**DEVELOPMENT OF A CO₂ SEQUESTRATION MODULE BY
INTEGRATING MINERAL ACTIVATION AND
AQUEOUS CARBONATION**

ANNUAL TECHNICAL PROGRESS REPORT

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Abstract

Mineral carbonation is a promising concept for permanent CO₂ sequestration due to the vast natural abundance of the raw minerals, the permanent storage of CO₂ in solid form as carbonates, and the overall reaction being exothermic. However, the primary drawback to mineral carbonation is the reaction kinetics. To accelerate the reaction, aqueous carbonation processes are preferred, where the minerals are firstly dissolved in solution. In aqueous carbonation, the key step is the dissolution rate of the mineral, where the mineral dissolution reaction is likely to be surface controlled. In order to accelerate the dissolution process, the serpentine can be ground to very fine particle size (<37 μ m), but this is a very energy intensive process. Alternatively, magnesium could be chemically extracted in aqueous solution. Phase I showed that chemical surface activation helps to dissolve the magnesium from the serpentine minerals (particle size $\sim$ 100 μ m), and furthermore, the carbonation reaction can be conducted under mild conditions (20°C and 650psig) compared to previous studies that required >185°C, >1850psig and <37 μ m particle size. Phase I also showed that over 70% of the magnesium can be extracted at ambient temperature leaving amorphous SiO₂ with surface areas $\sim$ 330m²/g.

The overall objective of Phase 2 of this research program is to optimize the active carbonation process developed in Phase I in order to design an integrated CO₂ sequestration module. During the current reporting period, Task 1 “Mineral activation” was initiated and focused on a parametric study to optimize the operation conditions for the mineral activation, where serpentine and sulfuric acid were reacted, as following the results from Phase 1. Several experimental factors were outlined as having a potential influence on the mineral activation. This study has focused to date on the effects of varying the acid concentration, particle size, and the reaction time. The reaction yields and the characterization of the reaction products by ICP/AES, TGA, and BET analyses were used to describe the influence of each of the experimental variables.

The reaction yield was as high as 48% with a 5M acid concentration, with lower values directly corresponding to lower acid concentrations. ICP/AES results are indicative of the selective dissolution of magnesium with reaction yields. Significant improvements in the removal of moisture, as observed from TGA studies, as well as in the dissolution can be realized with the comminution of particles to a D₅₀ less than 125 μ m. A minimum threshold value of 3M concentration of sulfuric acid was determined to exist in terms of the removal of moisture from serpentine. Contrary to expected, the reaction time, within this design of experiments, has been shown to be insignificant. Potentially coupled with this unexpected result are low BET surface areas of the treated serpentine. These results are issues of further consideration to be addressed under the carbonation studies. The remaining results are as expected, including the dissolution of magnesium, which is to be utilized within the carbonation unit. Phase 1 studies have shown that carbonation reactions could be carried out under a milder regime through the implementation of NaOH titration with the magnesium solution. The optimization of acid concentration, particle size, and reaction temperature will ultimately be determined according to the carbonation efficiencies. Therefore and according to the planned project schedule, research efforts are moving into Task 2 “Aqueous carbonation” as the redesign of the reactor unit is nearly completed.

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1. INTRODUCTION

1.1. Rationale

Fossil fuels have been the main energy supplier in the US for over a century. However, the current US fossil energy scenario is undergoing significant transformations, especially to accommodate stringently increasing environmental challenges. The Vision 21 Program in fact represents a paradigm shift from traditional power plants by proposing a 21st Century Energy Plant that integrates multiple technologies with unprecedented efficiency and no environmental impact, while using a diversified fossil fuel portfolio and opportunity feedstocks to generate electricity, transportation fuels, and chemicals (DOE, 1999a). The greatest challenge to achieve no environmental impact or zero emissions is probably greenhouse gases, especially CO₂ emissions that are inevitably associated with fossil fuel burning. Furthermore, issues related to anthropogenic CO₂ emissions are closely scrutinized by the public opinion, who may demand carbon reductions as a priority for the continuation of large scale utilization of fossil fuels. Carbon management can be achieved by (i) increasing the efficiency of energy conversion; (ii) using low-carbon or carbon-free energy sources; and (iii) capturing and sequestering CO₂ emissions. 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, 1999b).

