Ex-Situ and In-Situ Mineral Carbonation as a Means to Sequester Carbon Dioxide

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ABSTRACT

The U. S. Department of Energy's Albany Research Center is investigating mineral carbonation as a method of sequestering CO_2 from coal-fired-power plants. Magnesium-silicate minerals such as serpentine [$Mg_3Si_2O_5(OH)_4$] and olivine (Mg_2SiO_4) react with CO_2 to produce magnesite ($MgCO_3$), and the calcium-silicate mineral, wollastonite ($CaSiO_3$), reacts to form calcite ($CaCO_3$). It is possible to carry out these reactions either ex situ (above ground in a traditional chemical processing plant) or in situ (storage underground and subsequent reaction with the host rock to trap CO_2 as carbonate minerals).

For ex situ mineral carbonation to be economically attractive, the reaction must proceed quickly to near completion. The reaction rate is accelerated by raising the activity of CO_2 in solution, heat (but not too much), reducing the particle size, high-intensity grinding to disrupt the crystal structure, and, in the case of serpentine, heat-treatment to remove the chemically bound water. All of these carry energy/economic penalties. An economic study illustrates the impact of mineral availability and process parameters on the cost of ex situ carbon sequestration.

In situ carbonation offers economic advantages over ex situ processes, because no chemical plant is required. Knowledge gained from the ex situ work was applied to long-term experiments designed to simulate in situ CO_2 storage conditions. The Columbia River Basalt Group (CRBG), a multi-layered basaltic lava formation, has potentially favorable mineralogy (up to 25% combined concentration of Ca, Fe^{2+}, and Mg cations) for storage of CO_2. However, more information about the interaction of CO_2 with aquifers and the host rock is needed. Core samples from the CRBG, as well as samples of olivine, serpentine, and sandstone, were reacted in an autoclave for up to 2000 hours at elevated temperatures and pressures. Changes in core porosity, secondary mineralizations, and both solution and solid chemistry were measured.

INTRODUCTION

Carbon sequestration has been proposed as a method to decrease the amount of CO_2 released to the atmosphere. A significant worldwide effort is being made to assess the technological and economic feasibility of both in situ (below ground) and ex situ (above ground in a traditional chemical process) sequestration. Because of perceived economic advantages and the fact that in

situ processes are similar to known technologies such as enhanced oil recovery (EOR) and enhanced coal-bed methane recovery more work has focused on in situ sequestration. EOR processes pump CO_2 into an oil reservoir to increase oil recovery. The major difference between sequestration and EOR is that in EOR the goal is to recover as much CO_2 (and oil) as possible while in sequestration the goal is to store the CO_2 forever i.e. zero recovery. However, in any in situ process legacy issues such as leakage would be difficult to solve. And therefore ex situ processes that have the potential to minimize legacy issues, albeit at a price, are also being considered.
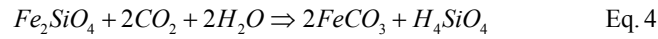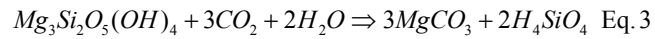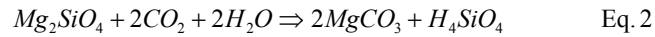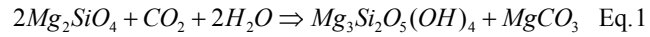
In 1998 the Department of Energy's Albany Research Center (ARC) began investigating ex situ carbon sequestration. At the onset it was recognized that any ex situ process would have to meet certain minimum requirements:

1) The resource used to store the CO_2 must be large enough to store a significant amount of the CO_2 produced from a point source such as a coal-fired power plant.
2) The mineral resource must be near the power plant to minimize transportation costs.
3) The product used to store the CO_2 must be environmentally benign and stable so that decomposition does not release CO_2.
4) The use of energy for the process must be kept to a minimum.
5) The economic impact of the process on the cost of electricity must be kept to a minimum.

Initially, work focused on a process proposed by Lackner (1997 a, b) at Los Alamos National Laboratory (LANL). The LANL process is based on a U.S. Bureau of Mines process to produce magnesium from olivine (Mg_2SiO_4) (Huston 1942, 1945). In this process olivine is dissolved in HCl to produce silica and $MgCl_2$ followed by electrolysis of the $MgCl_2$ to produce magnesium. The process is technically but not economically feasible. A significant problem is separating $MgCl_2$ from silica, which forms a gel. In the LANL aqueous mineral carbonation process, $MgCl_2$ undergoes a series of crystallization/dehydration steps and is converted to $Mg(OH)_2$. Silica gel is still a problem, but the primary problem is the energy required to remove the waters of hydration from the $Mg(OH)_2$ after the HCl dissolution. Nilsen (999) conducted a careful material and energy balance which revealed that the energy requirements of the process were approximately 4 times the amount that would be gained by burning coal to produce the CO_2.

