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Abstract

The greatest challenge to achieve no environmental impact or zero emissions for the Vision 21 plants is probably greenhouse gases, especially CO_2 emissions that are inevitably associated with fossil fuel combustion. Mineral carbonation, that involves the reaction of CO_2 with non-carbonate minerals to form stable mineral carbonates, has been lately proposed as a promising CO_2 sequestration technology due to the vast natural abundance of the raw minerals, the long term stability of the mineral carbonates formed, and the overall process being exothermic, and therefore, potentially economic viable. However, carbonation efficiency is being considered a major hurdle for the development of economically viable sequestration technologies, where present studies require extensive mineral particle communition, high pressures and prior capture of the CO_2. 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 process.

The objective of the proposed novel active carbonation concept is to promote and accelerate reaction rates and efficiencies through surface activation to the extent that extensive mineral particle communition and high temperatures and pressures are not required. In this research program, serpentine was used as the carbonation feedstock material. Physical and chemical surface activation studies were conducted to promote its inherent carbonation reactivity. The activated materials were characterized by a battery of analytical techniques to determine their surface properties and assess their potential as carbonation minerals. Active carbonation studies were conducted and the carbonation activity was quantitatively determined by the increase of the weight of solid products and the percent of stoichiometric conversion.

This work has shown that chemical activation was more effective than the physical activation in terms of increasing the surface area (330 vs. 17m^2/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, 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 m^2/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.

Finally, this project has been awarded a Phase II, where the active carbonation process developed during this Phase I will be optimized in order to design a CO_2 sequestration module.

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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 CO_2 emissions that are inevitably associated with fossil fuel burning. Furthermore, issues related to anthropogenic CO_2 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 CO_2 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 CO_2 concentrations in the atmosphere with over 30% compared to preindustrial levels (Keeling and Whorf, 1998).

Furthermore, it is estimated that future global CO_2 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 (Mg_2SiO_4), and serpentine ($Mg_3Si_2O_5(OH)_4$), react with CO_2 to form geologically stable mineral carbonates:

$$(Mg, Ca)_x Si_y O_{x+2y} + xCO_2 \quad x(Mg, Ca)CO_3 + ySiO_2$$
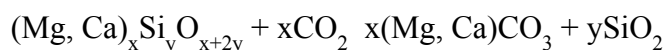
These processes basically mimic the naturally occurring weathering of rocks to form stable magnesium and calcium carbonates, and therefore, are based on exothermic reactions (Goff et al., 1997). For serpentine minerals, the above reaction can be written as follows:

$$CO_2 + 1/3\ Mg_3Si_2O_5(OH)_4 \quad MgCO_3 + 2/3\ SiO_2 + 2/3\ H_2O + 64\ KJ/mole \text{ (Yegulalp et al.,}$$

$$2000)$$
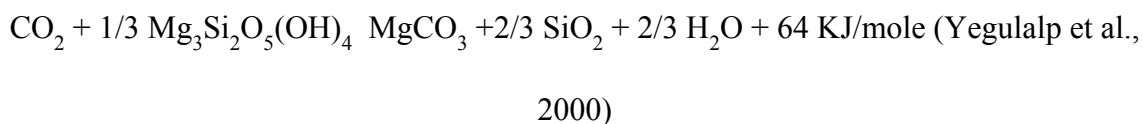
The mineral carbonation approach has several inherent advantages, including a vast natural abundance of the raw minerals, the permanent and benign storage of CO_2 in solid form, and the overall reaction being exothermic, and therefore potentially economically viable (Goff et al., 2000; Herzog, 1997). The 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 CO_2, 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 <37μm to promote surface reactions that are known to control most mineral dissolution reactions (O'Connor et al., 2000). These mineral carbonation studies require extensive communition of the raw minerals (<37μm), high partial pressures (>1950 psig), and long reaction times (>6 hours). However, all these operations are very energy intensive. For example, pilot scale communition tests to grind the serpentine minerals to minus 200 mesh (75 μm) 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). Accordingly, the novel active carbonation concept proposed here utilizes surface activation to accelerate the carbonation reaction efficiency.

1.2. Program objectives

The overall objective of the proposed research program is the development of an active carbonation process that can ultimately evolve into an integrated CO_2 sequestration module for Vision 21 plants. Carbonation efficiency is being considered a major hurdle

for the development of economically viable sequestration technologies. Accordingly, the objective of this project 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 communition and without heat treatment, while lowering the temperature and pressure conditions of the carbonation reactions.

