

ENERGY AND ECONOMIC CONSIDERATIONS FOR EX-SITU
AQUEOUS MINERAL CARBONATION

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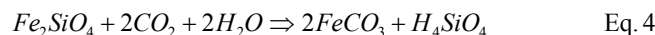
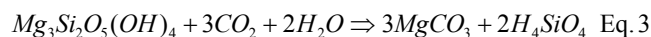
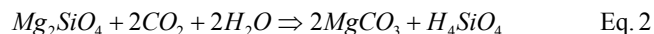
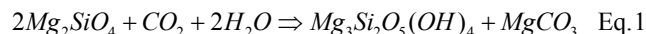
ABSTRACT

Due to the scale and breadth of carbon dioxide emissions, and speculation regarding their impact on global climate, sequestration of some portion of these emissions has been under increased study. A practical approach to carbon sequestration will likely include several options, which will be driven largely by the energy demand and economics of operation. Aqueous mineral carbonation of calcium and magnesium silicate minerals has been studied as one potential method to sequester carbon dioxide. Although these carbonation reactions are all thermodynamically favored, they occur at geologic rates of reaction. Laboratory studies have demonstrated that these rates of reaction are accelerated with increasing temperature, pressure, and particle surface area. Mineral-specific activation methods were identified, however, each of these techniques incurs energy as well as economic costs. An overview of the mineral availability, pretreatment options and energy demands, and process economics is provided.

MINERAL CHEMISTRY

Carbonation Reactions

The alteration of Mg-bearing ultramafic rocks by natural hydrothermal fluids is known as serpentinization, and produces hydrated Mg-silicate minerals (serpentine) and, when CO₂ is available, magnesite (eq. 1). Increasing the activity of CO₂ can by-pass the formation of the hydrated species to form the carbonates and silicic acid and/or free silica (eq. 2). Because this reaction occurs in nature and is thermodynamically favored, it became the basis for the aqueous mineral carbonation process. Studies demonstrated that the list of primary mineral reactants could be expanded beyond the Mg-rich silicates to include the Ca- and Fe²⁺-rich silicates as well. The theoretical carbonation reactions for the Ca-, Fe²⁺-, and Mg-silicates are included below for reference (eq. 1-5).



Carbonation Potential

A key theoretical yardstick for the value of a particular mineral reactant for mineral carbonation is its carbonation potential. The carbonation potential for a rock or mineral was described by Goff et al. (2000) regarding the hydrated magnesium silicate serpentine [Mg₃Si₂O₅(OH)₄]. Goff used the molar concentration of Mg in a serpentine sample to calculate the theoretical number of moles of CO₂ that could be converted to magnesite (MgCO₃) by reaction with the serpentine. This method was modified for the current study to include the cations Ca and Fe²⁺ in the calculation, because all three cations can potentially form stable carbonate compounds. The modified method thus permits the calculation of the carbonation potential for the alternative mineral feed stocks studied (Table I). The carbonation potential, R_{CO₂}, was calculated from the total molar concentration of Ca, Fe²⁺, and Mg in the feed, and is defined here as the mass ratio of rock or mineral necessary to convert a unit mass of CO₂ to the solid carbonate (eq. 6). By this definition, a low R_{CO₂} is preferable.

$$R_{CO_2} = \frac{100}{(\sum Ca^{2+} + Fe^{2+} + Mg^{2+})MW_{CO_2}} \quad \text{Eq. 6}$$

Where:

$\sum Ca^{2+} + Fe^{2+} + Mg^{2+}$ = The sum of the molar concentrations for the specified cations.

MW_{CO_2} = Molecular weight of CO₂.

Table I. Mineral chemistry, carbonation potential, and reactivity.¹

Rock/mineral group	Mineral	Formula	Concentration, wt pct				R _{CO₂} ²	ε _A , %	R _X ³ , %
			Feed			Prod.			
			Ca	Fe ²⁺	Mg	CO ₂			
Feldspar	Anorthite (An)	CaAl ₂ Si ₂ O ₈	10.3	3.1	4.8	1.9	4.4	23	9
Serpentine	Antigorite (Ant)	Mg ₃ Si ₂ O ₅ (OH) ₄	<0.1	2.4	24.6	24.2	2.1	47	92
Pyroxene	Augite (Aug)	CaMgSi ₂ O ₆ + (Fe,Al)	15.6	9.6	6.9	11.1	2.7	37	33
Basalt	An, Aug, Mt, Ol		6.7	6.7	4.3	2.9	4.9	37	15
Olivine (Ol)	Fayalite (Fa)	Fe ₂ SiO ₄	0.6	44.3	0.3	19.2	2.8	36	66
Olivine (Ol)	Forsterite (Fo)	Mg ₂ SiO ₄	0.1	6.1	27.9	29.7	1.8	56	81
Serpentine	Lizardite (Liz)	Mg ₃ Si ₂ O ₅ (OH) ₄	0.3	1.5	20.7	16.0	2.5	39	40
Oxide	Magnetite (Mt)	Fe ₃ O ₄	0.6	21.9	0.3	1.5	5.5	18	08
Ultramafic	Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	2.2	9.2	15.7	5.2	2.8	36	15
Ultramafic	Wollastonite (Wo)	CaSiO ₃	31.6	0.5	0.3	22.9	2.8	36	82

¹ Carbonation test conditions: 80% -37 μm feed; 1 hour; 185°C; P_{CO₂}=150 atm; 15% solids; 0.64 M NaHCO₃, 1 M NaCl.

² Mass ratio of ore necessary to carbonate unit mass of CO₂.

³ Reaction efficiency, percent stoichiometric conversion of Ca, Fe²⁺, and Mg cations in silicate feed to carbonate.

Carbonation Reactivity

While the R_{CO₂} is an inherent property of a rock or mineral, the carbonation reactivity of that rock or mineral is dependent on numerous factors, including the mineral composition, pretreatment, and solubility at the specific carbonation conditions of time, temperature, and pressure. An evaluation of the relative sequestration reactivity for the specific mineral feed stocks studied is included in Table I. The reactivity of the various feed materials was measured as the extent of reaction, R_X, or the percent stoichiometric conversion of the Ca-, Fe²⁺-, and Mg-silicates to their carbonate counterparts (eq. 7).

$$R_X = \frac{X_{CO_2}}{\epsilon_A(1 - X_{CO_2})} \quad \text{Eq. 7}$$

Where:

X_{CO₂} = CO₂ concentration in the solid products in weight percent.