At about the same time O'Connor (2000) proposed an alternate aqueous process based on the geochemical process known as serpentinization. In the geologic process, magnesium-silicates such as olivine are altered by hydrothermal fluids to produce hydrated magnesium silicates such as serpentine. If the hydrothermal fluid contains CO_2, then magnesite ($MgCO_3$) is also formed (eq.1). If the activity of CO_2 is high enough, only the carbonate and silicic acid and/or free silica form (eq. 2). Hydrated magnesium silicates will also carbonate (eq. 3). Some

magnesium silicate minerals also contain both Ca and/or Fe^{2+} and these will also carbonate contributing to the total carbon sequestration potential (eqs. 4 and 5).

$$2Mg_2SiO_4 + CO_2 + 2H_2O \Rightarrow Mg_3Si_2O_5(OH)_4 + MgCO_3 \quad \text{Eq.1}$$
$$Mg_2SiO_4 + 2CO_2 + 2H_2O \Rightarrow 2MgCO_3 + H_4SiO_4 \quad \text{Eq.2}$$
$$Mg_3Si_2O_5(OH)_4 + 3CO_2 + 2H_2O \Rightarrow 3MgCO_3 + 2H_4SiO_4 \quad \text{Eq.3}$$
$$Fe_2SiO_4 + 2CO_2 + 2H_2O \Rightarrow 2FeCO_3 + H_4SiO_4 \quad \text{Eq.4}$$
$$CaSiO_3 + CO_2 + 2H_2O \Rightarrow CaCO_3 + H_4SiO_4 \quad \text{Eq.5}$$

The advantage of these reactions is that the carbonate precipitates directly from the solution, thus avoiding the energy-intensive water removal steps. The process does not dissolve the silica, thus eliminating the solid liquid separation problems associated with silica gel.

MINERAL AVAILABILITY

The large tonnage of mineral reactant required for mineral sequestration makes it necessary to locate the mineral carbonation plant at the mine mouth, rather than at the CO_2 point source. In North America, large deposits of olivine and serpentine occur along both coasts, but not in the interior, which places limitations on the application of the mineral-carbonation technology. O'Connor (2004 a, b) identified seven regions (figure 1) in the U.S. that contain significant mineral deposits that could be used for ex situ mineral carbonation. Table 1 shows the total annual CO_2 emissions from

Figure 1. Ultramafic mineral carbonation regions.

coal-fired power pants within 100- and 200-mile radii of the deposits and the annual amount of ore from the deposit required assuming 100% carbonation of the ore and sequestration of 100% of the CO_2. R_{CO2} represents the ratio of the mass of ore required to carbonate one unit mass of CO_2, assuming 100% conversion of Fe^{+2}, Mg and Ca cations available in the mineral. The lower R_{CO2} (~1.6) for olivine as opposed to serpentine (R_{CO2} = ~ 2.2) means considerably more serpentine would have to be mined to sequester the same amount of CO_2, and more yet for the wollastonite (R_{CO2} = ~2.7). The regional ore demand totals are very large. However, with two exceptions (Regions 5 and 7), the ultramafic mineral resources far exceed these demands. Also note that the amount of ore is 4.6 (olivine) to 7.5 (wollastonite) times the amount of coal required.
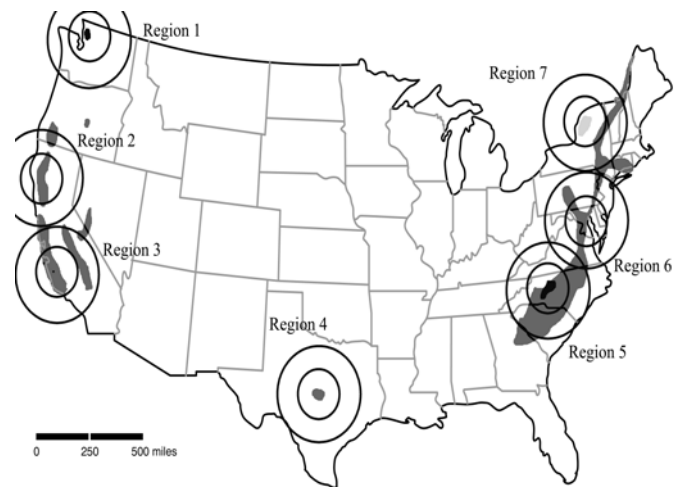
Table 1. Annual CO_2 emissions and minimum ore requirements within each region

Region	Mining District/Deposit	Mineral	Size of Deposit	R_{CO2}	Radius miles	Coal MT	CO_2 MT	Ore MT
1	Twin Sisters, WA	Olivine (Dunite)	1.8 Gt	1.8	0-100	5	13	23
					100-200	2	5	9
2	Trinity-Siskyou Mtn, CA-OR	Serpentine (Lizardite)	Large	2.5	0-100	4	10	26
					100-200	0	0	0
3	Coast range Southern CA	Serpentine (Lizardite)	Large	2.5	0-100	4	10	26
					100-200	0	0	0
4	Llano Uplift, TX	Serpentine (Lizardite)	>1 GT	2.5	0-100	13	30	75
					100-200	18	42	104
5	Asheville, NC	Olivine	200 MT	1.8	0-100	20	54	98
					100-200	49	133	239
6	State Line, MD-PA	Serpentine (Antigorite)	Large	2.1	0-100	39	106	222
					100-200	46	125	262
7	Willsboro, NY	Wollastonite	14 MT	2.8	0-100	4	11	30
					100-200	24	65	182