1.3. Research design

This research program can be divided into the following three tasks, as described in the research proposal. Under Task 1 "Surface activation", a selection of magnesium rich minerals was used as carbonation feedstock materials. Physical and catalytic surface activation studies were conducted in these minerals to promote their inherent carbonation reactivity. The activated materials were then characterized by N_2 and CO_2 adsorption isotherms, thermogravimetric studies, microscopy and X-ray to characterize their surface properties and assess their potential as carbonation minerals. Task 2 "Active carbonation" conducted integrated carbonation studies on the raw materials and their activated counterparts. The carbonation activity was quantitatively determined by the increase of the weight of solid products and the percent of stoichiometric conversion. Finally, Task 3 "Preliminary economic assessment" evaluated the economic viability of the proposed active carbonation concept from a thermodynamic standpoint.

2. EXECUTIVE SUMMARY

Mineral carbonation, that involves the reaction of CO_2 with non-carbonate minerals to form stable mineral carbonates, has been recently proposed as a promising CO_2 sequestration technology due to the vast natural abundance of these raw minerals, the long term stability of the mineral carbonates formed, and the overall process being exothermic, and therefore, potentially economic viable. However, current mineral carbonation studies require extensive pulverization of the raw minerals, long reaction times (>6 hours) and extremely high partial pressures of CO_2 at >115 atm. 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. The novel concept proposed here focuses on surface activation to accelerate the carbonation reaction efficiency. The overall objective of the proposed research program is the development of an active carbonation process that can ultimately evolve into an integrated CO_2 sequestration module for Vision 21 plants.

In this project, several activation methods were investigated, including physical activation with steam and air, and chemical activation using a suite of acids and bases. N_2 and CO_2 adsorption isotherms, SEM, and TGA studies were conducted to characterize the properties of the samples prior and after treatment. Carbonation experiments were also conducted on selected samples and the results are summarized below.

The studies conducted showed that the surface area of the raw serpentine, which is about 8 m^2/g, can be increased through physical and chemical activation methods to nearly 330 m^2/g. 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 17m^2/g. 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. Therefore, the proposed active carbonation concept can successfully increase the exposure of the reactive surface, and hence, accelerate the carbonation reactions presumably by orders of magnitude.

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, 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 m^2/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 communition (<37 μm).

Finally, this project has been awarded a Phase II, where the active carbonation process developed during this Phase I will be optimized in order to design a CO_2 sequestration module.

3. EXPERIMENTAL PROCEDURES

3.1. Study samples

Current samples available at our laboratories include serpentine (antigorite) from Cedar Hills Quarry, SE Pennsylvania, serpentine (lizardite) from Interstate 5 roadcut, SW Oregon; and olivine (forsterite) from Twin Sisters Deposit, NW Washington. These samples have been provided by the DOE-Albany Research Center and are widely used by other groups working on mineral carbonation. The Phase I of this project so far has focused on the serpentine sample from Cedar Hills.

3.2. Sample characterization

The raw and activated Cedar Hills serpentine samples were characterized by thermogravimetric analyses (TGA) to evaluate their weight loss upon heat treatment. Using a Perkin Elmer TGA 7 at atmospheric pressure, profiles were obtained for a temperature range of $25\,^{o}C$ to $900\,^{o}C$ with a constant heating rate of $10\,^{o}C$ per minute. TGA profiles were obtained in both N_2 and CO_2.

A Quantachrome Autosorb-1 Model ASIT adsorption apparatus was used to characterize the surface area and porosity of the samples, where adsorption isotherms were conducted under N_2 and CO_2 at 77K and 273K, respectively. The BET surface areas were calculated using the adsorption points at the relative pressures (P/P_0) 0.05 - 0.25. The total pore volume, V_{TOT}, was calculated from the amount of vapor adsorbed at the relative pressure of 0.95. The mesopore (pores 2-50 nm in width) size distribution

was calculated using the BJH (Barrett-Joyner-Halenda) equation (4,5), and the micropore volumes were derived from the t-method, where the t values were calculated using the deBoer equation(6). The mesopore volume was then calculated from the difference between the V_{TOT} and the micropore volume.

The chemical composition of the samples was obtained through ICP-AES analyses, using a Leeman Labs PS3000UV inductively coupled plasma spectrophotometer. Solutions and solid samples were analyzed, with the solids samples being dissolved using 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 by approximately 12 hours, followed by cooling in a dessicator.

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

The mineral phases present in each sample were determined by XRD analyses. A Scintag Pad V unit with a vertical theta/2-theta goniometer was used. The unit utilized a Cu-Kα X-ray source and was operated at a voltage of 35kV and a current of 30mA. A

quartz zero background was used to mount the powder samples during XRD analyses. The samples were analyzed over a 2-theta range of 5.0-90.0°, with a step scan rate of 0.1°/minute. Peaks were identified using the ICDD Powder Diffraction Files.

