have to be optimized.

Accordingly, the objective of this research was to conduct a parametric study to optimize the operating conditions, including leaching temperature, acid concentration and activation time in order to increase the efficiency of mineral activation process for subsequent CO_2 sequestration. The overall goal of this study was to dissolve the maximum amount of magnesium from serpentine minerals for its subsequent carbonation, while producing high surface silica solid byproducts.

Experimental Procedures

The serpentine sample for this research was from Cedar Hills Quarry, SE Pennsylvania. A concentration of 1.5 M sulfuric acid was used as the best agent to dissolve the magnesium and made it readily available for the carbonation reaction. There were six experiments conducted at various operating conditions, as listed in Table 1. For each experiment, approximately 50 grams of serpentine and 53 grams of sulfuric acid were reacted in a continuous-stirred pitcher for a given period of time. The first five experiments were conducted at 51-52°C while the last experiment was conducted at room temperature (25°C). After the reaction, the acid treated product was filtered and both the liquid and the solid products were analyzed by gas sorption and ICP method.

Table 1: Serpentine activation operating conditions

Experiment	Temp (°C)	Time (hr)
1	51	1
2	51	3
3	52	6
4	51	8
5	51	16
6	25	24

Gas adsorption was used to measure the surface area of the sample. The operation procedure as follows: degassing, or surface cleaning from contaminants such as water and oils, is first carried out by placing the powder sample in a glass cell and heating it under a vacuum; then the clean sample is brought to a constant temperature by means of an external bath; later small amounts of a gas are admitted in steps into the evacuated sample chamber. As more gas molecules are introduced into the system, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface. Based on the Brunauer, Emmett and Teller (BET) theory, the number of molecules required to cover the adsorbent surface with a monolayer of adsorbed molecules, Nm, can be estimated. Then multiplying Nm by the cross-sectional area of an adsorbate molecule yields the sample's surface area (http://www.quantachrome.com/SurfaceArea.htm).

Inductively Coupled Plasma (ICP) is a technique to determine the concentration of different elements of a sample. When an atom encounters a high-energy source, the electrons in the atom are excited to specified higher energy levels. When these electrons return to their ground state(s), they emit characteristic wavelengths of radiation. By determining what wavelengths are being emitted, the analyst can determine what

elements are present in the sample. Then by measuring the intensities of these wavelengths and comparing them to those generated by known standards, the concentrations of the different atoms can be determined (www.mri.psu.edu/mcl/techniques/icp.asp).

Results and Discussion

The ICP and BET data for the six experiments are presented in Table 2. As the reaction time increased (experiments 1-5), it is expected that the MgO concentration of the solid product in the first five experiments decreased, since more Mg^{2+} dissolves into the solution. The element Si does not dissolve, hence SiO% in the solid decreased as MgO% in the solid increased. Figure 1 also shows that MgO% in the mineral decreased after the acid treatment and leveled out between 3 hours to 16 hours reaction time. However, experiment four, which was conducted for 8 hours at 52°C showed relative low surface area (90.55m²/g) and Mg extraction yield percentage (61%) compared to the rest of the experiments. It is suggested that the experiment four needed further investigation and therefore would not be included for all the following analysis. Experiment six which was conducted at room temperature showed less competitive result (88.5 m²/g of surface area and 53% of Mg extraction yield percentage) and thus was not considered as optimum operating conditions.

Table 2: ICP and BET test results for MgO and SiO concentration, surface area of the solid product and Mg extraction yield%

Exp.	MgO%	SiO_2%	Fe_2O_3%	Surface Area (m^2/g)	Mg extraction yield %
1	30.30	51.30	2.33	91.oo	53%
2	25.60	56.00	1.86	172.40	63%
3	25.10	58.70	1.60	167.80	71%
4	27.00	57.10	1.97	90.55	61%
5	24.20	60.00	1.39	156.50	67%
6	32.00	50.20	2.85	88.50	53%