MINERAL PRETREATMENT

Magnesium-silicate minerals were initially chosen for study because of their abundance and occurrence near coal-fired power plants in the Northwest, the Northeast and Texas (O'Connor 2004). Specific minerals studied were Southwest Oregon lizardite (serpentine), Cedar Hill antigorite (serpentine), and Twin Sisters olivine (dunite). Later investigations included wollastonite. Head analyses of the mineral reactants are shown in table 2. The lower magnesium concentration in the serpentine minerals is due to the presence of ~14% chemically bound water.

Table 2. Head analyses.

	Serpentine (antigorite)	Serpentine (lizardite)	Dunite Olivine	Wollastonite
	%	%	%	%
Ca	0.019	0.314	0.0112	32.9
Fe^{+2}	2.61	2.40	6.0	0.53
Fe^{+3}	1.29	2.02	<0.01	0.001
Mg	26.1	23.9	31.1	0.274
Si	17.3	18.0	18.9	22.7
Water[1]	0.440	1.59	0.070	0.05
LOI[2]	15.1	14.8	0.390	3.23
R_{CO2}[3]	2.03	2.12	1.64	2.70

1 - Free moisture, measured as the weight loss after 1 hour at $105^{o}C$, in air.
2 - Loss on Ignition, measured as the weight loss after 1 hour at $1000^{o}C$, in argon.
3 - Ratio of ore mass that must be processed to carbonate 1 unit mass of CO_2, assuming 100% carbonation of all Ca, Fe^{+2}, and Mg.

In an actual commercial sequestration process not all the mineral will react. The amount that reacts is determined by the pretreatment of the mineral and the reaction conditions. Both thermal and mechanical means can be effective in accelerating the reaction rate. Mechanical pretreatment reduces the mean particle size of the minerals, while thermal pretreatment removes chemically bound water, which changes the structure of the mineral and may increase the porosity and surface area. McKelvy (2002) and Chizmeshya (2002) described thermal activation and computational modeling studies, respectively, conducted at Arizona State University. The extent of reaction has a substantial effect on the amount of mineral required and the cost of mineral carbonation. ALRC has run over 600 experiments to elucidate these variables and the results have been published in a series of papers by Gerdemann, Nilsen, O'Connor, Penner, and Rush 2004.

Because without some sort of activation the extent of carbonation of serpentine in one hour is approximately 10%, a great deal of study has focused on serpentine activation. Thermal activation, which removes the waters of hydration, significantly improves the reaction rate. One effective heat treatment is to heat the serpentine to 630°C under an inert atmosphere. The energy consumption required for this heat treatment is process is estimated to be 290 and 325 kW•h/ton for antigorite and lizardite, respectively. It is also possible to mechanically activate serpentine with very high-energy attrition grinding. This destroys the crystal structure, making a highly reactive amorphous material. Unfortunately the energy cost of this is significantly higher than the heat treatment and would probably use all the energy produced in the coal fired power plant.

For olivine, wollastonite and heat-treated serpentine, the most effect way to accelerate the reaction is to increase the surface area by decreasing the particle size. The energy required to re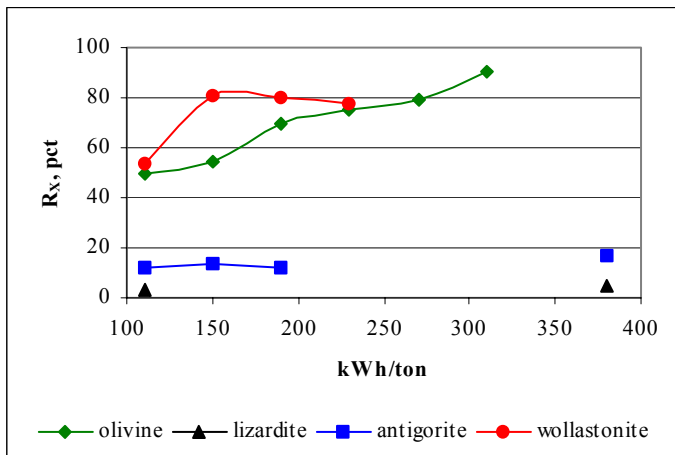duce the particle size to 200 mesh (75 microns μm) is estimated to be 11 kW•h/ton. However, with 200-mesh olivine particles the extent of reaction (R_x) is only 14% in one hour or 52% in 3 hours.

Figure 2. Grinding energy versus Rx.