ε_A = Percent weight gain assuming 100% stoichiometric conversion of the available cations to the carbonates.

Due to the variability in mineral solubility, partial pressure of CO₂ (P_{CO₂}) sensitivity, and precipitation kinetics, it was not practical to conduct all tests at a standardized set of pretreatment and carbonation conditions. Thus, the R_X values reported in Table I generally represent the best results achieved for each mineral reactant to date. The standardized test conditions are included as a footnote to the table. Variations from the standard conditions are noted below. For example, the wollastonite and forsterite exhibit comparable R_X, but both required an ultra-fine grinding pretreatment stage to achieve those reaction efficiencies. In addition, the P_{CO₂} for the wollastonite carbonation is much lower than that for the forsterite, at 40 atm versus 150 atm, respectively. Countering the reduced P_{CO₂} for wollastonite, however, is its higher R_{CO₂} relative to forsterite. Because Ca is a much heavier element than Mg, the Ca-bearing silicates have a lower molar concentration of cations suitable for carbonation, and thus a higher R_{CO₂}. Antigorite serpentine has the second lowest R_{CO₂} and the highest R_X of the minerals investigated. However, a heat pretreatment stage was necessary to achieve this degree of reactivity. Lizardite serpentine underwent an identical heat treatment stage to achieve the reported R_X, although to less effect. Heat treatment proved an effective activation methodology for the hydrated minerals. However, as with the ultra-fine grinding used to activate olivine and wollastonite, heat treatment has a significant impact on the process economics and CO₂ balance. Finally, the mafic rocks and/or minerals, including basalt, which is comprised in part of varying concentrations of anorthite, augite, magnetite, and olivine, all tended to exhibit the lowest R_X and the highest R_{CO₂}.

MINERAL AVAILABILITY

Ultramafic Mineral Carbonation Regions

The ultramafic minerals investigated for mineral carbonation generally occur within large ophiolite complexes that are described as remnants of oceanic crust that have been compressed and folded along convergent continental margins. In North America, these ultramafic belts occur along both coasts, rather than the interior, which places limitations on the application of the mineral carbonation technology. The large tonnage of ore required for mineral sequestration makes it necessary to locate the mineral carbonation plant at the mine mouth, rather than at the CO₂ point source. An evaluation of the scale of major CO₂ point sources and their proximity to the potential mineral sources resulted in the identification of 7 primary ultramafic mineral carbonation regions within the conterminous U.S. (Figure 1).

Coal Consumption and Ore Tonnage

To determine the potential scale for mineral sequestration, it was necessary to derive the total CO₂ point source emissions within a specified distance of the mineral sources within these 7 regions. To simplify this determination, CO₂ point sources were limited to coal-fired power plants that occur within 100- and 200-mile radii of the geographic center of the specific mining district or mineral deposit. Total CO₂ emissions were calculated from total regional coal consumption derived from Platts (2001), and carbon content of the coal used in that region after Babcock & Wilcox (1998). Assumptions for coal use by region include sub-bituminous/lignite Washington coal in Region 1, sub-bituminous Wyoming coal in regions 2 and 3, Texas lignite in region 4, and bituminous Pennsylvania coal in regions 5-7 (Table II). The total calculated CO₂ emissions for all 7 regions (604 Mt) represents ~30% of the total annual CO₂ emissions from U.S. coal-fired power plants, as reported by the EIA (2003).



Figure 1. Ultramafic mineral carbonation regions.

Total ore demand in Table II was calculated assuming sequestration of 100% of the CO₂ emissions in each region, at the R_{CO2} of the various mineral reactants, and the demonstrated extent of reaction (R_X). Experimental results were used for the latter at two levels of mineral pretreatment. Standard pretreatment for all minerals is defined as size reduction to 80% minus 400 mesh (37 μm). Activated pretreatment is specific to the mineral type: olivine and wollastonite were mechanically activated by the addition of an ultra-fine grinding stage; serpentine minerals were activated by the addition of a heat-treatment stage. The impact of the mineral pretreatment operations is dramatic, reducing the total ore tonnage by over 75%. However, these activation steps also impact process economics and the CO₂ balance.

Ultramafic Mineral Resources

The regional ore demand totals included in Table II are very large, even for the activated mineral reactants. However, with two exceptions, the ultramafic mineral resources far exceed these demands. Roskill (1990) reported reserves of 1.8 Gt of unaltered dunite (>90% olivine) at the Twin Sisters deposit in NW Washington, a 33-year supply.

Coleman and Irwin (1977) and Goff et al. (1997) described the vast belts of serpentine in SW Oregon and the California Coast Ranges, which dwarf the annual estimated ore demands for both Regions 2 and 3. Less certain is the availability of serpentine from the Llano Uplift to meet the estimated ore demand of ~200-400 Mt/year for mineral sequestration in Region 4. A resource of over 1 Gt of serpentine is inferred after Barnes et al. (1950), which may be a 5-10 year supply at full-scale mineral sequestration. In contrast, the serpentine resource in Region 6, the State Line district along the Maryland-Pennsylvania border, is vast, as described by Pearre and Heyl (1960). However, the 300-600 Mt/year ore demand would require 20-40 50-kt/day open pit mines.

Hunter (1941) provided a detailed description of the olivine deposits in western North Carolina, and Roskill (1990)

Table II. Annual coal consumption, CO₂ emissions, and ore demand by ultramafic mineral carbonation region.

