

Ex Situ Aqueous Mineral Carbonation

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The U.S. Department of Energy's National Energy Technology Laboratory (NETL) located in Albany, OR (formerly the Albany Research Center) has studied ex situ mineral carbonation as a potential option for carbon dioxide sequestration. Studies focused on the reaction of Ca-, Fe-, and Mg-silicate minerals with gaseous CO₂ to form geologically stable, naturally occurring solid carbonate minerals. The research included resource evaluation, kinetic studies, process development, and economic evaluation. An initial cost estimate of ~\$69/ton of CO₂ sequestered was improved with process improvements to ~\$54/ton. The scale of ex situ mineral carbonation operations, requiring ~55 000 tons of mineral to carbonate, the daily CO₂ emissions from a 1-GW, coal-fired power plant, may make such operations impractical.

Introduction

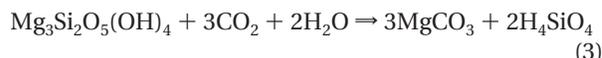
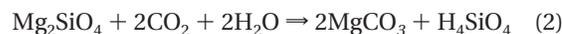
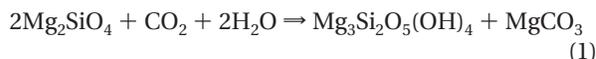
An estimated 22 gigatons (Gt) of anthropomorphic CO₂ was emitted worldwide in 1990, of which the U.S. contribution was ~5 Gt. By 2005, U.S. annual emissions of CO₂ increased to 5.9 Gt, and worldwide emissions were 25 Gt (1). In the absence of changes in policy, technology, or both, CO₂ emissions will continue to increase. Improving energy efficiency and using alternative energy sources could produce significant reductions in CO₂ emissions, but these alone may not achieve desired levels, making it necessary to capture and sequester CO₂.

Reaction of mineral oxides with CO₂ to form stable mineral carbonates is one potential way to sequester CO₂. Some of the earliest discussion of mineral sequestration of anthropogenic CO₂ occurred at the Los Alamos National Laboratory (LANL), where an aqueous process was proposed for mineral carbonation of serpentine [Mg₃Si₂O₅(OH)₄] ores (2, 3). The LANL process is based on technology developed during World War II by the Tennessee Valley Authority (TVA) and U.S. Bureau of Mines (USBM) for production of Mg metal from olivine (Mg₂SiO₄). In the TVA/USBM process, olivine was leached with HCl to extract magnesium as MgCl₂, followed by electrolysis of the MgCl₂ to recover Mg and regenerate HCl (4, 5).

The LANL process substituted a complex MgCl₂ dehydration and crystallization operation for the electrolytic stage of the TVA/USBM process. During the acid-recovery step, crystallized MgCl₂ is converted to Mg(OH)₂, which is then reacted with CO₂ to form magnesite (MgCO₃). Feasibility studies of the LANL process at the National Energy Technology Laboratory (NETL) and International Energy Agency (IEA)

found that the energy required for the dehydration and crystallization steps was four times the electrical energy produced by burning the coal, resulting in a negative CO₂ balance (6, 7).

These results led NETL to propose an alternate process based on the naturally occurring alteration of Mg-bearing ultramafic rocks. Nature's carbon cycle sequesters CO₂ as mineral carbonates for geologic periods of time, primarily by precipitation from the ocean. A less common but significant part of this cycle is the hydrothermal process called serpentinization, in which ultramafic rocks bearing Mg-silicate minerals such as olivine are altered to produce hydrated Mg-silicate minerals (e.g., serpentine) and carbonates (e.g., magnesite) (eq 1). This reaction is thermodynamically favored and occurs in nature, and large quantities of Mg-silicate minerals exist, making it a logical basis for CO₂ sequestration. If the concentration of CO₂ is increased, formation of serpentine may be suppressed, and only carbonate and silicic acid, free silica, or both are produced (eq 2). Experimental work at NETL demonstrated that the list of potential mineral reactants can be expanded to include hydrated Mg-silicate minerals (eq 3) and Ca- and Fe²⁺-rich silicates (eqs 4 and 5) (8).