Further particle size reduction was investigated by use of conventional rod- and ball-milling techniques, as well as ultra-fine grinding using a scalable stirred-media detritor (SMD) mill. The grinding energy

required for specific size reduction was calculated for olivine and the two serpentine minerals using data derived from pilot-scale comminution tests conducted on the ores and a formula described by Bond (1952). Energy consumption for ultra-fine grinding was determined by direct measurement from the SMD mill. Four test series were conducted on the primary mineral reactants to evaluate the sensitivity of mineral reactivity (R_X) to grinding energy (Figure 2). While olivine showed a nearly linear relationship between mechanical energy input and R_X, wollastonite activation peaked at a much lower energy input, with no gain at higher energies. In contrast, both serpentine minerals show virtually no increase in R_X at energies up to nearly 400 kW•h/ton.

Additional studies using a laboratory-scale attrition-grinding mill showed significant activation of the serpentines but the estimated energy consumption was extremely high, and activation of serpentine by mechanical means alone appears impractical. The attrition mill is a chamber filled with 3-mm stainless-steel balls stirred at 800 rpm by a shaft with 3 pins (impellors) mounted such that the top and bottom impellers are parallel with the middle one but offset by 90°. One hour in the attrition mill reduces particle size to ~ 50% (D_{50}) minus 2 to 4 μm depending on whether the mill is run wet or dry. Wet milling results in smaller particles, but under the right conditions, dry milling can produce non-crystalline material that is significantly more reactive. Unfortunately, attrition grinding is more energy-intensive than conventional grinding and may not be scaleable to the size required for carbon sequestration.

CHEMICAL REACTION

The magnesium-silicate mineral reactions were carried out in an aqueous solution of 0.64M $NaHCO_3$, 1M NaCl in a batch autoclave. The 0.64M $NaHCO_3$ solution concentration is the solubility limit of the bicarbonate at room temperature. This bicarbonate solution was found to significantly improve the reaction rate for magnesium-silicate minerals. The rate of carbonation of the calcium-silicate mineral, wollastonite, was not increased significantly by the carbonate solution and therefore most of the wollastonite experiments were carried out in distilled water.

Because the reaction rate is sensitive to particle size, which is determined largely by feed preparation, it is difficult to compare test series with differently prepared feeds. For this reason and to make comparisons easier, the extent of reaction in one hour was normalized by dividing it by the maximum extent of reaction in one hour for that particular material. Figure 3 shows the effect of raising the reaction temperature from room temperature to 250°C on the extent of reaction. For Twin Sisters olivine, the maximum extent of reaction in one hour (50%) occurred at 185°C. Two factors work against raising the temperature: (1) aqueous CO_2 activity in solution decreases, and (2) the reaction becomes thermodynamically less favorable. Thus, above some temperature, the extent of reaction decreases.

This temperature is approximately 185°C for olivine and 155°C for heat-treated serpentine. Wollastonite has a broad peak beginning at 100°C.
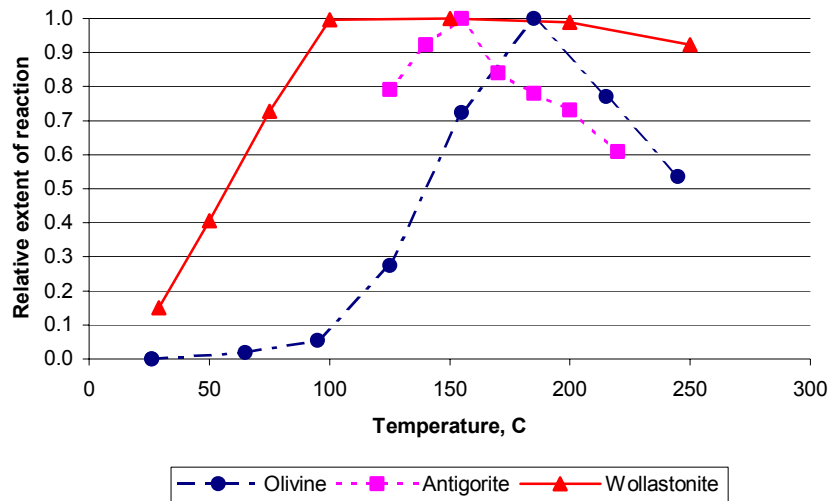

Figure 3. The effect of temperature.

Raising the partial pressure of CO_2 also increases the extent of reaction in one hour. This is due to the increased activity of aqueous CO_2, and pressure also pushes the reaction towards completion because the pressure decreases due to the conversion of $CO_2(g)$ into solid $MgCO_3$.

Previous work by Ityokumbu (2001) and Gerdemann (2003) has shown that olivine reacts according to the shrinking-particle model while, serpentine follows the shrinking-core model. In both models, surface area, and thus the particle size, has a significant impact on the reaction rate. O'Connor (2000, 2002) found large unreacted olivine particles and small particles (10 μm) of magnesium-carbonate product. No variation in magnesium content was seen from the surface to the center of the larger particles. This is consistent with the particle surface reacting to release magnesium into solution and then precipitation of small magnesium-carbonate particles from the solution (the shrinking-particle model). Experiments with wollastonite are also consistent with. Thus the most effective way to increase the reaction rate and the extent of reaction is to grind the minerals to as small a size as possible. This, however, carries a significant energy cost and also minimizes the size difference between product and unreacted ore making, the separation and recycle of unreacted ore more difficult.