3.3. Activation studies

The Cedar Hills serpentine sample was chosen to undergo the activation experiments due to the availability of existing data from previous studies. The physical activations were performed using steam at $650\,^{o}C$ and air at $630\,^{o}C$ for three hours. The chemical activations utilized using a suite of acids and bases, including H_2SO_4, HNO_3, H_3PO_4, HCl, and NaOH. Typically around 50 g of serpentine were mixed with 200mL of water and 200mL of acid or base at room temperature for approximately 24 hours.

3.4. Carbonation studies

A series of aqueous carbonation experiments using a continuous stirred tank reactor (CSTR) on the parent serpentine sample and the activated samples were conducted at NETL, as previously described (Fauth et al., 2002). The high temperature and pressure experiments were conducted using a 1L Hastelloy C-2000 CSTR unit, while lower temperature and pressure carbonation reactions were performed in a 500mL Hastelloy C-276 CSTR vessel.

4. RESULTS AND DISCUSSION

Several activation methods were investigated, including physical activation with steam and chemical activation using a suite of acids and bases (Maroto-Valer et al., 2001; 2002a; and 2002b). N_2 and CO_2 adsorption isotherms, SEM, and TGA studies were conducted to characterize the properties of the samples prior and after treatment. Carbonation experiments were also conducted on selected samples and the results are summarized below.
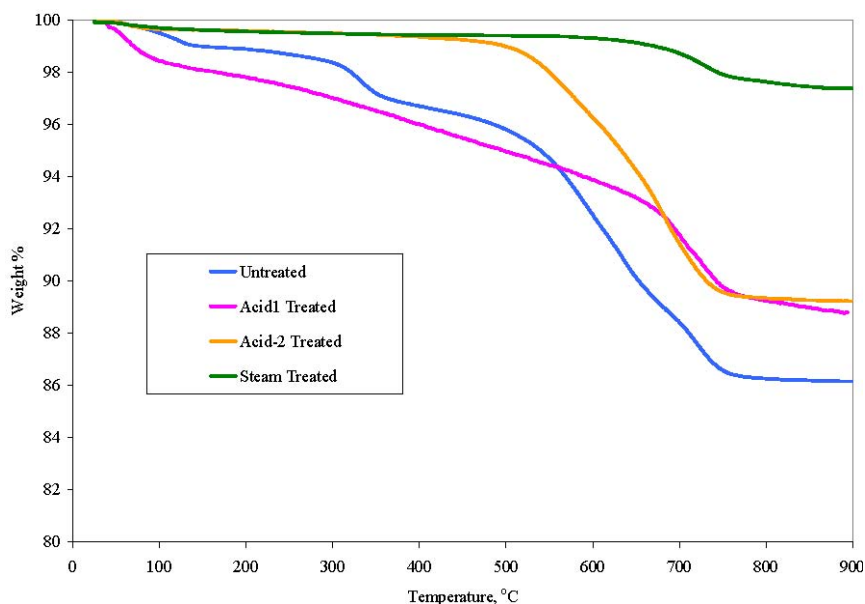
4.1. TGA characterization of raw and activated samples