Region	Mining district/deposit	Mineral	R _{CO2}	R _X , %		Radius, miles	Coal, Mt	C, wt pct	CO ₂ , Mt	Ore, Mt	
				Std.	Act.					Std.	Act.
1	Twins Sisters, WA	Olivine	1.8	61	81	100	5	70	13	38	29
							2	70	5	15	11
2	Trinity-Siskyou Mtn, CA-OR	Serpentine (lizardite)	2.5	9	40	100	4	70	10	303	64
							0	70	0	0	0
3	Coast Range, Southern CA	Serpentine (lizardite)	2.5	9	36	100	4	70	10	303	71
							0	70	0	0	0
4	Llano Uplift, TX	Serpentine (lizardite)	2.5	9	40	100	13	63	30	888	187
							18	63	42	1229	259
5	Asheville, NC	Olivine	1.8	61	81	100	20	74	54	160	121
							49	74	133	392	295
6	State Line, MD-PA	Serpentine (antigorite)	2.1	12	92	100	39	74	106	1822	242
							46	74	125	2149	285
7	Willsboro, NY	Wollastonite	2.8	43	82	100	4	74	11	70	37
							24	74	65	422	222
Total	Region 1-7, ultramafic ores						228		604	7790	1823

reported ~200 Mt of reserves. These reserve estimates indicate that the olivine supply in Region 5 could meet the ore demand for only 1-2 years, assuming ~120 Mt/year within the more limited 100-mile radius. Serpentine resources would have to substitute for olivine in Region 5. Virta (2001) reported wollastonite reserves in Region 7 at ~14 Mt, roughly a 6-month supply for the 100-mile radius ore demand. Alternatives to wollastonite would be needed, although increased demand could spur exploration that might extend the wollastonite supply.

Mafic Mineral Carbonation Regions

The most likely targets for mafic mineral exploitation are the three massive flood basalt provinces that occur within the conterminous U.S. (Figure 2). These flood basalt provinces contain vast amounts of material for mineral sequestration, although experimental studies indicate that reaction efficiencies are low and R_{CO_2} high compared to the ultramafic minerals (Table I). Mafic regions 8 and 10 overlap ultramafic regions 1 and 6, respectively. The CO_2 emissions and ore demand totals were calculated separately, but by the same methods, with the results included in Table III.



Figure 2. Mafic mineral carbonation regions.

The Columbia River Basalt Group (CRBG) of Region 8 has been described by Reidel et al. (1989), among other authors. Green (1972) described the geology of the Keweenaw Rift System Basalts (KRSB) in Region 9, while Olsen et al. (1996) provided similar discussion of the Newark Basin Basalts (NBB) of Region 10. In each case, the tremendous tonnages required for *ex situ* mineral sequestration and the layered structure of each flood basalt province suggest they may hold greater promise for *in situ* mineral sequestration rather than the *ex situ* process. Reidel et al. (2002) reported on the potential for natural gas storage within the CRBG and speculated on the potential for CO_2 injection into its deep saline aquifers. Initial laboratory pressure-leach studies conducted at ARC on core from the CRBG were reported by O'Connor et al. (2003). The favorable basalt mineralogy could make these flood basalt provinces attractive targets for geological sequestration.

Table III. Annual coal consumption, CO_2 emissions, and ore demand by mafic mineral carbonation region

Region	Mining district/deposit	Mineral	R_{CO_2}	R_x , %	Radius, miles	Coal, Mt	C, wt pct	CO_2 , Mt	Ore, Mt
8	CRBG, WA-OR	Basalt	4.9	15	100	2	70	5	170
					100-200	5	70	13	420
9	KRSB, MN-WI-IA	Basalt	4.9	15	100	13	69	33	8100
					100-200	18	69	46	1500
10	NBB, NJ-NY-PA	Basalt	4.9	15	100	23	74	62	2000
					100-200	34	74	92	3000
Total	Region 8-10, mafic ores					95		251	15200

MINERAL PRETREATMENT

Activation of the mineral reactants has been achieved by both thermal and mechanical means, although the mechanism for this activation is not clearly understood. Because most mineral dissolution reactions are surface controlled, it is possible that the two pretreatment methods proved successful primarily due to increased surface area. Mechanical pretreatment reduces the mean particle size of the minerals, while thermal pretreatment removes chemically-bound water, which may increase the porosity and the resulting surface area. Zhang et al. (1996) provided some discussion of the enhancement of Mg silicate solubility by mechanical means, while McKelvy et al. (2002) and Chizmeshya et al. (2002) described thermal activation and computational modeling studies, respectively, conducted at Arizona State University, a collaborating laboratory with ARC. All suggest that the activation is due to destruction or disordering of the mineral lattice. It is likely that both phenomena are responsible to some degree for the improvements in mineral reactivity achieved by pretreatment. However, the following discussion focuses on the energy consumption for the various mineral pretreatment options, rather than the root causes for enhanced reactivity.

Mechanical Activation

Mechanical activation 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 Work Index (grinding energy) necessary 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 the 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 3).

The carbonation test conditions varied by mineral, using the best demonstrated reaction parameters: 1 hour duration (all minerals); 185°C (olivine), 155°C (serpentines), 200°C (wollastonite); P_{CO_2} of 150 atm (olivine and serpentines), 40 atm (wollastonite); carrier solution of 1 M NaCl, 0.64 M $NaHCO_3$ (olivine and serpentines), distilled water (wollastonite). 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 kWh/ton.

Thermal Activation

Thermal activation of the hydrated Mg-silicate species was accomplished by the addition of a heat treatment stage in the mineral pretreatment process. An effective heat treatment methodology was developed experimentally and confirmed by differential thermal analysis and thermal gravimetric analysis (DTA/TGA) of the antigorite serpentine ore sample (Figure 4).

The most effective heat-treatment temperature determined experimentally was approximately 630°C. This is reflected in the TGA plot, which shows the most significant weight loss, due to dehydroxylation or removal of the chemically-bound water, initiating at about 600°C. The DTA plot shows an endotherm in this temperature range centered on approximately 650°C, which corroborates the experimental data derived from bulk heat treatment of the ore. A second endotherm evident on the DTA plot occurs at about 390°C, coinciding with a weight loss of roughly 2% based on the TGA. This may be indicative of brucite [$Mg(OH)_2$] dehydroxylation, which occurs at roughly 375°C. X-ray diffraction (XRD) analysis of the same sample identified brucite as a minor phase (1-10%).