ENERGY CONSUMPTION

Using the energy data from the mechanical and thermal activation studies plus the extent of reaction measured in the chemical studies, energy consumption can be calculated for mineral carbonation in each of the 7 ultramafic mineral regions (Table 3). The table also includes the total energy consumed in the mineral

preparation, the extent of reaction in one hour achieved with that feed preparation, the amount of ore required to sequester 100% of the CO_2, and finally the parasitic energy loss.

Table 3. Parasitic energy losses

Region	Ore & grade	Pretreatment	Energy kW•h/ton	Rx %	Ore, Kt/day	% Total plant energy
1	Olivine, 100%	-200 mesh	18	16	286	15
		-400 mesh	83	61	75	26
		Ultra fine	233	81	56	55
2-4	Serpentine (lizardite) 100%	-200 mesh	13	9	706	37
		Heat treat – 200mesh	339	40	158	222
5	Olivine, 70%	-200 mesh	19	16	286	22
		-400 mesh	89	61	75	28
		Ultra fine	239	81	56	56
6	Serpentine (antigorite) 100%	-200 mesh	13	12	445	24
		Heat treat – 200mesh	306	62	86	110
		Heat treat – 400mesh	376	92	58	90
7	Wollastonite, 50%	-400 mesh	97	165	165	67
		Ultra fine	167	87	87	61

While the daily ore requirements decrease dramatically with mineral activation, the improved reactivity achieved by the additional pretreatment operations is negated for the most part by the higher energy demand. For example, 15% of the total plant energy is necessary to produce minus 200-mesh Twin Sisters olivine and results in 16% extent of carbonation in one hour. Ultra-fine grinding increases the extent of reaction to 81% but increases the parasitic energy loss to 55%. Parasitic energy losses exceeding 100% indicate that the CO_2 avoided is negative, meaning that more CO_2 is emitted by the pretreatment operation than is sequestered. These problems are most acute for the thermal-activation operations on the serpentine minerals, but the high-energy consumption for the mechanical activation operations on the olivine and wollastonite minerals are also problematic. These calculations assume a single pass of the mineral through the carbonation plant; the successful addition of a recycle stream could reduce the virgin ore demand significantly. However, ultra-fine grinding may make the separation of product from reactant - to produce the recycle stream - difficult.

Even in the best-case scenario, 200-mesh Twin Sisters olivine, 15% of the total energy produced from the coal-fired power plant is used in the carbonation process. In some cases, typically heat-treated serpentine, all of the plant's generated energy is consumed in the mineral pretreatment step. Separating the CO_2, transporting it to the sequestration plant, and operating the sequestration plant will only increase the cost.

PROCESS FEASABILITY STUDY

The National Energy Technology Laboratory (NETL) commissioned a process feasibility study based on using olivine and using a preliminary process design and basis developed at ARC by Nilsen and Penner (2001). In this study by Lyons (2003), a steady-state simulation of the process was created in Aspen® process simulation software, from which capital and operating cost estimates were generated. The study evaluated an olivine-based mineral-carbonation process scaled for sequestration of 100% of the CO_2 emissions from a 1.3 GW coal-fired power plant and was based on the following assumptions:

1) Twin Sisters olivine (Region 1) is utilized for the process, with the sequestration plant located next to the mine site.
2) The mining operation is open pit, and the process products are re-deposited in the depleted pits.
3) Olivine is the mineral reactant, with an ore grade of 100% and MgO concentration of 49%.
4) Olivine is ground to 80% minus 400 mesh (37 μm).
5) 65% reaction efficiency (R_X) with each pass through the process.
6) 60% of the unreacted olivine from the products is separated at 20 μm size and recycled.
7) CO_2 is transported to the plant via pipeline (CO_2 separation costs arenot included in cost estimates).
8) Carbonation conditions include: 2 hour residence time; T = 185°C; P_{CO2} = 150 atm; P_{H2O} = 6.5 atm; 30% solids; carrier solution = 0.64M $NaHCO_3$, 1 M NaCl.

The NETL study evaluated sequestration of approximately 1,100 tons of CO_2 per hour, requiring roughly 2,500 tons of virgin olivine ore plus an additional 800 tons of olivine from an unreacted product recycle loop every hour. Power requirements total 352 MW, with nearly 75% of the total power required for the ore grinding operations. This power represents a 27% energy penalty on the power plant for which the sequestration operation was designed. Sensitivity analyses were conducted to evaluate the impact of reduced reactor residence time and P_{CO2} on the overall sequestration cost and energy demand. These results were used to derive the carbonation costs for the alternative mineral feedstocks described in this report, as well as the overall carbonation costs and CO_2 balance for each mineral-carbonation region. The results of these calculations are summarized in table 4.

Standard pretreatment was assumed to be ball milling to –200 mesh for olivine and serpentine and –400 mesh for wollastonite. Activated pretreatment is heat treatment for serpentine and ultra-fine grinding for olivine and wollastonite. For the purposes of this table, capital costs for the processing equipment are ignored

and, thus the costs are lower than would be expected. While it is recognized that these costs are significant, perhaps as high as the operating costs, values calculated in Table 4 are only intended to provide a relative comparison of carbonation costs between mineral reactants and carbonation regions, rather than absolute carbonation costs. The feasibility study also to identifies where the major costs of the process occur and assess the technological and economic feasibility of the ex situ process.