The N_2 TGA profile for the raw serpentine presents a weight loss of approximately 14%, as shown in Figure 1. At lower temperatures, a small portion of the water is removed and the largest weight loss begins to occur at temperatures approaching $500\,^{o}C$. This weight loss can be attributed to the removal of hydroxyl groups, that are known to inhibit the carbonation reaction by occupying active sites on the mineral surface. Heat treatment can remove these groups and has been shown to increase carbonation efficiency, but it must be performed at elevated temperatures $(600 - 650\,^{o}C)$ to be effective (5). The TGA profiles of the steam and the air activated samples, also shown in Figure 1, show that most of the water has been removed during the high temperature activation. However, these temperatures are higher than those of a typical flue gas, and activation at such high temperatures would require additional energy input.
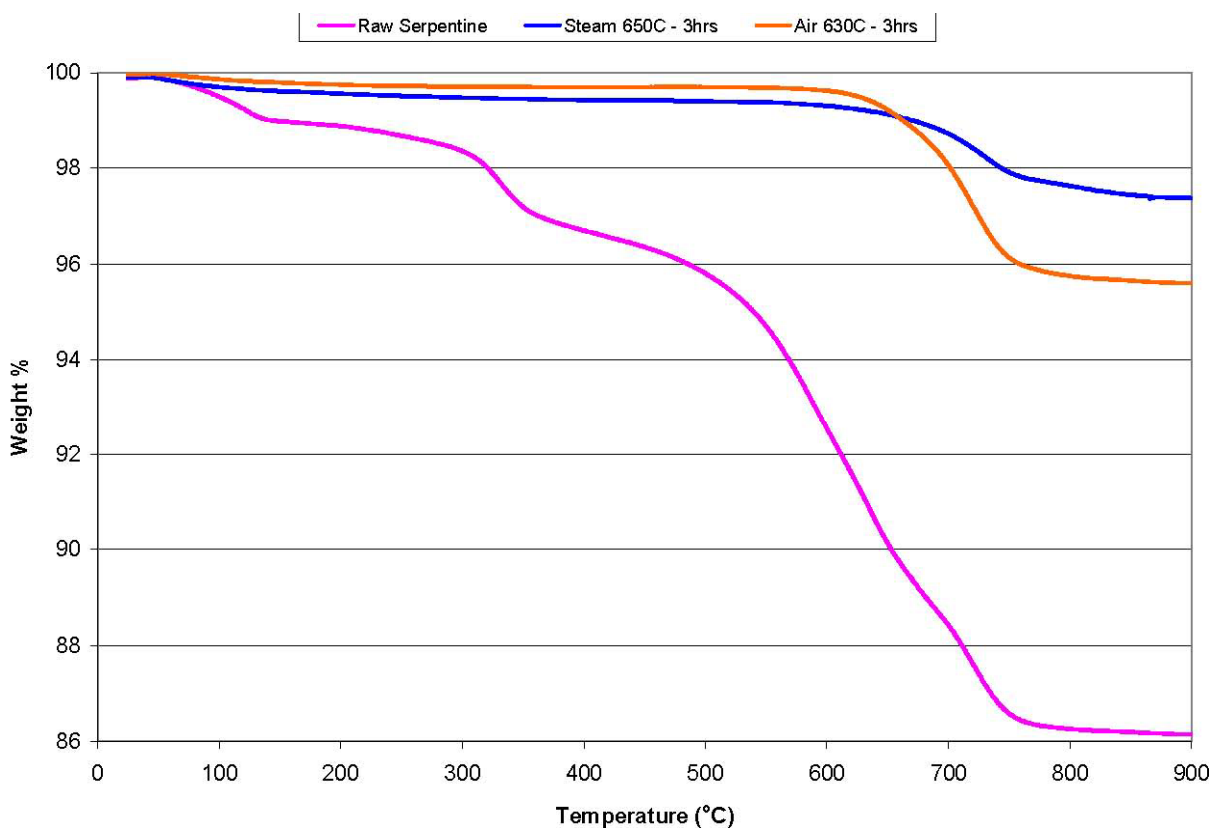
Figure 1. N_2 TGA profile of the raw and physically activated Cedar Hills serpentine.

Thermogravimetric analysis in N_2 and CO_2 were also conducted on the parent serpentine and its chemically activated counterparts, and Figure 2 shows the TGA profiles in N_2. The parent serpentine lost around 15wt%, where this weight loss can be attributed to the removal of hydroxyl groups that are known to inhibit the carbonation reaction by occupying active sites on the mineral surface. In contrast, the chemically activated samples (acid-1: HNO_3, and acid-2: H_2SO_4) lost ~11wt%, and their weight loss is shifted to higher temperatures indicating that the activation process acted selectively removing low-temperature (< 600°C) hydroxyl groups. The TGA profile of the steam activated sample shows that most of the water has been removed during the high

temperature activation (Figure 2), and its weight loss is only ~3%. Therefore, physical activation is more effective than chemical activation in terms of removing the weight loss.


Figure 2. N_2 TGA profile of the raw and activated serpentines.

4.2. Porous texture characterization of raw and activated samples

Adsorption isotherms (N_2-77K) conducted on the raw and treated serpentine samples. Figure 3 shows the N_2-77K adsorption isotherms for the raw sample and the chemically activated samples. The BET surface area, total pore volume, and average pore diameter of the raw sample and the activated samples calculated from the above isotherms are presented in Table 1.