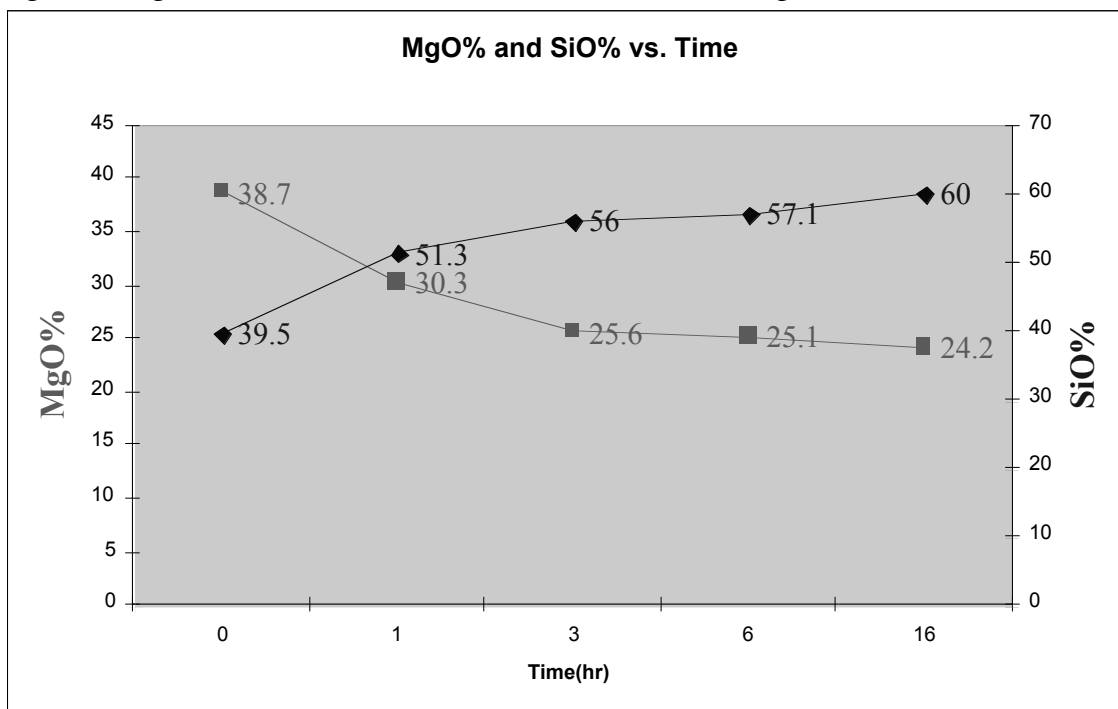Figure 1: MgO concentration and SiO concentration in solid product

Figure 2 shows the variation of surface area with reaction time. As the reaction time increased, the surface area of sample also increased. This is because the acid treatment dissolved Mg and left more fine pores on the mineral, and thus increased its surface area. The surface area of serpentine sample could reach as high as 172 m^2/g compare to the original sample of 8m^2/g. As reported for the MgO and SiO concentration, the surface area did not change much from 3 hours to 16 hours reaction time. Therefore, 3 hours seem to be the optimum reaction time for the experimental conditions used here (51°C and 1.5 M acid).

Figure 3 shows the relationship between the MgO% in the solid and surface area of solid product. It can be seen that the surface area increased as more Mg dissolved into liquid and left less amount of Mg in the solid.

Figure 2: Surface areas of activated samples
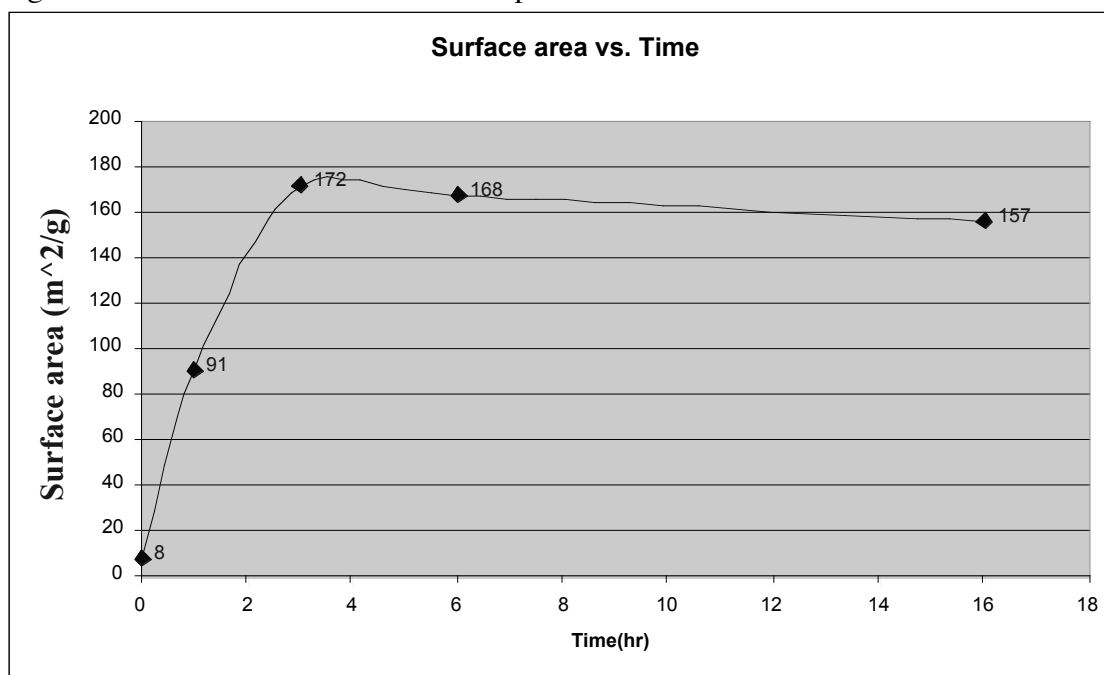