Table 4. Economics of sequestration.

		Sequestration costs					
		$/kW•h		CO_2 avoided, MT		$/tCO_2$ avoided	
Region	Ore	std.	act.	std.	act.	std.	act.
1	Olivine	0.06	0.06	13	7	78	167
2	Serpentine	0.49	0.23	8	0	537	NC
3	Serpentine	0.49	0.25	8	0	538	NC
4	Serpentine	0.43	0.20	59	0	521	NC
5	Olivine	0.06	0.06	126	63	81	173
6	Serpentine	0.26	0.08	187	0	309	NC
7	Wollastonite	0.09	0.06	62	43	112	110

std. = standard treatment
std. = activated treatment

The lowest costs were for standard pretreatment olivine ores from Regions 1 and 5, at $78-$81/ton CO_2 avoided. These costs more then doubled with the addition of the activation step. Wollastonite ore from Region 7 that was activated by ultra-fine grinding has the second lowest carbonation cost, at $110/ ton CO_2 sequestered. Wollastonite exhibited greater reactivity than any of the other minerals, but its higher R_{CO2} value and lower ore grade combined with the ultra-fine grinding activation step, resulted in slightly higher costs than the olivine ores. Even with the activation step, the limited wollastonite resource in Region 7 makes it unlikely that the ore could support an ex situ mineral-carbonation operation without a significant increase in proven ore reserves. All of the four regions utilizing serpentine as the mineral reactant had significantly higher costs and, heat activation reduced the CO_2 avoided to 0.

This work has shown that ex situ sequestration can meet the first two minimum requirements for a successful carbonation process (availability and location). Both calcite and magnesite occur in nature as end products of geologic reactions and therefore it is reasonable to assume that stability and environmental safety are not a problem. However, the energy and economic costs are serious problems. The crucial problem is increasing the reaction rate, especially in the case of serpentine. A slow reaction means that a large reactor is required to obtain the required residence time. If the reaction is too slow, it may not even be possible to build a large enough reactor.

IN SITU CARBONATION

The high parasitic energy losses as well as the high cost of CO_2 avoided make ex situ carbonation look unfeasible. Even with a significant improvement in the reaction rate, the quantity of ore mined would be a significantly more than the quantity of the coal being burned. The knowledge gained in the ex situ experiments can be applied to in situ processes. In any in situ process the reaction rate in not a problem as long as the CO_2 remains confined to the in situ reaction zone.

While a considerable amount of work has gone into investigation of in situ processes, very little of that work has considered the rock/solution interactions. Rush (2004) published the results of a series of batch autoclave experiments at conditions found in natural aquifers. In these experiments core samples from the Columbia River Basalt Group (CRBG) were subjected to simulated aquifer conditions for up to 2000 hours. The CRBG is a series of up to 300 separate basalt lava flow. Each flow contains a massive non-porous section and porous flow top and bottom. The porous zones host extensive aquifers (Whitehead 1994 a, b). This extensive aquifer sequence makes the CRBG an ideal candidate for geological sequestration, with potential for both hydrodynamic and mineral trapping of injected CO_2 (O'Connor 2003). These core samples came from depths between 3000 and 4000 feet and include sections from the porous inter-flow zone, with porosity from 17% to 40% and from a massive section with porosity of 0% to 5%.

Figure 4 shows dissolution of basalt at 300 psi and 35°C. The Ca, Fe and Mg ions show a steady increase with time. After 2000 hours their concentrations are still increasing, indicating that equilibrium has not been reached. Very little Silicon goes into solution. The dissolution is accompanied by an increase in the porosity of the core. When the pressure was increased to 1500 psi, the results were similar, but the dissolution rate is slightly faster. No magnesite was found in any of the basalt-core experiments, however a small amount of unknown carbonate was detected by X-ray diffraction (XRD) analysis.
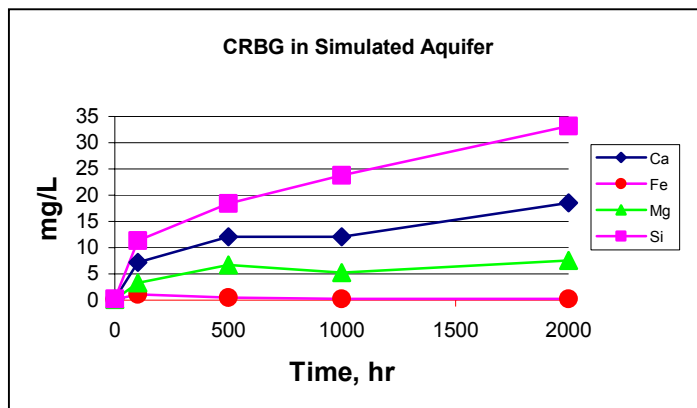

Figure 4. Dissolution of Basalt.