A key theoretical measure of the carbonation potential of a mineral reactant is its R_{CO_2} , which is defined as the mass of ore necessary to convert a unit mass of CO₂ to a carbonate. By this definition, a low R_{CO_2} is preferable to a high R_{CO_2} . R_{CO_2} was introduced for hydrated Mg-silicate serpentine [Mg₃Si₂O₅(OH)₄], where the molar concentration of Mg in a serpentine sample was used to calculate the theoretical number of moles of CO₂ that could be converted to magnesite by reaction with the serpentine (9). 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. This modified method also permits calculation of the carbonation potential for alternative feed stocks. Because the R_{CO_2} calculated here incorporates Ca and Fe²⁺ in addition to Mg in the calculation, the values differ slightly from those reported by Goff.

In 1998, NETL, in collaboration with other laboratories, began an extensive research program to estimate the cost to sequester all of the CO₂ from a 1-GW, coal-fired power plant into a mineral carbonate. The goal of this program was to estimate how much additional cost CO₂ sequestration would add to the price of electricity. The approach began with the proposed ex situ carbon-sequestration process shown in Figure 1. An extensive experimental program sought to define what minerals to use, particle size and methods of comminution, mineral pretreatment options, solution chemistry, reaction parameters such as time, temperature, and pressure, and suitable reactor designs.

The experiments established realistic but not necessarily optimal process conditions, which were then used in a feasibility study to calculate the cost of the process; separation

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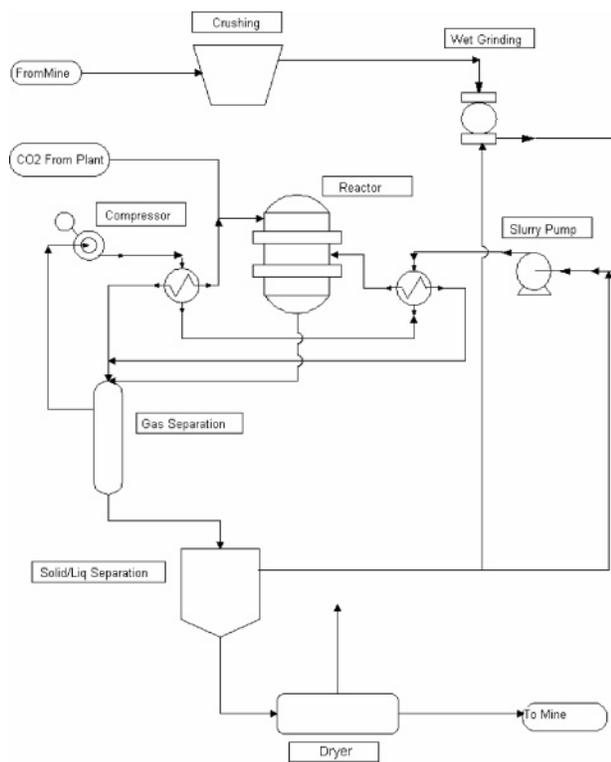


FIGURE 1. Aqueous mineral carbonation process flow diagram.

and transportation costs for CO₂ were not included. The feasibility study also allowed for substitution of alternative processes and equipment. While the process and conditions may not be optimized, they provide a basis for comparison. For example, replacing the autoclave reactor with a continuous plug-flow reactor generates some savings, but this change does not significantly affect the economics of the process.

Materials and Methods

Materials used in this study were chosen for their availability in large quantities near coal-fired power plants and ability to form carbonates. The United States contains large ultramafic resources that may be suitable for carbon sequestration (10, 11). Wollastonite (CaSiO₃) is another mineral that can be carbonated. Seven regions within the continental United States (Figure 2) were identified that contain these mineral resources with potential for mineral carbonation (12). Regions 1 and 5 contain olivine; regions 2–4 contain lizardite serpentine; region 6 contains antigorite serpentine; and region 7 contains wollastonite.

Pretreatment. The carbonation process requires size reduction of the mined ore. Field samples of the minerals were crushed and then ground to minus 75 μm or minus 38 μm in conventional laboratory rod or ball mills, and the energy requirements for these operations were estimated. Additional size reduction, if desired, was accomplished in a stirred-media detritor (SMD), from which direct energy measurements were possible.

Heat treatment was investigated as a means to remove water of hydration from the serpentine samples. Ground samples were typically heated to 630 °C for 2 h.

A blended head sample of each prepared feed material was analyzed for chemical composition. The head analysis and the analysis of the product solids were used to determine the extent of reaction in the carbonation tests.