Anthropogenic emissions have increased the CO₂ concentrations in the atmosphere with over 30% compared to preindustrial levels (Keeling and Whorf, 1998).

Furthermore, it is estimated that future global CO₂ emissions will increase from ~7.4 GtC (billion tons of atmospheric carbon)/year in 1997 up to ~ 26 GtC/year in 2100 (Houghton et al., 1996; Keeling, and Whorf, 1998), and therefore, there is a clear need to develop carbon sequestration processes. Mineral carbonation is a process in which magnesium-rich minerals, such as olivine (Mg₂SiO₄), and serpentine (Mg₃Si₂O₅(OH)₄), react with CO₂ to form geologically stable mineral carbonates:

These processes basically mimic the naturally occurring weathering of rocks to form stable magnesium and calcium carbonates, and therefore, are based on exothermic reactions (Goff et al., 1997). For serpentine minerals, the above reaction can be written as follows:

The mineral carbonation approach has several inherent advantages, including a vast natural abundance of the raw minerals, the permanent and benign storage of CO₂ in solid form, and the overall reaction being exothermic, and therefore potentially economically viable (Goff et al., 2000; Herzog, 1997). The key challenge to mineral carbonation is the reaction kinetics, since these naturally occurring processes are extremely slow of the order of a hundred of thousand years (Herzog, 2002). Accordingly, direct carbonation, where the minerals react directly with the CO₂, has been abandoned in favor of processes where the minerals are firstly dissolved, since they have been proved to have much faster kinetics than direct carbonation processes (Herzog,

2002). Previous studies have focused on crushing magnesium-rich minerals, such as serpentine and olivine, to particle size $<37\mu\text{m}$ to promote surface reactions that are known to control most mineral dissolution reactions (O'Connor et al., 2000). These mineral carbonation studies require extensive comminution of the raw minerals ($<37\mu\text{m}$), high partial pressures (>1950 psig), and long reaction times (>6 hours). However, all these operations are very energy intensive. For example, pilot scale comminution tests to grind the serpentine minerals to minus 200 mesh ($75\mu\text{m}$) have reported an energy penalty of 11.5kWh/ton of mineral processed (O'Connor et al., 2002a). Previous studies have also reported that preheating the serpentine minerals to about 650°C increases significantly its carbonation reactivity, probably due to dehydroxylation and increase in the surface area and destabilization of the crystal structure (Bearat et al., 2002, McKelvy et al., 2000). However, this pretreatment is very energy intensive, requiring around 200kWh/ton of serpentine, or in other words, a 20% energy penalty for a coal-fired power plant (Herzog, 2002). 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 novel active carbonation concept proposed in Phase I of this project utilizes surface activation to accelerate the carbonation reaction efficiency. The objective of Phase I was to increase significantly the reaction rates and efficiencies for forming carbonates from minerals, and thus allowing the integration of various synergistic features for the development of a cost-effective sequestration technology, including acceleration of carbonation efficiency without extensive mineral particle comminution and without heat

treatment, while lowering the temperature and pressure conditions of the carbonation reactions.

Phase I of this project showed that the surface area of the raw serpentine, which is about 8 m²/g, can be increased through physical and chemical activation methods to nearly 330 m²/g (Maroto-Valer et al., 2002a). Previous studies have shown that the carbonation reaction is terminated when the reactive surface of the mineral is either depleted and/or becomes inactive by mass transfer resistance (Fauth et al., 2000). Therefore, the proposed active carbonation concept aimed to increase the exposure of the reactive surface, and hence, accelerate the carbonation reactions presumably by orders of magnitude. It has been reported that low temperature dehydroxylation prior to carbonation can cause the formation of porous intermediate materials with enhanced reactivities (Bearat et al., 2002). Some studies have indicated that the mineral dissolution reaction is likely to be surface controlled, and the formation of silica-enriched zones could indicate that the reaction is diffusion controlled (O'Connor et al., 2002b). Furthermore, the formation of silica rims on the reaction surfaces of the minerals may slow the magnesium dissolution (Fauth et al., 2002).