A great deal of study has focused on serpentine activation, both recently within the DOE Mineral Carbonation Study Group, and prior to the current research. Barnes et al. (1950) described extensive studies on the utilization and heat activation of Texas serpentine. Zhang et al. (1997) reported on the enhancement of acid extraction of Mg and Si from serpentine by mechanochemical treatment. From a process standpoint, the energy consumption required for activation is more significant than the methodologies themselves, which led to an effort to determine the relative energies for thermal activation of the serpentine minerals used in the current study.

The theoretical energy required for the heat activation process must include the energy to heat the mineral to the specified temperature and the enthalpy of dehydroxylation. The latter includes the energy to decompose the serpentine, removing the hydroxyl molecule and producing a pseudo-amorphous silicate phase. Thermodynamic data reported by King et al. (1967) was used to calculate the effective heat capacities at temperature for antigorite serpentine. The theoretical energy required to heat the mineral to the specified temperature was calculated by equation 8.

$$Q = C_p \Delta T \quad \text{Eq. 8}$$

Where:

Q = heat, cal/mol

C_p = cal/K•mol @ temperature T_1 , (K)

ΔT = $T_1 - T_0$ (298K)

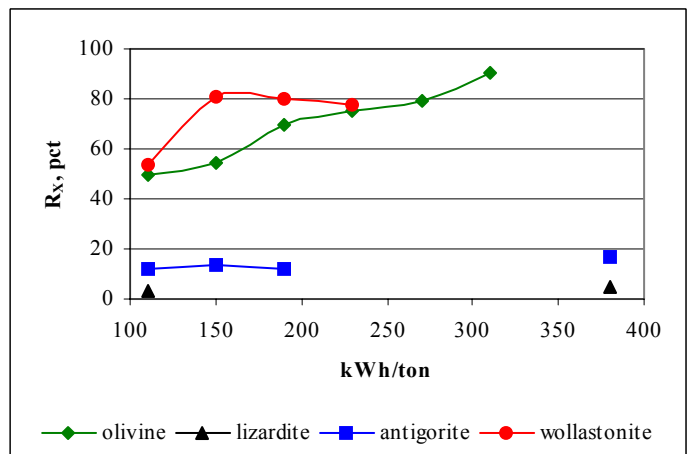


Figure 3. Grinding energy versus R_x .

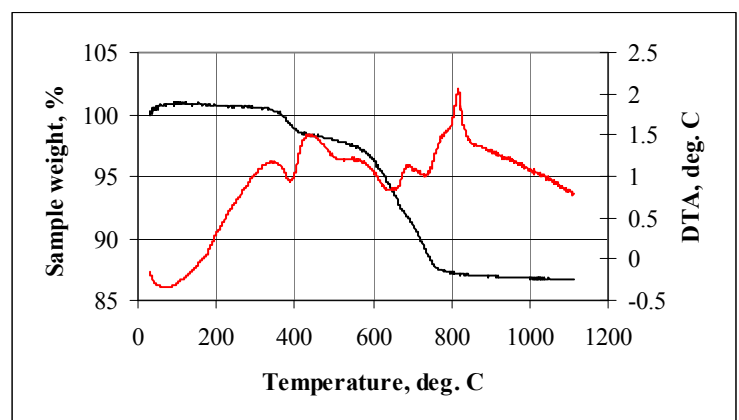


Figure 4. DTA (red) & TGA (black) for antigorite serpentine.

Quantitative DTA analysis was utilized to determine the dehydroxylation energies (E_d) for antigorite and lizardite serpentine, which were reported by Govier and Arnold (2004) to be approximately 95 and 131 kJ/mol, respectively. Combining the C_p data derived for antigorite serpentine coupled with these mineral-specific E_d values results in the total theoretical energy requirement for the heat-activation process. For example, heat treatment of the serpentine at 630°C ($C_p = 89.26$ cal/K mol) requires 206 kW•h/ton to heat the mineral, while dehydroxylation of the antigorite and lizardite requires an additional 87 and 120 kW•h/ton, respectively. Total energy consumption for the heat treatment process is thus 293 and 326 kW•h/ton, for antigorite and lizardite, respectively.

Energy Consumption

Using the energy data compiled during the mechanical and thermal activation studies, a compilation of comparative energy consumption values was prepared for each of the 7 ultramafic mineral carbonation regions (Table IV). The feed material histories are summarized in the first three columns of the table, with a code specific to each material included in column 4. This code is used in subsequent tables to conserve space. The rest of the table includes the energy consumption values determined for the various mineral pretreatment methodologies by stage.

For example, crushing energy for all materials is estimated at 2 kW•h/ton, based on mining cost data produced by the U.S. Bureau of Mines (1987). Ore grade is assumed to be 100% for the Twin Sisters olivine and all serpentine mineral districts (Regions 1-4, 6), based on first-hand observation of several of the mining operations, which are essentially open-pit quarries that require no concentration steps. However, laboratory analysis of olivine samples collected from the Asheville Mining District (Region 5) identified alteration minerals, serpentine and talc, with an estimated ore grade of 70% olivine. Bench-scale tests conducted on the Region 5 olivine ore indicated that gravity separation could be an effective beneficiation process, with an energy penalty of approximately 2 kW•h/ton. It is assumed that the beneficiation step would be conducted following the first grinding stage, which appears to provide sufficient liberation of the olivine from the alteration products based on the laboratory studies. Thus, the grinding energy for the stage 1 grind is based on the tonnage of raw ore processed, while subsequent pretreatment energies are based on processing the olivine concentrate.

Table IV. Energy consumption by feed material and specific pretreatment methodology.