Two thousand hours is not long compared to the time CO_2 will be stored in the
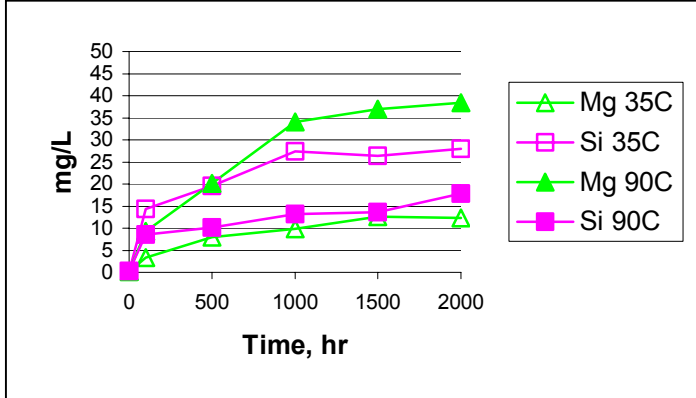

Figure 5. Effect of temperature on Si and Mg dissolution

aquifer. Therefore there is a need to simulate longer test times by accelerating the reaction rate without changing the chemistry. The traditional way to do this would be to raise the temperature. However raising the temperature changes the chemistry. Figure 5 shows the results of two tests at the same conditions except that one is at $35^{\circ}C$ and the other is $90^{\circ}C$. Raising the temperature decreases the silicon in solution while increasing the magnesium in solution. Because aqueous CO_2 solubility decreases as the temperature is raised, the bicarbonate ion becomes favored over carbonic acid (figure 6) and this changes the pH from ~5.5 to ~8. One way to solve this problem is to increase the pressure enough to maintain constant aqueous CO_2 solubility and thus pH.

This change in pH driven by the amount of CO_2 in solution may make it possible to control the conditions in the aquifer. At the point where CO_2 is introduced into the aquifer the pH will be acidic, causing dissolution of silicon from the silicate minerals. Further away from the point of introduction the pH may drop, allowing the precipitation of carbonates.
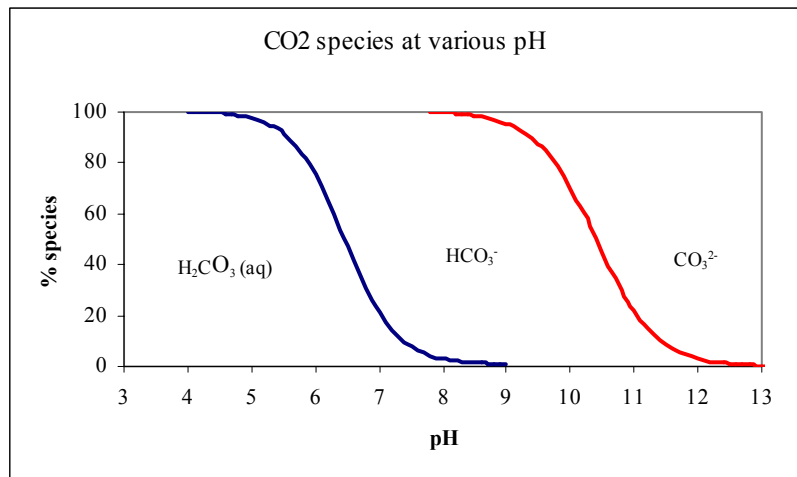
A second series of simulated in situ tests was conducted on Twin Sisters olivine from north-central Washington,

Figure 6. Effect of pH on solution chemistry.

two serpentines, -antigorite from northwestern Pennsylvania and lizardite from southwest Oregon - and Tyee sandstone from western Oregon. The olivine and serpentines were chosen because of their abundance, particularly of the serpentines, and much is known of their carbonation potential from previous ex situ work. Both rocks tend to form massive jointed formations containing few or no aquifers, so their practicality for in situ carbonation needs to be evaluated.

Test conditions for the serpentines, olivine, and sandstone were 60°C and 1500 psi, 90°C and 1500 psi for the basalt. The standard bicarbonate solution (0.64M $NaHCO_3$, 1M NaCl) was used. Samples other than the basalt were rough 1-inch cubes. Solution samples were analyzed at 100, 500, 1000, and 2000-hour intervals during the second series of tests.
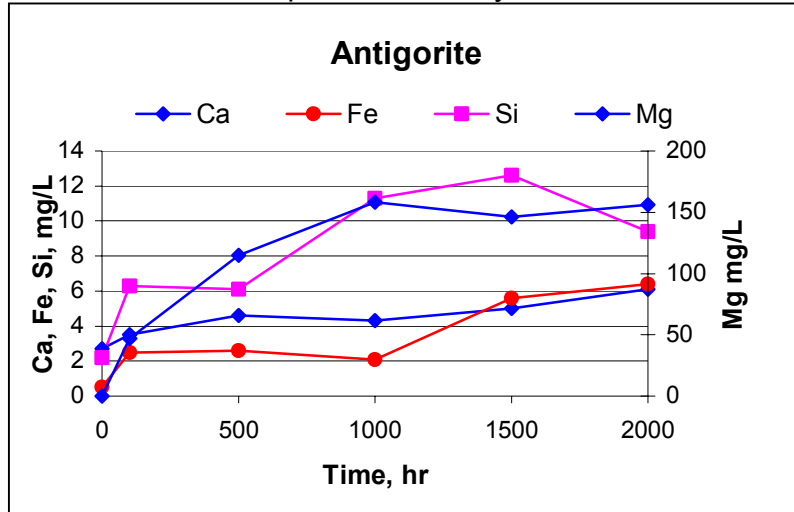
Antigorite

Figure 7. Dissolution of antigorite serpentine.