The isotherms showed that the adsorbed volume increases significantly for the activated samples compared to that of the raw serpentine sample, indicating that the activation process has increased the porosity of the activated samples (Figure 3).
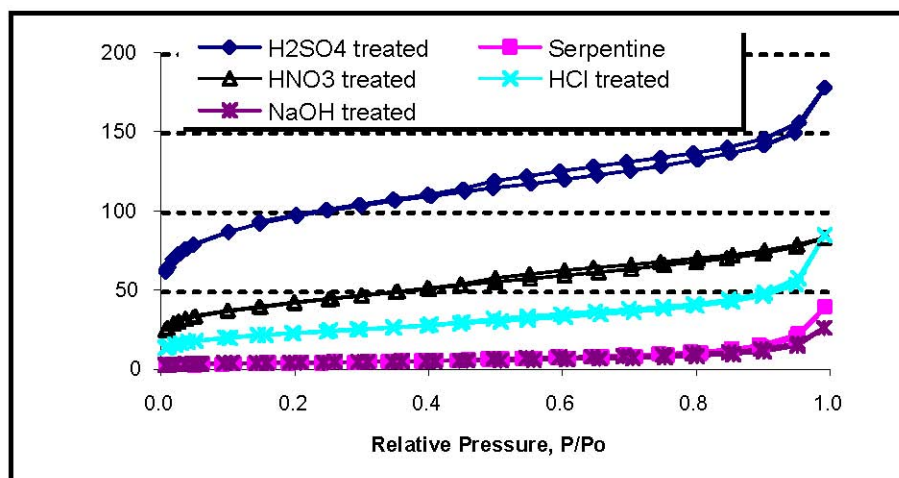
Figure 3. N_2 77K adsorption isotherms of the raw and chemically activated serpentine samples.

The raw sample has a type 2 isotherm, which is concave to the P/Po axis at the low relative pressure, then almost linear and finally convex to the P/Po axis. This isotherm type is due to the formation of an adsorbed layer whose thickness increases progressively with increasing relative pressure and is typical for non-porous or macroporous adsorbents. The isotherms of the chemically treated samples, with the exception of the NaOH treated, are different from that of the parent serpentine and show an increase in the surface area compared to the raw Cedar Hills serpentine (Table 1). The isotherm for the H_2SO_4 treated sample has a sharp increase at low relative pressures that is due to micropore filling. The isotherm exhibits then a hysteresis loop at high relative pressures that is associated with the filling and emptying of mesopores by capillary

condensation, where mesopores were also observed for the parent samples. Therefore, the chemical treatment produces a significant amount of micropores in the sample, and also some mesopores.

The porosity data in Table 1 shows that the surface area of the raw serpentine, which is about 8 m^2/g, can be increased through physical and chemical activation methods to nearly 330 m^2/g. 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 active carbonation of this invention is 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).

The chemical activation seems to be more effective than the physical activation in terms of increasing the surface area (330 vs. 17m^2/g, Table 1). The pore volume shows a similar trend, where the activation increases the pore volume to values up to 0.234 ml/g compared to only 0.017 ml/g for the parent untreated sample (Table 1). The pore

diameter of the chemically activated samples is smaller than the parent serpentine, particularly for the chemically activated samples, whose diameter is only 2.8 nm compared to 8.5 nm for the parent sample.

Table 1. BET surface area, pore volume and average pore size of the samples investigated.

Sample	BET surface area m^2/g	Pore Volume ml/g	Average Pore Diameter nm
Untreated sample	8	0.017	8.5
Steam treated, 650°C	16	0.035	7.9
Air treated, 630°C	17	0.034	7.9
Sulfuric acid	330	0.234	2.8
Nitric acid	147	0.120	3.3
Phosphoric acid	122	0.097	3.2
Hydrochloric acid	104	0.092	3.5
Sodium hydroxide	15	0.023	6.1

CO_2 adsorption isotherms at 277K were also conducted on the sulfuric activated serpentine sample and the raw sample, and the Langmuir reported surface area of the activated serpentine was $242m^2/g$, compared to only $9m^2/g$ for the raw sample. Therefore, compared to the raw serpentine, the chemically activated samples have

developed significant microposity (i.e. pores < 2nm). This is consistent with other studies that have shown that optimization of acid treatment of antigorite with sulfuric acid resulted in dissolution of magnesium leaving solid silica (purity over 99%) with high surface areas of over 400 m^2/g (Kosuge et al, 1995). Similarly, previous studies have shown that using concentrated hydrochloric acid (40%) at temperatures above 250°C resulted in surface areas up to 200 m^2/g (Girgis et al., 1976). 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., 2001). Therefore, the proposed mineral activation is expected to facilitate the magnesium dissolution reactions.

4.3. ICP/AES studies

The objective of the acid treatment process is to extract the Mg^{2+} for its subsequent reaction with CO_2. Accordingly, the Mg^{2+} content of the solutions as well as the produced solids were measured by ICP/MS, and Table 2 summarizes the % of Mg^{2+} extracted in solution. The sulfuric acid extraction presented the highest extraction yield, where over 70% of all the magnesium present in the parent serpentine samples was dissolved in solution. For the other acid activations investigated, the extraction yields are significantly lower. For the purposes of comparison, Table 2 also includes the maximum extraction yield reported for acetic acid (Kakizawa et al., 2001), which is lower than that reported using sulfuric acid (48% vs. 71%). Furthermore, the optimization of acid

treatment of antigorite with sulfuric acid has been reported to result in dissolution of magnesium leaving high purity (>99%) solid silica (Kosuge et al, 1995).