Surface area vs. Time

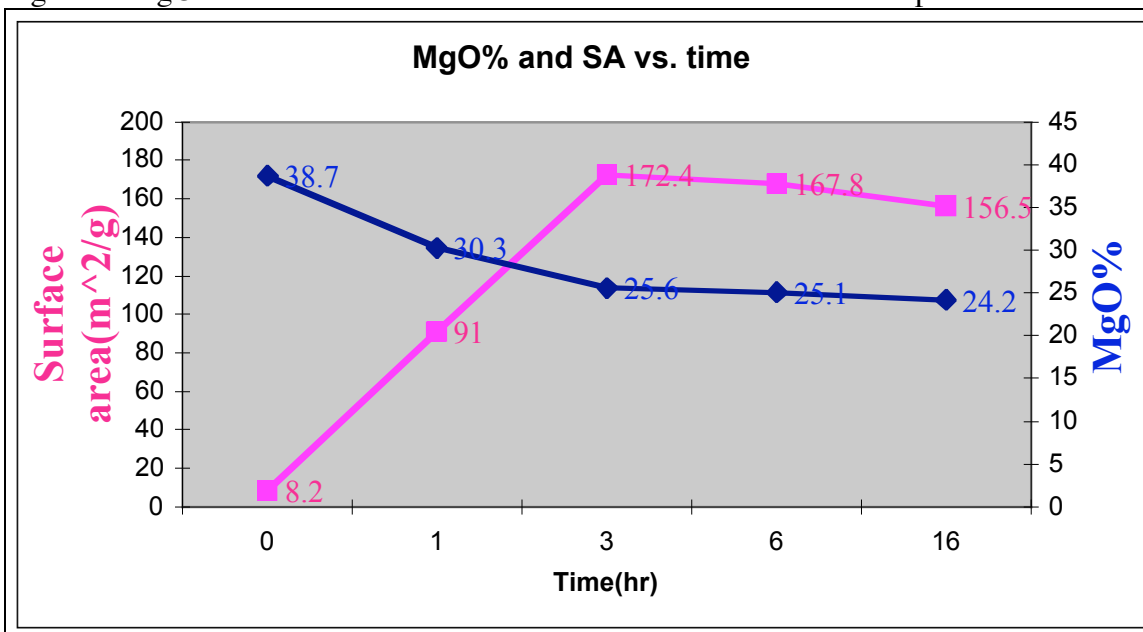Figure 3: MgO concentration in solid and surface area of activated sample

Figure 4 compares the surface area of the parent sample and the sample activated for 3-hours (experiment 3) with previous samples that were produced in Phase I. Although the sample showed much large surface area after treatment of 24 hours at room temperature, the sulfuric acid concentration was significantly higher (6.7M vs. 1.5M), and consequently, increased the cost of the process. The experiment conducted here for only 3 hours with 1.5M of sulfuric acid showed relatively close surface area, around 10% difference, to the experiment conducted for 12 hours using 2.3M of sulfuric acid.