Kinetic Experiments. Kinetic experiments were conducted in a continuously stirred batch autoclave. For each test, the desired amount of mineral reactant was mixed with carrier solution (usually distilled water or bicarbonate/salt

solution) to make a slurry (normally 15% solids). The slurry was poured into the autoclave, the autoclave sealed, purged with CO₂, and heated to the desired test temperature. Heating time was typically 1 h. A gas booster pump was used to inject enough CO₂ to obtain the desired pressure. The pump was controlled by a pressure transducer on the autoclave that allowed injection of additional CO₂ during the test to make up for pressure losses due to reaction, leaks, or both. Mixing of all three phases was achieved with a gas-dispersion agitator. Tests showed a dramatic increase in the extent of reaction in 1 h when the stirring rate was increased to 1000 rpm, after which no increase occurred. The autoclave was held at temperature and pressure for the desired amount of time, after which the autoclave was cooled, the pressure bled off, and the slurry removed and filtered. The solids were dried, weighed, and sampled for analysis. The solution was also analyzed.

Solutions. Distilled water was used as the carbonation carrier solution in the initial tests and was considered the carbonic acid route. However, reaction rates for most minerals were low in distilled water. Based on the results from early tests, a buffered saline solution (0.64 M NaHCO₃ and 1 M NaCl) became the standard solution. The NaHCO₃ in this system served the dual purpose of modifying the solution to slightly alkaline pH to facilitate carbonate precipitation while acting as an effective CO₂ carrier.

Feasibility Study. A feasibility study (13) was conducted based on a process design developed at NETL (14). A steady-state simulation of the process was created in Aspen process simulation software, from which capital- and operating-cost estimates were generated.

Results and Discussion

Kinetic Experiments. Nearly 700 individual tests were conducted to investigate the effect of temperature, partial pressure of CO₂ (P_{CO_2}), solution chemistry, particle size, amount of chemically bound water removed during heat treatment, and effect of high-energy attrition grinding on the carbonation reaction rate. Figure 3 shows the results of a set of kinetic experiments for serpentine, olivine, and wollastonite ground to <75 μm. The reaction rate for serpentine is quite slow, unless the chemically bound water is removed by heat treatment. Heat-treated serpentine reacts rapidly, reaching 50% extent of reaction in 1 h, but the maximum never exceeded 65%. Similar results were obtained with high-energy attrition grinding, but this carries a substantial energy penalty. Olivine carbonation proceeds to over 80% in 6 h. Wollastonite is the most reactive, reaching over 70% in 1 h, and unlike the magnesium minerals, the wollastonite reaction proceeds rapidly in distilled water.

The reaction rate for olivine is controlled by the surface area (15). Thus, olivine is activated simply by reducing the particle size to increase the surface area. Larger, partially reacted olivine particles and smaller (<10 μm) particles of MgCO₃ are observed in the reaction product (16). Olivine particles had a Mg-depleted surface and an olivine core, consistent with the shrinking-core model, in which the particle surface reacts to release magnesium into solution, leaving a shrinking core. Then MgCO₃ precipitates from the solution. The composition and effect of this passivating layer on the carbonation of olivine have been studied (17). Experiments with wollastonite are also consistent with the shrinking-core model. For serpentine, however, the extent of reaction was low, even when the mineral was ground to a very small size or the test time was increased to 24 h.

Because reaction rate is a function of particle size, which is determined largely by feed preparation, comparison of reaction rates is difficult in test series with differently prepared feeds. To make comparisons easier, the extent of reaction (R_t) in 1 h was normalized by dividing R_t in 1 h for a particular



FIGURE 2. Ultramafic mineral carbonation regions.

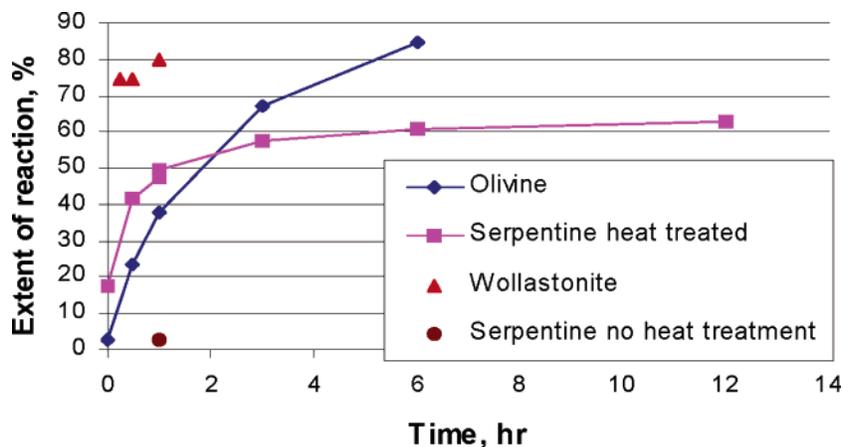


FIGURE 3. Extraction at 185 °C and 150 atm CO₂ in NaCl NaHCO₃ solution.