Table 2. Percentage of magnesium extracted for the treated samples, as determined by ICP/MS.

Treatment	% Mg^{2+} in solution	Activation conditions
Sulfuric acid	71	25°C, 12 hours
Hydrochloric acid	21	25°C, 12 hours
Phosphoric acid	25	25°C, 12 hours
Acetic acid	48*	60°C, 4 hours*

*Maximum extraction yield reported in the literature using acetic acid (Kakizawa et al., 2001)

4.4. SEM studies

Figure 4 shows the SEM pictures of the raw and of the HNO_3 chemically activated serpentines. The SEM studies show that at the same magnification level, the activated sample presents more needle-like particles than the raw material. Images taken at greater magnification level showed that the structure of the activated serpentine had been significantly altered.
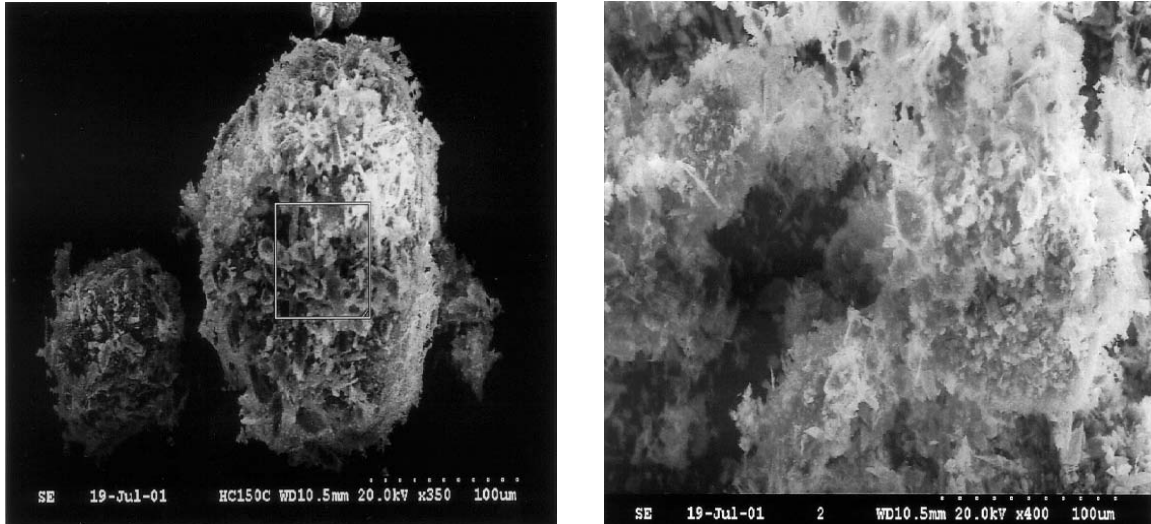
Figure 4. SEM images of the raw (left) and HNO3 chemically activated (right) serpentine samples.

4.5. Carbonation studies

A series of aqueous carbonation experiments using a CSTR reactor on the parent serpentine sample and the activated samples were also conducted, and the results are summarized in Table 3. The parent serpentine is very unreactive and it only shows 8% conversion at high temperatures and pressures confirming the need to activate the mineral prior to carbonation. The steam activated serpentine had a 73% conversion to magnesite at 155°C and 1850 psig after 1 hour reaction. However, as previously described, heat treatment is very energy intensive, and therefore, this steam activation route was not further considered. Following the serpentine extraction (100μm) with H_2SO_4, the $MgSO_4$

was reacted with CO_2 in solution at 20°C and low pressures (600psi) and the conversion as determined by the CO_2 consumption was ~54%. After extraction with H_2SO_4, the $MgSO_4$ was reacted with NaOH to precipitate $Mg(OH)_2$ that was subsequently reacted with CO_2 at 20°C and 600psi, and the conversion was ~73%. This is indeed a significant improvement over previous studies that required temperatures over 185°C and very high pressures (>1950 psi) as well as extensive communition (37µm) (Fauth et a., 2002; O'Connor et al., 2000).

Table 3. Carbonation condition and % conversion from CO_2 consumption.

Sample	% Conversion	Carbonation conditions
Parent	8	155°C, 1850psig, 1 hour
Steam	70	155°C, 1850psig, 1 hour
$Mg(OH)_2$	73 (77[a])	20°C, 650psig, 3 hours
$MgSO_4$	54	20°C, 650psig, 6 hours
Mg acetate	30	20°C, 650psig, 3 hours

[a] Value in brackets calculated from the amount of carbonate measured on the precipitate.