In Phase I of this project, several activation methods were investigated, including physical activation with steam and chemical activation using a suite of acids and bases. The chemical activation was more effective than the physical activation in terms of increasing the surface area, since steam activated serpentines at 650°C presented surface areas only up to 17m²/g. The steam activated serpentine had a 73% conversion to magnesite at 155°C and 1850 psig after 1 hour reaction, while under the same operating

conditions, the parent sample only had 8% conversion. However, as previously described, heat treatment is very energy intensive, and therefore, this steam activation route was not further considered. For the chemical activation, the most effective acid used was sulfuric acid, that resulted in surface areas of over 330 m²/g, and more than 70% of the magnesium was dissolved from the serpentine (100µm), and therefore, made available for carbonation. As a consequence, the subsequent carbonation reaction could be conducted at ambient temperatures (20°C) and low pressures (600psi) and it was possible to achieve 73% conversion after only 3 hours. This is indeed a significant improvement over previous studies that required temperatures over 185°C and very high pressures of around 1950 psig, as well as extensive comminution (<37 µm) (Fauth et al., 2002; O'Connor et al., 2000).

1.2. Program objectives

The overall objective of the proposed research program is to optimize the active carbonation process developed in Phase I in order to design an integrated CO₂ sequestration module for Vision 21 plants. As previously described, chemical surface activation helps to dissolve the magnesium from the serpentine minerals, and furthermore, the carbonation reaction can be conducted under ambient operating temperature and mild pressure conditions. A basic flow diagram of the proposed sequestration module is presented in Figure 1. The module consists basically of two integrated units for the activation and carbonation processes.

Figure 1. Basic flow diagram of the proposed sequestration module.

In the activation unit, serpentine is mixed with sulfuric acid to activate the mineral. During the activation process, the magnesium is extracted from the serpentine mineral and forms a Mg^{2+} solution that is sent to the carbonation reactor. As a consequence of the extraction process, a high-surface SiO_2 rich solid ($>300\text{m}^2/\text{g}$) is formed and precipitated. In the carbonation reactor, the CO_2 that has been separated from the flue gas of a power plant is reacted with the Mg^{2+} solution to precipitate MgCO_3 . During this process, the sulfuric acid will be regenerated and recycled.

1.3. Research design

This research program can be divided into the following four tasks, as described in the research proposal. Task 1 ‘Mineral activation’ will conduct a parametric study to optimize the operation conditions for the mineral activation, where serpentine and

sulfuric acid are reacted. The optimization of these processing parameters will yield a maximum dissolution of magnesium cations and also produce a high surface SiO₂ solid. Under Task 2 “Aqueous carbonation” the extracted Mg²⁺ will then be reacted with CO₂ at various temperatures and pressures in a CSTR to optimize the variables (temperature, pressure, pH, and stirring speed) that predominantly affect the carbonation reactions. Task 3 “Integration of the activation and carbonation units into a CO₂ sequestration module” will involve the integration of the two CSTR reactors and their optimum operating conditions into a module. Finally, Task 4 “Economic assessment” will be conducted to evaluate the economic viability of the proposed CO₂ sequestration module.

2. EXECUTIVE SUMMARY

Mineral carbonation is a promising concept for permanent CO₂ sequestration due to the vast natural abundance of the raw minerals, the permanent storage of CO₂ in solid form as carbonates, and the overall reaction being exothermic. However, the primary drawback to mineral carbonation is the reaction kinetics. To accelerate the reaction, aqueous carbonation processes are preferred, where the minerals are firstly dissolved in solution. In aqueous carbonation, the key step is the dissolution rate of the mineral, where the mineral dissolution reaction is likely to be surface controlled. In order to accelerate the dissolution process, the serpentine can be ground to very fine particle size (<37μm), but this is a very energy intensive process. Alternatively, magnesium could be chemically extracted in aqueous solution. Phase I showed that chemical surface activation helps to dissolve the magnesium from the serpentine minerals (particle size ~100μm), and furthermore, the carbonation reaction can be conducted under mild conditions (20°C and 650psig) compared to previous studies that required >185°C, >1850psig and <37μm particle size. Phase I also showed that over 70% of the magnesium can be extracted at ambient temperature leaving amorphous SiO₂ with surface areas ~330m²/g. The increase in surface area obtained is particularly important because the extraction process only occurs on the surface.