Feed Material History				Pretreatment Energy Consumption, kW•h/ton						
Region	Ore mineral & grade	Pretreatment methodology	Code	Crush.	Bene.	Grinding			Heat treatment	Total
						Stage 1	Stage 2	Stage 3		
1	Olivine, 100%	Ball mill (-200 mesh)	1A	2		11				13
		Ball mill (-400 mesh)	1B	2		11	70			83
		SMD mill	1C	2		11	70	150		233
2-4	Serpentine, 100% (lizardite)	Ball mill (-200 mesh)	2-4A	2		11				13
		Heat treatment (-200)	2-4B	2		11			326	339
5	Olivine, 70%	Ball mill (-200 mesh)	5A	2	2	15				19
		Ball mill (-400 mesh)	5B	2	2	15	70			89
		SMD mill	5C	2	2	15	70	150		239
6	Serpentine, 100% (antigorite)	Ball mill (-200 mesh)	6A	2		11				13
		Heat treatment (-200)	6B	2		11			293	306
		Heat treatment (-400)	6C	2		11	70		293	376
7	Wollastonite, 50%	Ball mill (-400 mesh)	7A	2	4	21	70			97
		SMD mill	7B	2	4	21	70	70		167

Virta (2001) reported wollastonite grade in the Region 7 deposits at 40-60%. Information provided with samples from the largest wollastonite mining operation in Region 7 described a two-stage concentration process, including size separation to remove calcite and magnetic separation to remove garnet. The wollastonite ore grade was assumed to be 50% for the subject calculations, and a beneficiation energy penalty of 4 kW•h/ton was added to the overall pretreatment energy consumption figure. As with the Region 5 olivine beneficiation, the size and gravity separation steps would be conducted on the raw wollastonite ore following the first-stage grind, which increases the grinding energy for that stage accordingly, compared to the non-beneficiated ore materials. Subsequent pretreatment energies are based on processing the wollastonite concentrate.

This compilation was used to calculate the theoretical parasitic energy loss from the power plant, based on the measured mechanical/thermal activation energies and experimental carbonation data. The basis for this calculation was a 1 GW coal-fired power plant, burning coal with an as-fired heat value of 12,500 Btu/lb and carbon content of 74%, at 35% plant efficiency. The CO₂ emissions of 25.4 kt/day were then used to calculate the daily ore requirement to sequester 100% of the CO₂ emissions at the R_{CO2} and demonstrated R_X of each mineral reactant in a single pass through the carbonation reactor (Table V).

While the daily ore requirements decrease dramatically with increased mineral activation, the coincident parasitic energy loss on the power plant becomes problematic. This assumes that the energy required for the pretreatment operation is generated by burning the same coal at the same efficiency as stated for the power plant. Adding the sequestration plant energy requirement decreases the CO₂ avoided even further. Parasitic energy losses exceeding 100% indicate that the CO₂ avoided is negative, meaning that more CO₂ is emitted by the pretreatment operation than is sequestered. The improved reactivity achieved by the additional pretreatment operations is negated for the most part by the higher energy demand. However, the higher ore requirements at the lower pretreatment energies require massive increases in mining output, exceeding the available resources in some regions. 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.

Table V. Parasitic energy loss by pretreatment.

Feed Code	R _{CO2}	R _x , %	Ore/conc., kt/day	Pct total plant energy
1A	1.8	16	286	15
1B	1.8	61	75	26
1C	1.8	81	56	55
2-4A	2.5	9	706	37
2-4B	2.5	40	158	222
5A	1.8	16	286	22
5B	1.8	61	75	28
5C	1.8	81	56	56
6A	2.1	12	445	24
6B	2.1	62	86	110
6C	2.1	92	58	90
7A	2.8	43	165	67
7B	2.8	82	87	61

PROCESS DEVELOPMENT

Mineral Carbonation History

Lackner et al. (1997a,b, 1998) provided some of the earliest discussion of mineral sequestration of anthropogenic CO₂ emissions. Together with colleagues from the Los Alamos National Laboratory (LANL), he proposed the LANL aqueous process for mineral carbonation of serpentine ores. The LANL process is a derivation from an earlier technology developed during World War II by the Tennessee Valley Authority and U.S. Bureau of Mines for production of Mg metal from olivine. Houston and Rankin (1942) and Houston and Kerr (1945) described an HCl acid-leach process for Mg extraction, followed by electrolysis of the MgCl₂ leach product for metal recovery and acid regeneration.

The LANL process substituted a complex MgCl₂ dehydration and crystallization operation for the electrolytic stage of the TVA/USBM process. The crystallized MgCl₂ is converted to Mg(OH)₂ during an acid recovery step, which is followed by carbonation of the Mg(OH)₂. Nilsen and Hundley (1999) conducted a preliminary feasibility study of the LANL process to quantify the energy-intensive dehydration and crystallization steps. Power requirements for the sequestration operation result in a negative CO₂ balance, such that CO₂ produced by generating the energy to run the process far exceeds the CO₂ sequestered by the process, which led to investigation of the ARC aqueous process as an alternative method.

Reactor Design

The ARC aqueous mineral-carbonation process has been demonstrated using a batch autoclave with continuous stirring and constant temperature and P_{CO2} capability. An industrial-scale process clearly requires continuous processing, and the elevated P and T conditions make reactor design a critical issue. Because required wall thickness for a pressure vessel is directly related to pressure and diameter, large-scale conventional autoclave reactors operating at 150 atm would be extremely thick-walled and very capital intensive. An ideal reactor design would entail minimal diameter to limit wall thickness without limiting scale. A continuous pipeline reactor meets these criteria; a conceptualized view of such a reactor is shown in Figure 6. As a proof-of-concept, a loop reactor would permit operation in the pipeline design without the need to build a full-scale reactor. Figure 7 shows the loop reactor constructed at ARC prior to installation of insulation.

Slurry is circulated for specified residence times while critical performance parameters such as three-phase mixing with static mixers,

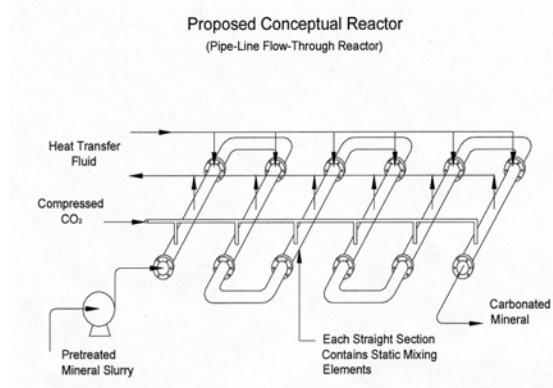


Figure 6. Conceptual pipeline reactor.