test by the maximum observed in 1 h ($R_{x(max)}$) for that particular material, and these normalized results are presented in Figure 4A and B. The actual maximum R_x values were 49.5, 81.8, and 73.5 for olivine, wollastonite, and HT serpentine respectively.

Figure 4A shows the effect that raising the reaction temperature from room temperature to 250 °C has on the extent of reaction. For Twin Sisters olivine, the maximum occurred at 185 °C, and for heat-treated serpentine, the maximum occurred at 155 °C. In contrast, wollastonite has a broad peak beginning at 100 °C. The carbonation process includes two distinct reactions, silicate mineral dissolution followed by carbonate precipitation. Dissolution kinetics improve with increasing temperature, but carbonate precipitation is retarded at higher temperatures due to reduced CO₂ solubility. A similar phenomenon regarding wall-rock alteration in CO₂-charged waters was described as the “unreactivity of CO₂ at higher temperatures” (18).

Similarly, the mineral-specific trends in Figure 4B show that Mg-silicate minerals exhibit a nearly linear increase in R_x with increasing P_{CO_2} , while R_x for wollastonite appears to be nearly independent of P_{CO_2} above ~40 atm.

The carrier solutions also had mineral-specific effects on R_x . The highest relative R_x for Mg-silicates was achieved in the NaHCO₃/NaCl solution. Ca-silicate carbonation was not as sensitive to solution chemistry, with similar results achieved in both the carbonate solution and distilled water. This may be indicative of a relatively higher solubility for

wollastonite compared to the Mg-silicates used, but seems more likely due to the much higher precipitation rate for CaCO₃ compared to MgCO₃. MgCO₃ precipitation rates are at least 4 orders of magnitude lower than those of CaCO₃ (19). Thus, wollastonite carbonation may not require as high a CO₂ concentration as does Mg-silicate carbonation.

The optimum mineral-specific carbonation conditions found in this study are reported in Table 1. These conditions represent the best-demonstrated reaction parameters to date and do not preclude future advancements. Process considerations were considered in this evaluation. For example, increasing P_{CO_2} above 150 atm for olivine was considered impractical.

Activation Studies. Mineral activation by aggressive pretreatment improves reactivity and could change the optimal carbonation conditions. For example, the reaction rates for olivine, wollastonite, and heat-treated serpentine can all be increased by decreasing the particle size and, thus, increasing the surface area. This can be done with traditional rod and ball mills or in a SMD mill. However, even very finely ground serpentine reacts very slowly.

High-intensity attrition grinding to less than 4 μm significantly increases reaction rate by increasing the surface area and disrupting the crystal structure of the mineral. Wet attritioning results in smaller particles, but dry attritioning produces noncrystalline material that is significantly more reactive. In some experiments, the carbonation reaction proceeded at room temperature and minimally elevated P_{CO_2} .