The overall objective of this research program is to optimize the active carbonation process developed in Phase I in order to design an integrated CO₂ sequestration module. The module consists basically of two integrated units for the activation and carbonation processes. In the activation unit, serpentine is mixed with sulfuric acid to activate the mineral. During the activation process, the magnesium is extracted from the serpentine mineral and forms a Mg²⁺ solution that will be sent to the carbonation reactor. As a consequence of the extraction process, a high-surface SiO₂ rich solid will be formed and precipitated. In the carbonation reactor, the CO₂ that has been separated from the flue gas of a power plant will be reacted with the Mg²⁺ solution to precipitate MgCO₃. During this process, the sulfuric acid will be regenerated and recycled to the activation reactor.

During the current reporting period, Task 1 “Mineral activation” was initiated and focused on a parametric study to optimize the operation conditions for the mineral activation, where serpentine and sulfuric acid were reacted, as following the results from Phase 1. Several experimental factors were outlined as having a potential influence on the mineral activation. This study has focused to date on the effects of varying the acid concentration, particle size, and the reaction time. The reaction yields and the characterization of the reaction products by ICP/AES, TGA, and BET analyses were used to describe the influence of each of the experimental variables.

The initial evaluation of the effect of serpentine acid treatment comes from the yield. It is apparent that a particle size reduction to a D_{50} less than or equal to $125\mu\text{m}$ is necessary for the enhancement of dissolution. In addition to particle size effects, it can be seen that an increase in acid concentration leads to an increase in the mass removal of serpentine. ICP results then indicate that the increases in mass removal are primarily due to magnesium dissolution. Concurrent to this magnesium dissolution, there is an increase in surface reactivity through the removal of hydroxyl groups. TGA results clearly indicate that acid concentrations at and above 3M are favorable with the particle size at a D_{50} of $125\mu\text{m}$ being ideal. Again, reactions have shown to be indifferent to variations in reaction time. BET surface area results are substantially lower than anticipated due to previous results. The effects of acid concentrations of at least 3M and particle comminution to a D_{50} less than $125\mu\text{m}$ can be realized in the optimization of surface activation. The effects of time within this study have shown to be insignificant.

Further activation studies will prove beneficial to the overall optimization of the sulfuric acid pretreatment stage. Currently, a seemingly intrinsic tie between the reaction time and the low surface area is being investigated. This tie may be through the oxidation of the serpentine surface or via sulfate crystallization. The optimization of the pretreatment reaction conditions is dependent only with respect to carbonation results. The characterization of serpentine treatment with the other techniques is indicative of successful activation. Therefore and according to the planned project schedule, research efforts are moving into Task 2 “Aqueous carbonation” as the redesign of the reactor unit is nearly completed.

3. EXPERIMENTAL

3.1. Study samples

Serpentine samples from the Cedar Hills quarry in SE Pennsylvania is used in this work as the mineral carbonation feedstock. The samples were provided by the Department of Energy - Albany Research Center (ARC). The samples consist of a -5/32" (4mm) head sample and a -400 mesh (-37.5 μm) ground sample that has underwent magnetic separation from a separation pilot-plant study (O'Connor, 2004).

The Department of Energy and Geo-Environmental Engineering's Mineral Processing laboratory was used to grind the provided 4mm head sample to the desired size fractions and secondly, to minimize any unknown preparation variables. A 4.75L batch ball mill with a ball charge of 30% was charged with 1500g samples of serpentine and ground for 9 minutes on a drive roll. The ground serpentine was sieved to the following size fractions: 300-150 μm , 150-75 μm , 75-37.5 μm , and -37.5 μm and with a hand magnet, wet separated to remove magnetite.