Figure 7. Laboratory-scale flow loop reactor.

fluid flow at supercritical CO₂ pressures, and pre- and post-test slurry injection and removal are evaluated. Engineering data acquired by operation of the flow-loop reactor may be used for the design and construction of a pilot-scale continuous pipeline reactor. However, before any discussion of construction of a second-generation pipeline reactor was warranted, a feasibility study of the current aqueous mineral carbonation process was necessary.

Process Feasibility Study

The feasibility of mineral carbonation as a method for CO₂ storage has been the subject of several previous studies. The EIA (1999) commissioned an exhaustive study of several methods proposed by LANL, including the original LANL aqueous process, and several molten salt processes described by Wendt et al. (1998a,b,c). Sequestration costs were estimated at \$60-80 per ton CO₂ for the favored molten salt process, which is yet to be demonstrated, to over \$200 per ton CO₂ for the LANL aqueous process. Both methods were found to be currently untenable, due to the excessive energy demand for the aqueous process, and excessive chemical make-up volumes for the molten salt process.

A second feasibility study was conducted by NEXANT (2000) for an anaerobic hydrogen/electric power generation plant with CO₂ disposal by mineral carbonation. This was the first study to include the ARC aqueous process for the mineral-carbonation step, in this case applied to serpentine carbonation. Sequestration costs were estimated at \$70 per ton CO₂, including a heat-activation step. The estimated energy demand for the heat-treatment step was much lower than that reported here, at 153 kW•h/ton compared to 293 kW•h/ton (antigorite) or 326 kW•h/ton (lizardite). The sequestration cost was calculated assuming a plant efficiency of 65% for the anaerobic hydrogen/electric power production technology, compared to a typical coal-fired power plant efficiency of 35%. Sequestration costs applied to conventional coal-fired technology were roughly \$130 per ton CO₂.

A third mineral carbonation feasibility study was commissioned by the National Energy Technology Laboratory (NETL) and completed by Lyons et al. (2003), using a preliminary process design and basis developed at ARC by Nilsen and Penner (2001). A steady-state simulation of the process was created in Aspen® process simulation software, from which capital- and operating- cost estimates were generated. This study evaluated an olivine-based mineral-carbonation process scaled for the sequestration of 100% of the CO₂ emissions from a 1.3 GW coal-fired power plant. Olivine was selected as the mineral reactant in part to simplify the process by eliminating the heat-pretreatment stage. The process flow diagram is shown in Figure 8. Because the proposed pipeline reactor design referred to above was unproven at the time, a conservative approach was adopted and conventional continuous-flow leach-type autoclave reactors were selected for the study (Figure 9).

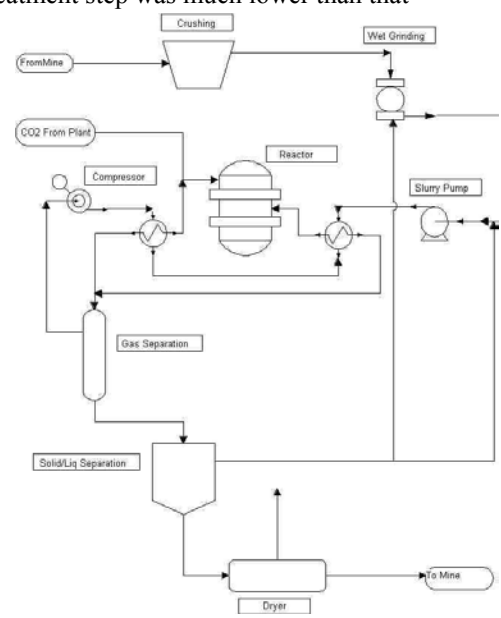


Figure 8. Process flow diagram.

The impact of the conventional reactor design on the process economics is significant. The design required 12-foot diameter vessels with 14-inch thick walls, which accounted for roughly 50% of total capital costs. Additional assumptions and selected bases for the feasibility study follow:

- Olivine is the mineral reactant, with an ore grade of 100% and MgO concentration of 49 wt pct;
- Olivine ore is ground to 80% minus 400 mesh (37 microns);
- 65% reaction efficiency (R_X) with each pass through the process;
- 60% of the unreacted olivine from the products is separated at 20 μ m size and recycled;
- Twin Sisters olivine (Region 1) is utilized for the process, with the sequestration plant located next to the mine site;
- The mining operation is open pit, and the process products re-deposited in the depleted pits;
- CO₂ is transported to the plant via pipeline (CO₂ separation costs not included in cost estimates);

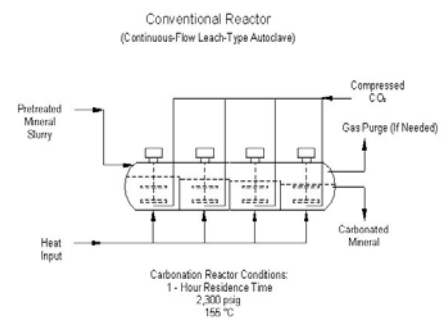


Figure 9. Conventional reactor design used in feasibility study.

- Carbonation conditions include: 2 hour residence time; $T = 185^{\circ}\text{C}$; $P_{\text{CO}_2} = 150 \text{ atm}$; $P_{\text{H}_2\text{O}} = 6.5 \text{ atm}$; 30% solids; carrier solution = 0.64 M 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_{CO_2} 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 by mineral-carbonation region.