The results for antigorite serpentine are shown in figure 7. Magnesium shows a rapid rise followed by a leveling off indicating that the solution is approaching equilibrium with respect to magnesium. It is interesting to note that, XRD analysis of the solids showed the presence of magnesite, unlike the CRBG work where the magnesium concentration was still rising at the end of the test. The dissolution of silicon was low, which is consistent with the ex situ work.

Results for lizardite serpentine were similar, and again magnesite was detected by XRD. Both of these samples had limited initial porosity (~5%); after the test the porosity remained the same in the lizardite, but it increased from 6.8% to 10.2% in the antigorite.

Dissolution of sandstone was slow, reaching only 30 mg/L; of Mg after 2000 hours. Fe, Ca and Si were ~15,10 & 5% respectively. The purity of the sandstone greatly affects these levels. Porosity of the sand stone remained constant at 20%.

CONCLUSIONS

Mineral carbonation may be a potentially viable regional solution to CO_2 emissions. Enough appropriate mineral feedstock is available in some regions of the country within a 100- or 200-mile radius of point CO_2 sources – such as coal-fired power plants – to supply an ex situ plant. Unfortunately the economic and energy costs are high. The major problems are the slow reaction rate and the steps, such as mineral activation, that are required to accelerate the reaction. An energy requirement of 352 MW was determined for a process scaled for the sequestration of 100% of the CO_2 emissions from a 1.3-GW coal-fired power plant (1,100 tons CO_2 per hour). After accounting for the sequestration energy

demand, CO_2 avoided was 72% of the total CO_2 sequestered, at a cost of $78 per ton of CO_2 avoided.

Based on the results of these studies, olivine and wollastonite exhibit the best potential for utilization in an industrial mineral-carbonation process. Current mineral-resource estimates indicate that only olivine could meet regional ore demands. While serpentine availability makes it the most attractive mineral reactant, having the broadest occurrence and the greatest abundance, current process developments have been unsuccessful at activating the serpentine without a heat-treatment step which cannot be supported due to excessive energy demands. Utilization of serpentine may yet find promise as a reactive matrix for geological sequestration, where reaction rate would be defined on the order of years rather than minutes. Preliminary studies of simulated in situ mineral carbonation of serpentine minerals show promise, and may point to viable application of the experience gained from the *ex situ* studies.

Seven ultramafic mineral-carbonation regions, located primarily along both coasts of the conterminous U.S, were identified in the course of the studies. Carbonation costs for the seven regions ranged from $89 to $191 per ton of CO_2 sequestered, at an energy cost of $0.09 to $0.20 per kW•h, depending on the intensity of mineral-pretreatment operations. The CO_2 avoided for all seven Regions was 76% of the CO_2 sequestered, when using standard pretreatment methodologies.

Effective thermal and mechanical mineral activation methodologies were identified that could decrease ore demand by up to 75%. However, energy-consumption determinations for both activation methodologies dramatically impact the process economics and the CO_2 balance. Mechanical activation of olivine is not recommended, primarily because it reduces the CO_2 avoided by nearly 50%, and sufficient mineral resources are available in one region to meet the ore demand without the activation step. Mechanical activation of wollastonite is recommended, due to its limited availability and the improvement in process economics and minimal impact on CO_2 avoided by inclusion of the activation step. Serpentine carbonation costs were reduced to roughly $78 per ton of CO_2 sequestered, at an energy cost of $0.08 per kW•h, with inclusion of a heat-treatment step. However, thermal activation of serpentine, while extremely effective, results in more CO_2 generated than is sequestered by the process, making it an impractical methodology. These calculations assume no heat recovery from the thermal-activation step, but plausible heat recovery would be unlikely to dramatically alter the CO_2 balance.

Because of the high cost of ex situ sequestration, a study was begun to apply the knowledge gained from the ex situ sequestration to solution/rock interactions under conditions for in situ carbon sequestration. In all cases, Ca, Mg and Fe^{+2} cations were released into the solutions, making aqueous carbonation possible. However, only in the case of serpentine was any magnesite identified in the

solids by XRD. Equilibrium had not been reached for basalt in solution by 2000 hours as Ca, Mg and Fe^{+2} concentrations in solution were still increasing.

Care must be taken in attempts to simulate longer reaction times, as the solution chemistry is a function of temperature and pressure. Increasing the temperature without changing the pressure changes the CO_2 solubility and thus the pH both of which affect Si or Mg solubility.

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