3.2. Statistical design

A Taguchi design of experiment (Minitab® software package) was used in this work to evaluate an optimum combination of control factors for Task 1. As discussed under the proposal, Task 1 specifies varying the following factors; sulfuric acid concentration, particle size, reaction time, and temperature. In order to provide a balanced design, where no factor is weighted disproportionately, temperature variations were carried out upon optimization of concentration, particle size, and time. The

orthogonal array of the above three factors with as many levels provides a balanced design, where no factor is weighted disproportionately (see section 3.3 below).

3.3. Activation studies

Chemical activation was carried out on 50g samples of ground Cedar Hills serpentine. The size fractions were 300 μ m-150 μ m, 150 μ m-75 μ m, and 75 μ m-37.5 μ m. An additional experiment was performed with -37.5 μ m samples, to establish the value of further size reduction. The serpentine was reacted in 500mL of prescribed concentrations of sulfuric acid for predetermined times (Table 3.1), as determined by the Taguchi design. The samples were then filtered and dried overnight at 105°C.

Table 3.1 Orthogonal design of experiment

Experiment	Molar Acid Concentration	Particle Size Fraction (D_{50}), μ m	Reaction Time, hrs
1	1.5	300-150 (163)	1
2	1.5	150-75 (125)	3
3	1.5	75-37.5 (61)	6
4	3	300-150 (163)	3
5	3	150-75 (125)	6
6	3	75-37.5 (61)	1
6A	3	-37.5 (10)	1
7	5	300-150 (163)	6
8	5	150-75 (125)	1
9	5	75-37.5 (61)	3

3.4. Sample characterization

Particle size analysis for the individual size fractions was completed on a Malvern Mastersizer “S” utilizing laser scattering, coupled with Mie theory and Fraunhofer analysis.

Analyses of chemical composition, solutions and solids, were carried out on a Leeman Labs PS3000UV Inductively Coupled Plasma Spectrometer (ICP). Solid samples, prior to analysis, were dissolved using a lithium metaborate fusion technique. Loss-on-ignition (LOI) values were determined by measuring the weight loss after heating at 900°C for 12 hours.

The serpentine samples, raw and treated, were characterized by a Perkin Elmer Thermogravimetric Analyzer (TGA) 7. Analysis conditions were at atmospheric pressure, the temperature increased incrementally from 25°C to 900°C at 10°C per minute, and carried out under nitrogen.

A Micrometrics Gemini BET was used to measure the specific internal surface area of the parent and acid treated samples. Adsorption isotherms at relative pressures,

$\left(\frac{P}{P_o} \right)$ 0.05 – 0.25 were carried out under liquid nitrogen at 77 K.

3.5. Carbonation studies

The carbonation reactor system is in the process of being redesigned, as outlined under Task 2, and is slated to be in operation in December of 2004. In order to carry out the carbonation experiments at pressures of 1850 psi, a gas transfer cylinder has been constructed for CO₂ delivery. The development of this reactor system and transfer

cylinder will allow for the carbonation reactions to be completed in house. Design capabilities for the integration of the activation and carbonation units within Task 3 are being put in place as well.

Figure 3.1 Redesign of reactor system (left: drive magnet assembly, cover face, and reactor housing, right: inside of cover face with impeller and thermowell)

4. RESULTS AND DISCUSSION

Under Task 1, the optimization of the sulfuric acid activation was investigated (Maroto-Valer et al., 2001; 2002a; and 2002b). Reaction yields, TGA, BET, and ICP analyses were conducted to characterize the properties of the serpentine before and after chemical treatment, and were evaluated within Minitab. The results from the chemical activation and optimization are summarized in the sections below.

4.1. Particle size characterization

To better understand the effects associated with the individual particle size fractions, the parent serpentine was grounded to different size fractions. Particle size analysis was carried out for each fraction to ensure that the desired size fractions have been prepared.