Carbonation Costs

The final carbonation cost determined in the NETL feasibility study was \$69 per ton CO_2 sequestered for the baseline olivine process described above. This baseline process applies directly to ultramafic mineral carbonation in Region 1, as described in Table II. However, the R_X reported in the subject study were achieved in 1-hour reactor residence times rather than the 2-hour residence time assumed for the NETL study. Thus, the sequestration cost was lowered to \$54 per ton CO_2 , based on the reactor residence-time sensitivity analysis. Dividing the modified sequestration cost of \$54 per ton CO_2 by the ore demand value (R_{CO_2}/R_X) for the ore in Region 1 results in a cost of ~\$18 per ton ore. It was necessary to derive the sequestration cost per ton of ore in order to account for variations in the pretreatment operations, which are mineral-specific and are reported as an energy cost per ton of ore in Table IV. This made it possible to determine an adjusted carbonation cost, including the pretreatment and sequestration costs, for each of the ultramafic mineral-carbonation regions defined in Table II. Multiplying the final adjusted cost per ton of ore by the calculated total ore demand provides the total carbonation cost for each region. Dividing the total calculated regional CO_2 emissions by the total carbonation costs provides the carbonation cost per ton of CO_2 sequestered. Using this method, the estimated carbonation costs were determined for each ultramafic mineral carbonation region and are reported in Table VI.

The sequestration costs for wollastonite ore in Region 7 were reduced by \$5 per ton ore (to \$13 per ton ore) due to the lower P_{CO_2} (40 atm) utilized in the reactor, based on the P_{CO_2} sensitivity analysis included in the NETL study. However, the pretreatment costs for the wollastonite ore were adjusted for the beneficiation process required due to the lower grade of ore. The size and magnetic separation processes used to produce a wollastonite concentrate were estimated to incur an energy penalty of $4 \text{ kW}\cdot\text{h}/\text{ton ore}$. Because the beneficiation processes were assumed to be conducted at minus 200-mesh ($75 \mu\text{m}$) particle size, the grinding costs to that stage increase accordingly, adding $10 \text{ kW}\cdot\text{h}/\text{ton ore}$ to the pretreatment costs. Using the electricity cost of \$0.054 per $\text{kW}\cdot\text{h}$ cited in the NETL study as a basis, the final adjusted carbonation cost is approximately \$14 per ton ore. For simplicity, this adjustment ignores capital costs for the beneficiation operation. Similar adjustments due to lower ore grade and the required beneficiation costs were made for the olivine ores in Region 5, for a final adjusted sequestration cost of \$19 per ton ore.

Table VI. Annual coal consumption, energy generation, CO_2 emissions, ore requirements, and carbonation costs by ultramafic mineral carbonation Region.

Region	Coal, Mt	Heat value, Btu/lb ¹	Energy, GW•h (x 1000)	CO_2 seq., Mt ²	Ore demand, Mt		Sequestration costs							
					std.	act.	\$/ton ore ³		\$, billions		\$/ton CO_2 seq.		\$/kW•h	
							std.	act.	std.	act.	std.	act.	std.	act.
1	7	12300	18	18	53	40	18	26	1.0	1.1	54	59	0.06	0.06
2	4	11030	9	10	302	64	15	44	4.4	2.0	427	199	0.49	0.23
3	4	11030	9	10	303	71	15	44	4.4	2.3	427	222	0.49	0.25
4	31	11360	72	72	2117	446	15	44	30.7	14.3	427	199	0.43	0.20
5	69	13080	184	187	552	416	19	27	10.3	11.1	55	59	0.06	0.06
6	85	13080	320	231	3971	527	15	48	57.7	17.9	250	78	0.26	0.08
7	28	13080	75	76	492	259	14	19	6.9	4.8	91	64	0.09	0.06
Total	228		687	604	7790	1823	15	37	115.4	53.7	191	89	0.20	0.09

¹ As-fired coal heat value based on primary coal used in each Region, after Babcock & Wilcox (1998).

² Total CO_2 emissions based on coal consumption and carbon content by region (Table II); CO_2 sequestered assumes sequestration of 100% of emissions.

³ Carbonation cost per ton of ore, derived from NETL feasibility by Lyons et al. (2003), with adjustments described in text.

The non-heat-treated serpentine ores (Regions 2-4, 6) were ground to 80% minus 200-mesh ($75 \mu\text{m}$), a savings of approximately $70 \text{ kW}\cdot\text{h}/\text{ton}$ of ore compared to the finer grind assumed for the NETL study. Thus, the final adjusted sequestration cost for the non-heat-treated serpentine ores is roughly \$15 per ton ore.

Table VI includes two sets of carbonation costs. The first set is for what has been termed standard pretreatment, with the associated costs described above. The second set of carbonation costs refers to the activated pretreatment methodologies, which were defined previously in the discussion for Table II. Ultrafine grinding was utilized for activation of the olivine and wollastonite ores and/or concentrates, while heat-treatment was utilized for activation of the serpentine ores. The grinding energy necessary to grind beyond the 400-mesh (37 μm) size assumed in the NETL study, or the energy required to add a heat-treatment step for the serpentine ores, was reported in Table IV. Using these energies and the \$0.054 per kW•h basis from the NETL study, the adjusted carbonation costs per ton ore and per ton CO₂ were calculated.

DISCUSSION

Carbonation Costs

The carbonation cost summary in Table X illustrates the complex relationship between mineral reactivity, degree of pretreatment, ore demand, and ultimate costs. For example, the ore demand is decreased by roughly 75% for all seven Regions with the addition of the activation step, which reduces the mean sequestration cost from \$191 to \$89 per ton CO₂ sequestered, and cuts the cost per kW•h to \$0.09 per kW•h. The lowest costs were found for the standard pretreatment olivine ores from Regions 1 and 5, at \$54 and \$55 per ton CO₂ sequestered, respectively. These costs increased by roughly \$5 per ton CO₂ with the addition of the activation step. Considering the mineral resources described previously for each region, the activation step would only be recommended for the Region-5 olivine ore, due to its limited availability. The wollastonite ore from Region 7 that was activated by ultrafine grinding has the second lowest carbonation cost, at \$64 per ton CO₂ sequestered. The wollastonite exhibited greater reactivity than any of the other minerals, but its higher R_{CO₂} value and lower ore grade, and the ultrafine grinding activation step resulted in slightly higher costs than the olivine ores.

Of the four regions utilizing serpentine as the mineral reactant, only the antigorite ore from Region 6 has carbonation costs reasonably close to those for the olivine and wollastonite ores. The heat-activated antigorite ore has a carbonation cost of \$78 per ton CO₂ sequestered. This is roughly 35-40% of the cost for the heat-activated lizardite ores from Regions 2-4, and suggests that only the Region 6 serpentine could be reasonably considered for *ex situ* mineral carbonation, with the current process developments, based on economics alone.