XRD and SEM studies have also being conducted to confirm the formation of magnesite following the carbonation reaction. Figure 5 shows SEM pictures of the serpentine mineral before and after it has sequestered CO_2. The SEM picture on the left corresponds to amorphous serpentine mineral $(Mg_3Si_2O_5(OH)_4)$, while the SEM picture

on the right corresponds to crystalline hydrated magnesite mineral (Mg_3CO_3), as also confirmed by XRD and ICP analyses.
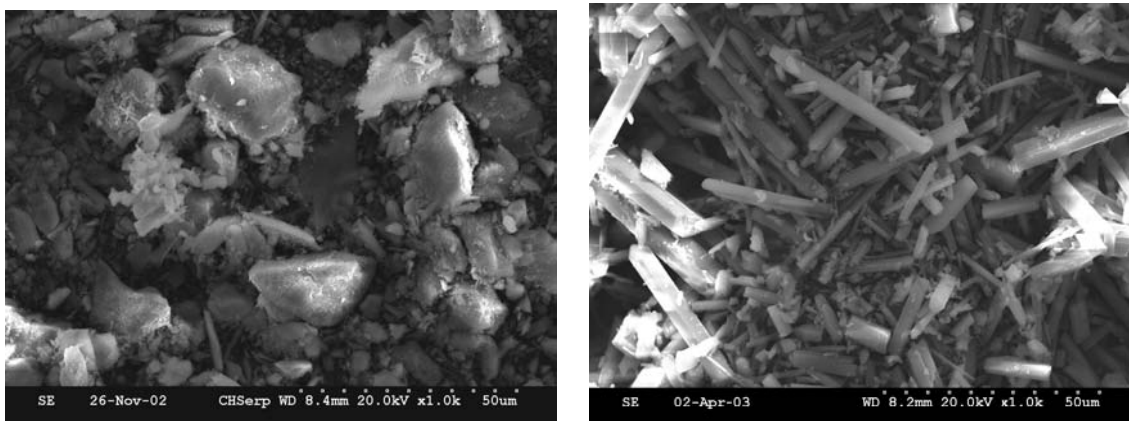
Figure 5: SEM pictures of a serpentine mineral sample before and after it has sequestered CO_2: serpentine mineral before carbonation (left); and after carbonation (right).

4.6. Preliminary economic/thermodynamic analysis

For a sequestration process to have the potential to become industrially feasible, it must have acceptable kinetics as well as acceptable energy needs. Accordingly, we have conducted a preliminary study of the thermodynamics involved in the process using sulfuric acid by using standard thermodynamic data at 298K has been conducted (Dean, 1992; Weast et al., 1988). The reaction of serpentine with sulfuric acid is exothermic, as shown below, and therefore, can provide energy to the overall sequestration process:
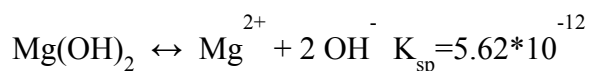
$$Mg_3Si_2O_5(OH)_4 + 3H_2SO_4 \quad 3MgSO_4 + 5H_2O + 2SiO_2 + 236 \text{ kJ/mole}$$

After extraction with H_2SO_4, the $MgSO_4$ can be reacted with NaOH to precipitate $Mg(OH)_2$ following an exothermic reaction:

$$MgSO_4 + 2NaOH \quad Mg(OH)_2 + Na_2SO_4 + 139 \text{ kJ/mole}$$

Furthermore, the $Mg(OH)_2$ precipitates very readily due to its low solubility product constant, K_{sp}:

$$Mg(OH)_2 \leftrightarrow Mg^{2+} + 2 \, OH^- \quad K_{sp}=5.62*10^{-12}$$

The $Mg(OH)_2$ was subsequently reacted with CO_2 in solution at 20°C and 600psig and the conversion was ~75% again in an exothermic reaction under very mild conditions, 25°C and 600psig:

$$Mg(OH)_2 + CO_2 \quad MgCO_3 + H_2O + 79 \text{ Kcal/mole}$$
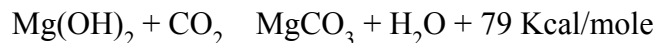
Consistent with this work, previous studies have reported that carbonation of $Mg(OH)_2$ has conversions as high as 90% at low temperatures and pressures, 20°C and 255psig, and formed a precipitate that was mainly $MgCO_3*3H_2O$ (Park et al., 2002). Therefore, the formation of $Mg(OH)_2$ is a very interesting alternative because of the inherent low carbonation processing conditions of $Mg(OH)_2$ compared to other processes (>185°C and >1950 psi) and the reaction being exothermic. Finally, an inherent advantage of carrying out the carbonation reaction at lower temperatures is that CO_2 solubility in water decreases with increasing temperature (Crovetto and Wood, 1992), where the CO_2 solubility at 0°C is 0.3346 g of gas/100g of water, and at 60°C the solubility decreases to 0.0576 g of gas/100g of water.