Figure 4.1 shows the particle size distribution of the fractions prepared. The analysis confirms the distribution of particles within each of the respective size fractions. In the following sections, the size fractions are referred to by the median particle size, or D_{50} , as determined from Figure 4.1,

Figure 4.1 Particle size distribution of the fractions prepared

4.2. Magnesium dissolution

Sulfuric acid has been determined to be an effective agent in the dissolution of magnesium from serpentine for its subsequent carbonation (Maroto-Valer et al., 2003). As described under Section 3.3, a selection of acid concentrations has been used, ranging from the stoichiometric equivalent to a molar excess of acid. Upon reaction, the yield was calculated from dividing the treated and dried filter cake weight by the initial weight of the serpentine sample.

The main effects plot in Figure 4.2 represents the influence of acid concentration and particle size on yield. The dissolution of serpentine (or reaction yields) clearly increases with higher acid molar concentration. The particle size dependence shows that the benefits of grinding serpentine are realized at less than 75 microns. Characterization of serpentine with respect to time consistently shows that results are independent of reaction time. Ongoing research into the effects of reaction time and settling time before filtration remains open in Task 1, and studies will be conducted to ascertain these effects.

Figure 4.2 Effect of time, concentration, and size on yield

4.3. ICP-AES studies

As previously shown in Phase I (Maroto-Valer et al., 2003), sulfuric acid treatment is used to extract magnesium from serpentine, concurrently producing a high

surface area silicate. ICP-AES analyses were conducted to measure the concentrations of the solutions and solids and they are presented in Table 4.1 and Figure 4. 3 shows the effect of time, size, and acid concentration on the MgO content of solids. The acid concentration presented the largest degree of control on magnesium dissolution (Figure 4.3). Experiments 8 and 9, which correspond to a 5M acid concentration, were the most effective in terms of removing magnesium. ICP studies confirm that the serpentine mass removal primarily targeted magnesium (Table 4.1). Accordingly, lower % MgO in the solids generally corresponds to higher Mg^{2+} concentrations in solution, and vice versa.

Table 4.1 ICP results for the treated solids and solutions

Experiment	ICP % Solids			ICP Solutions (ppm)			
	SiO₂	MgO	Fe₂O₃	Mg	Fe	Ca	Si
Parent*	36.4	43.3	3.42	-	-	-	-
1	49.3	34.5	1.94	8728	1290	560	146
2	43.0	26.7	1.94	9539	1280	541	157
3	44.3	28.9	1.99	8160	1495	499	158
4	54.4	32.7	1.75	9255	1401	252	21
5	46.9	20.7	1.42	9751	1480	251	60
6	49.4	24.1	1.58	10556	1717	261	62
6A	55.1	29.2	1.20	9170	1952	247	70
7	59.3	27.5	1.46	9627	2251	72	86
8	48.5	14.0	0.76	6825	1400	65	11
9	62.7	17.7	0.82	10385	1569	80	21

ICP results for the parent sample were from the 4mm ARC provided sample

The ICP results also indicate some additional benefits of comminution, as the lowest particle size fractions have the lowest iron concentration. This is of interest during the carbonation, since it has been shown that as magnetite oxidizes, the carbonation of

serpentine is inhibited due to the formation of a passive surface layer of hematite (Fauth, 2000).

Figure 4.3 Effect of time, size, and acid concentration on the MgO content of solids

4.4. TGA characterization of raw and activated samples

It has been shown that the removal of the hydroxyl groups present in serpentine minerals increase the chemical reactivity and carbonation efficiencies, probably due to hydroxyl groups inhibiting carbonation by occupying active sites on the serpentine surface (Lackner, 1995). The evolution of these hydroxyl groups is known to occur around 600°C (Maroto-Valer et al., 2003). Therefore, thermogravimetric analyses, TGA, were conducted on the parent and treated serpentine samples to determine the influence of acid treatment, and the TGA profiles are presented in Figure 4.4. The weight loss of

the parent sample (Figure 4.4) shows the evolution of adsorbed water, crystallized water, and finally of the chemically bound hydroxyl groups that occur at approximately 120°C, 300°C, 500°C, respectively. The treated samples demonstrate that the sulfuric acid pretreatment led to the removal of crystallized water and hydroxyl groups for each experiment, as illustrated by the disappearance or decrease in the weight loss at 300°C, 500°C, respectively.

Figure 4.4 TGA profile of the parent and physically activated Cedar Hills serpentine.