CO₂ Balance

The total energy generation by region reported in Table VI was included for calculation of the carbonation cost per kW•h, and to determine the net CO₂ avoided by the mineral-carbonation process. The NETL study determined a total energy demand of 352 MW for the baseline process. This baseline value was adjusted to account for the lower energy consumption required for the 1-hour carbonation residence times (all minerals), lower P_{CO₂} utilized for wollastonite carbonation, and the coarser particle size used for the non-heat-treated serpentine ores. The adjusted energy-consumption figures are reported by region in Table VII, in GW•h per Mt CO₂ sequestered, along with the energy consumption required for the activation steps, with the sum of the two being the total energy consumption for the activated ores. Assuming the energy required for the mineral-carbonation process was supplied by the same coal-fired power plants generating the CO₂ to be sequestered, the CO₂ generated by the mineral-carbonation process was calculated, and subtracting the latter from the total CO₂ sequestered results in the net CO₂ avoided. The CO₂ avoided with the standard pretreatment methodology for all seven regions is roughly 76% of the total CO₂ sequestered. Carbonation costs increase accordingly for each of the mineral reactants.

Table VII. Energy consumption for the mineral carbonation process, with derived CO₂ avoided.

Region	Energy, GW•h (x1000)	CO ₂ seq., Mt ¹	Energy consumption, GW•h/Mt CO ₂ seq.			CO ₂ avoided, Mt		Carbonation cost, \$/t CO ₂ avoided	
			std. ²	act. ³	Total	std.	act.	std.	act.
1	18	18	300	333	633	13	7	78	167
2	9	10	180	2022	2202	8	0	537	NC
3	9	10	180	2251	2431	8	0	538	NC
4	72	72	180	2022	2202	59	0	521	NC
5	184	187	320	333	653	126	63	81	173
6	320	231	180	829	1009	187	0	309	NC
7	75	76	190	239	429	62	43	112	110
Total	687	604				463	112	249	479

¹ Total CO₂ emissions based on coal consumption and carbon content by Region (Table II), CO₂ sequestered assumes sequestration of 100% of said emissions.

² Energy consumption for complete sequestration operation, including energy for standard pretreatment methodology and carbonation energy derived from White (2003).

³ Energy for activated pretreatment methodology, mechanical or thermal (from Table IV).

Inclusion of the activation steps dramatically lowers the CO₂ avoided and essentially eliminates the heat-activated serpentine ores from consideration. Inclusion of the heat-activation step results in negative CO₂ avoided, which means more CO₂ is generated than sequestered by the process. The ultrafine grinding step used to activate the olivine and wollastonite more than doubles the olivine carbonation cost, but has little impact on that of the wollastonite. The reason for the latter lies in the lower total energy consumption required for the activated wollastonite compared to the activated olivine. Because the two activated minerals have nearly identical R_X, the lower energy consumption for the activated wollastonite outweighs its higher R_{CO₂} and results in a lower carbonation cost compared to the olivine ores. These results suggest that inclusion of an activation step may be warranted for the wollastonite ore but not recommended for the olivine ores, while heat activation of the serpentine ores is not tenable.

CONCLUSION

Carbon dioxide sequestration by an aqueous mineral carbonation process was demonstrated in laboratory-scale batch autoclave tests, using three primary silicate-mineral reactants. These reactants, generally characterized from most reactive to least reactive, include the Ca-silicate wollastonite, Mg-silicate olivine, and hydrated Mg-silicate serpentine. The studies conducted on the Mg-silicate olivine provided the basis for a process feasibility study, which determined a carbonation cost of \$69 per ton of CO₂ sequestered. The study included sensitivity analyses for carbonation reactor residence time and P_{CO₂}, which were utilized to adjust the carbonation costs for more recently developed mineral-specific process improvements. The adjusted carbonation cost for the baseline olivine process is \$54 per ton of CO₂ sequestered. An energy requirement of 352 MW was determined for a process scaled for the sequestration of 100% of the CO₂ emissions from a 1.3-GW coal-fired electric generation plant (1,100 tons CO₂ per hour). After accounting for the sequestration energy demand, CO₂ avoided was 72% of the total CO₂ sequestered, at a cost of \$78 per ton of CO₂ avoided.

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 CO₂ sequestered, at an energy cost of \$0.09 to \$0.20 per kW•h, depending on the intensity of mineral-pretreatment operations. The CO₂ avoided for all seven Regions was 76% of the CO₂ sequestered, when using standard pretreatment methodologies.

The studies included an investigation of mineral availability in the seven carbonation regions identified. Total coal-fired electric generation CO₂ emissions within these regions account for roughly 1/3 of the U.S. total, and would require 1.8 to 7.8 Gt per year of silicate ore to carbonate 100% of the emissions, depending on the degree of mineral pretreatment utilized. Two regions utilized olivine, four utilized serpentine, and one utilized wollastonite as the mineral reactant. However, mineral availability followed a reverse trend compared to reactivity, with the order from most abundant to least abundant being serpentine, olivine, and finally wollastonite. Based on ore demand calculations made as part of the study, current resource estimates for wollastonite could not support the regional ore demand, and only one of the regions utilizing olivine could meet the demand for a significant time. Serpentine resources likely exceed the ore demands in three of the four regions but would require dozens of mines on the scale of 50 kt per day to meet the regional demand.

Effective thermal and mechanical mineral activation methodologies were identified that could decrease ore demand by up to 75%. However, energy-consumption for both activation methodologies dramatically impact the process economics and CO₂ balance. Mechanical activation of olivine is not recommended, primarily because it reduces the CO₂ avoided by nearly 50%, and sufficient mineral resources are available in the one region to meet the ore demand without the activation step. However, mechanical activation of wollastonite is recommended, due to its limited availability and the improvement in process economics and minimal impact on CO₂ avoided by inclusion of the activation step. Serpentine carbonation costs were reduced to roughly \$78 per ton of CO₂ 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 CO₂ 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 CO₂ balance.

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 the 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. The latter can not 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.

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