The solubility product constant for magnesite, $MgCO_3$ is also very low and therefore favors its precipitation:

$$MgCO3 \leftrightarrow Mg^{2+} + CO3^{2-} \quad Ksp=6.82*10^{-6}$$
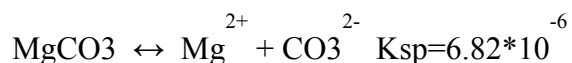
Furthermore, this work also calculated that for all the pH values (1-14), the $MgCO_3$ has lower solubility than the $Mg(OH)_2$ and therefore, will precipitate preferentially.

Finally, in order to minimize the costs associated with the use of acids in a process, it should be possible to recover or regenerate the acid. In order to achieve this, the $MgSO_4$ was reacted directly with CO_2 at (20°C) and low pressures (600psi) and the conversion as determined by the CO_2 consumption was ~54%. Again the overall reaction is exothermic:

$$MgSO_4 + H_2CO_3 \quad MgCO_3 + H_2SO_4 + 49kJ/mole$$

Alternatively, the acid can be recovered following Step 4 of this invention disclosure.

5. CONCLUSIONS

The objective of the proposed novel active carbonation concept is to promote and accelerate reaction rates and efficiencies through surface activation to the extent that extensive mineral particle communition and high temperatures and pressures are not required. In this project, several activation methods were investigated, including physical activation with steam and air, and chemical activation using a suite of acids and bases. N_2 and CO_2 adsorption isotherms, SEM, and TGA studies were conducted to characterize the properties of the samples prior and after treatment. Carbonation experiments were also conducted on selected samples and the results are summarized below.

The studies conducted showed that the surface area of the raw serpentine, which is about 8 m^2/g, can be increased through physical and chemical activation methods to nearly 330 m^2/g. 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 17m^2/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, heat treatment is very energy intensive. For the chemical activation, the most effective acid used was sulfuric acid, that resulted in surface areas of over 330 m^2/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 communition (<37 μm).

In summary, this work has developed a method to extract the Mg^{2+} from serpentine, either as $MgSO_4$ or $Mg(OH)_2$ for its subsequent reaction with CO_2. This allows to conduct the CO_2 sequestration at only 20°C, 650psig, while previous work needs higher temperatures and pressures (155°C, 1850psig). Finally, this project has been awarded a Phase II, where the active carbonation process developed during this Phase I will be optimized in order to design a CO_2 sequestration module.

6. LIST OF PUBLISHED JOURNAL ARTICLES, COMPLETED PRESENTATIONS, PATENTS, AND STUDENTS RECEIVING SUPPORT FROM THE GRANT

Conference Presentations and Proceedings

• M. M. Maroto-Valer, D. J. Fauth, M. E. Kuchta, Y. Zhang, J. M. Andrésen, and Y. Soong, Study of magnesium rich minerals as carbonation feedstock materials for CO_2 sequestration, 18th Annual International Pittsburgh Coal Conference, 2001, Paper 23-01.pdf (CD-ROM publication).

• M.M. Maroto-Valer, M.E. Kuchta, Y. Zhang and J.M. Andrésen, Integrated carbonation: a novel concept to develop a CO_2 sequestration module for power plants, Sixth International Conference on Greenhouse Gas Control Technologies, 2002, Paper ZEP1.pdf (CD-ROM publication).

• M.M. Maroto-Valer, Y. Zhang, M.E. Kuchta, and J.M. Andrésen, Activation of serpentine minerals for enhanced CO_2 sequestration, 19th Annual International Pittsburgh Coal Conference, 2002, Paper 127.pdf (CD-ROM publication).

• M. M. Maroto-Valer, D. J. Fauth, M. E. Kuchta, Y. Zhang, J. M. Andrésen, and Y. Soong, Development of a CO_2 sequestration module by integrating mineral activation and aqueous carbonation, Second Annual Conference On Carbon Sequestration, In Press.

Provisional Patent

The following provisional patent was partially based on work supported by this grant.

Title: Process for Sequestering Carbon Dioxide and Sulfur Dioxide

Inventors: M. M. Maroto-Valer, D. J. Fauth, M. E. Kuchta, Y. Zhang, and J. M. Andrésen.

Date: May 9, 2003

Students supported under this grant

• Matthew E. Kuchta, MSc graduate student in the Department of Energy and Geo-Environmental Engineering, The Pennsylvania State University. His thesis to be defended this summer on the topic of this project.

7. ACKNOWLEDGEMENTS

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