A statistical evaluation of the TGA samples is based on the percent weight loss at 800°C and it is presented in Figure 4.5. Values at this temperature were chosen based on the components of interest being sufficiently driven off and due to an apparent drift. A blank run was performed with the TGA, a result of which showed a weight gain

beginning at 800°C. Figure 4.4 illustrates the susceptibility of serpentine to specific treatment conditions, in terms of volatiles. TGA values again demonstrate that time does not have a significant role in the increased reactivity from acid treatment of serpentine. However, the effects of varying the size of particles and the acid concentration are visible in Figure 4.5. The particle size analysis for the TGA requires further consideration as it is surprisingly not to find an optimum particle size range. Figure 4.5 also illustrates that a 3M acid concentration is favored over 1.5M and that there are not additional gains with increasing the acid concentration to a 5M solution. These variations in percent weight loss between the experiments show the sensitivity of serpentine to varying environments.

Figure 4.5 Effect of time, size, and acid concentration on TGA

4.5. Porous texture characterization of raw and activated samples

Previous studies have demonstrated that parent samples with a surface area of 8 m²/g, can be increased through chemical activation to nearly 330 m²/g due to low

temperature dehydroxylation (Bearat, 2002; Maroto-Valer et al., 2003). The carbonation of serpentine has been shown to be surface controlled, as the reaction is limited when the magnesium at the mineral surface is depleted and/or inactivity by mass transfer resistance (Fauth, 2000). Therefore, it is assumed that an increase in surface area will promote carbonation.

Table 4.2 shows the surface area results for the BET characterization of the parent and treated serpentines. With values being substantially lower than expected and achieved during Phase I, there is an ongoing evaluation of the pretreatment stage. Further investigation of the acid treatment on surface area values and ultimately surface reactivity is to be conducted upon carbonation under Task 2.

Table 4.2 BET results for treated serpentine samples

Experiment	Surface Area, m²/g
1	24.13
2	18.53
3	24.02
4	25.17
5	18.96
6	23.49
6A	25.65
7	36.09
8	20.87
9	27.9

5. CONCLUSIONS

The overall objective of this research program is to optimize the active carbonation process developed in Phase I in order to design an integrated CO₂ sequestration module. Chemical activation, through sulfuric acid treatment, has been proven to be an effective mechanism for increasing the reactivity of serpentine. Accordingly, under Task 1, several variables have been characterized in an attempt to optimize the acid treatment step. These variables include acid concentration, particle size, reaction time, and reaction temperature. A design of experiments has been used in this work to evaluate an optimum combination of these variables, with the results showcasing a range of sensitivities and trends.

The initial evaluation of the effect of serpentine acid treatment comes from the yield. It is apparent that a particle size reduction to a D₅₀ less than or equal to 125µm is necessary for the enhancement of dissolution. In addition to particle size effects, it can be seen that an increase in acid concentration leads to an increase in the mass removal of serpentine. ICP results then indicate that the increases in mass removal are primarily due to magnesium dissolution. Concurrent to this magnesium dissolution, there is an increase in surface reactivity through the removal of hydroxyl groups. TGA results clearly indicate that acid concentrations at and above 3M are favorable with the particle size at a D₅₀ of 125µm being ideal. Again, reactions have shown to be indifferent to variations in reaction time. BET surface area results are substantially lower than anticipated due to

previous results. The effects of acid concentrations of at least 3M and particle comminution to a D_{50} less than 125 μ m can be realized in the optimization of surface activation. The effects of time within this study have shown to be insignificant.

Further activation studies will prove beneficial to the overall optimization of the sulfuric acid pretreatment stage. Currently, a seemingly intrinsic tie between the reaction time and the low surface area is being investigated. This tie may be through the oxidation of the serpentine surface or via sulfate crystallization. The optimization of the pretreatment reaction conditions is dependent only with respect to carbonation results. The characterization of serpentine treatment with the other techniques is indicative of successful activation. Therefore, work is now being conducted under Task 2 to conduct carbonation experiments, as the remainder of the results is promising.

6. ACKNOWLEDGEMENTS

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