Figure 4: Comparison of the surface areas of the parent sample and its counterparts activated under different conditions
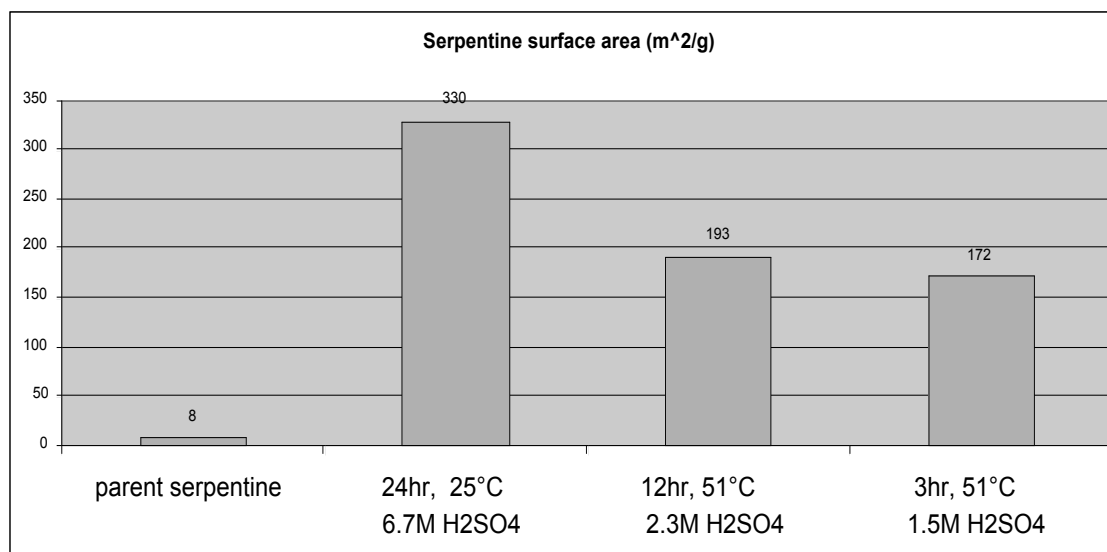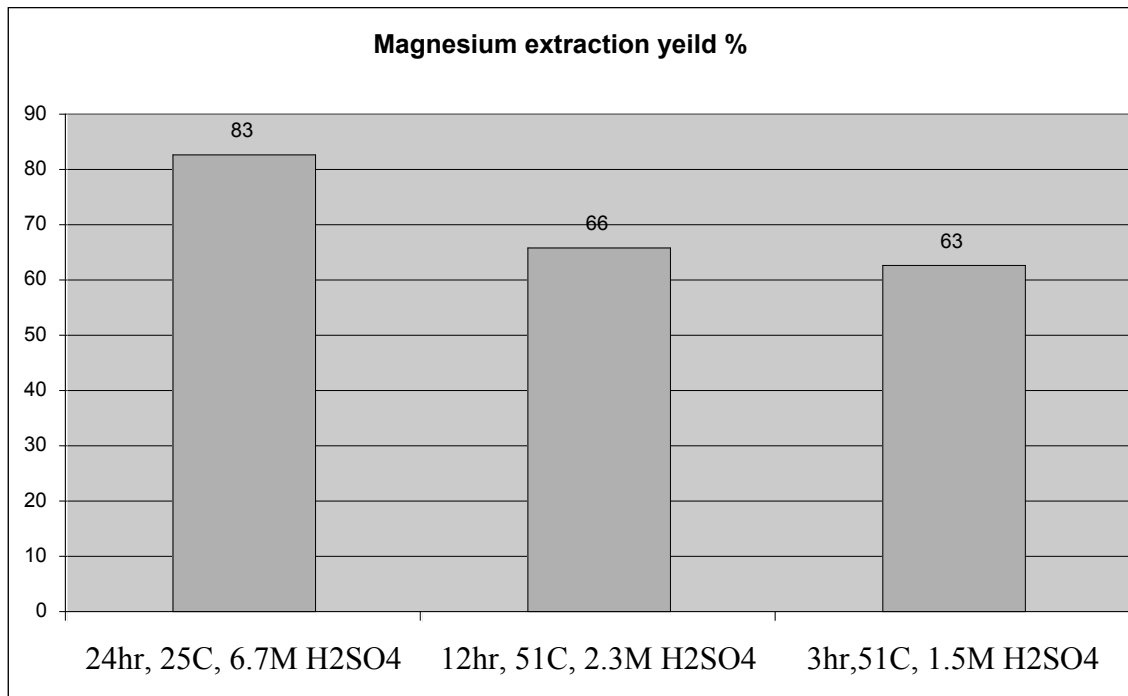
Figure 5 compares the Mg extraction yield percentage among these three experiments. As previously described, the purpose of this research was to dissolve the maximum amount of magnesium from serpentine mineral. The 24-hours experiment showed the highest percentage of Mg extracted, but it used relatively high concentration of 6.7M sulfuric acid and increased the cost. The 3-hours experiment with low acid concentration showed only 5% difference of Mg extraction yield percentage compare to the 12-hour experiment with 2.3 M sulfuric acid. This is a definite improvement considering the fact that short reaction time and low acid concentration were used.

Figure 5: Mg extraction yield%

Magnesium extraction yeild %

Bar chart showing Magnesium extraction yield %: 24hr, 25C, 6.7M H2SO4 = 83; 12hr, 51C, 2.3M H2SO4 = 66; 3hr, 51C, 1.5M H2SO4 = 63.

Conclusions

Findings from this summer research conclude that it is possible to increase the surface area of serpentine from $8m^2/g$ of untreated parent sample to $177m^2/g$ after 3 hours sulfuric acid treatment. This research has also optimized the operating conditions for mineral activation and, therefore, has led toward the development of CO_2 sequestration module. The best operating conditions for mineral activation were identified: 3 hours reaction time at 51 C with reduced concentration of 1.5M sulfuric acid.

The mineral carbonation project is still ongoing. After completing the optimization of mineral activation, the extracted magnesium in solution from serpentine will be reacted with CO_2 for aqueous carbonation. For the completion of the project, integration of the activation and carbonation units into a CO_2 sequestration module will be developed.

Acknowledgements

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