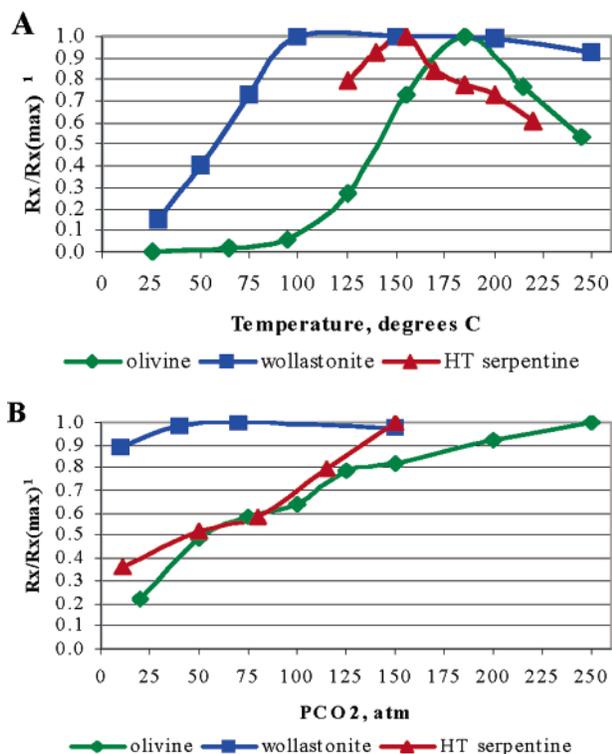


FIGURE 4. (A) Carbonation temperature sensitivity diagram. (B) Carbonation P_{CO_2} sensitivity diagram.

TABLE 1. Optimum Carbonation Conditions, by Mineral

mineral	carbonation conditions		
	$T, ^\circ C$	P_{CO_2}, atm	carrier solution
olivine	185	150	0.64 M $NaHCO_3$, 1 M NaCl
wollastonite	100	40	distilled water
HT serpentine	155	115	0.64 M $NaHCO_3$, 1 M NaCl

However, high-intensity attrition grinding is prohibitively energy intensive.

Heating serpentine above 630 °C removes chemically bound water from the lattice and produces a pseudoamorphous silicate phase (20). The theoretical energy required for the heat-activation process is the sum of the energy to heat the mineral to 630 °C and the enthalpy of dehydroxylation. Using data for heat capacities (21) plus quantitative differential thermal analysis for the dehydroxylation energies (95 kJ/mol for antigorite and 131 kJ/mol for lizardite) (22), the theoretical energy required for the heat-activation process was calculated to be 293 and 326 kW·h/ton for antigorite and lizardite, respectively.

Energy Analysis. The energy required to prepare the mineral feed to the size necessary for efficient carbonation is substantial. The energy required for the initial crushing step was estimated to be 2 kW·h/ton for all materials (12). Grinding to minus 75 μm (stage-1 grinding) adds another 11 kW·h/ton. Further grinding to minus 38 μm in ball mills is estimated to add 70 kW·h/ton (stage 2), and high-intensity grinding in an SMD (stage 3) adds an estimated 150 kW·h/ton.

A beneficiation step (e.g., gravity separation) would likely be necessary for ores that are significantly less than 100% of the desired mineral, and this step was incorporated into the process flowsheet for those minerals after the first stage of grinding. This increases the pretreatment energy required compared to that for nonbeneficiated ore materials. For these

cases, subsequent energies for additional grinding are based on processing the concentrated mineral.

Based on first-hand observation of several of the mining operations (open-pit quarries), ore grade was assumed to be 100% for the Twin Sisters olivine (region 1) and all of the serpentines (regions 2–4 and 6). However, analysis of olivine samples collected from the Asheville Mining District (region 5) identified alteration minerals (serpentine and talc), reducing the estimated ore grade to 70%. Bench-scale tests conducted on ore from region 5 indicated that gravity separation effectively concentrated the olivine, at an estimated energy penalty of ~2 kW·h/ton.

Wollastonite ore grades in region 7 are reported to be 40–60% (23). For this study, the grade was assumed to be 50%, and beneficiation energy was estimated to be 4 kW·h/ton, based on information provided with the samples from the largest wollastonite mine in region 7.

Table 2 summarizes the energy data from the mechanical and thermal activation studies for each of the minerals in the seven carbonation regions in Figure 2. The feed-material histories are summarized in the first three columns of the table. The table also includes energy consumption for the various mineral-pretreatment methodologies by stage. The reported energy for crushing includes all the energy costs including mining and transportation up to and including the crushing stage.

The theoretical energy cost to a power plant due to the mineral carbonation process is presented in Table 3. This is based on the mechanical/thermal activation energies calculated in Table 2 and experimental carbonation data. The basis for this calculation is a 1-GW, coal-fired power plant, burning coal with an as-fired heat value of 29 100 kJ/kg and carbon content of 74%, at 35% plant efficiency. The calculated CO₂ emissions (25.4 kt/day) were then used to calculate the daily ore requirement to sequester 100% of the CO₂ emissions at the R_{CO_2} and demonstrated R_x of each mineral reactant in a single pass through the carbonation reactor. It must be stressed that the energy calculations for this table do not include the energy costs of CO₂ capture and transportation.

The grinding-energy costs are high, but the reactivity of coarse feed is low. Inclusion of additional activation steps increases energy requirements and effectively eliminates SMD-ground materials and heat-activated ores from consideration. Only for wollastonite does the increased reactivity from pretreatment save energy.

Economic Analysis. The energy costs calculated above do not address the affect of the process on the price of electricity, and the feasibility study (15) helped answer that question. It evaluated sequestration of 100% of the CO₂ emissions from a 1.3-GW, coal-fired power plant using an olivine-based mineral-carbonation process. Assumptions for the feasibility were as follows: (1) Twin Sisters olivine (region 1) utilized, with the sequestration plant located next to the mine site; (2) ore is 100% olivine with MgO analysis of 49%; (3) open-pit mining, with process products redeposited in the depleted pits; (4) olivine ore ground to 80% minus 38 μm ; (5) 65% conversion achieved with each pass through the process; (6) 60% of the unreacted olivine from the products separated at 20 μm and recycled; (7) CO₂ transported to the plant via pipeline (CO₂ separation costs not included); (8) carbonation conditions, 2-h residence time, $T = 185^\circ C$, $P_{CO_2} = 150 atm$, $P_{H_2O} = 6.5 atm$, 30% solids, and carrier solution 0.64 M $NaHCO_3$, 1 M NaCl.

Approximately 2500 tons of fresh olivine and an additional 800 tons of olivine from the unreacted-product recycle loop are required to treat the ~1100 tons of CO₂/h generated under the above assumptions. Power requirements total 352 MW, nearly 75% of which is power required for ore-grinding operations. This represents a 27% energy penalty on the

TABLE 2. Energy Consumption by Feed Material and Specific Pretreatment Methodology

feed material			pretreatment energy consumption, kW· h/ton						
region	ore mineral and grade	pretreatment methodology	crush.	bene	grinding			heat treatment	total
					stage 1	stage 2	stage 3		
1	olivine, 100%	ball mill (-75 μm)	2		11				13
		ball mill (-38 μm)	2		11	70			83
		SMD mill	2		11	70	150		233
2-4	serpentine (lizardite), 100%	ball mill (-75 μm)	2		11				13
		heat treatment (-75 μm)	2		11			326	339
5	olivine, 70%	ball mill (-75 μm)	2	2	15				19
		ball mill (-38 μm)	2	2	15	70			89
		SMD mill	2	2	15	70	150		239
6	serpentine (antigorite), 100%	ball mill (-75 μm)	2		11				13
		heat treatment (-75 μm)	2		11			293	306
		heat treatment (-38 μm)	2		11	70		293	376
7	wollastonite, 50%	ball mill (-38 μm)	2	4	21	70			97
		SMD mill	2	4	21	70	70		167

TABLE 3. Energy Cost by Pretreatment

region	ore mineral and grade	pretreatment methodology	R _{CO2}	R _x , %	ore or conc, kt/day	% of total plant energy
2-4	serpentine (lizardite), 100%	ball mill (-38 μm)	1.8	61	75	26
		SMD mill	1.8	81	56	55
		ball mill (-75 μm)	2.5	9	706	37
5	olivine, 70%	heat treatment (-38 μm)	2.5	40	158	222
		ball mill (-75 μm)	1.8	16	286	22
6	serpentine (antigorite), 100%	ball mill (-38 μm)	1.8	61	75	28
		SMD mill	1.8	81	56	56
		ball mill (-75 μm)	2.1	12	445	24
7	wollastonite, 50%	heat treatment (-75 μm)	2.1	62	86	110
		heat treatment (-38 μm)	2.1	92	58	90
		ball mill (-38 μm)	2.8	43	165	67
		SMD mill	2.8	82	87	61

TABLE 4. Annual Coal Consumption, Energy Generation, CO₂ Emissions, Ore Requirements, and Carbonation Costs by Ultramafic Mineral-Carbonation Region

region	coal, Mt	heat value, Btu/lb ^a	energy, GW·h (1000 s)	CO ₂ seq, Mt ^b	ore demand, Mt	sequestration costs			
						\$/t ore ^c	\$, billions	\$/ton CO ₂ seq	\$/kW·h
1	7	12 300	18	18	53	18	1.0	54	0.06
2	4	11 030	9	10	302	15	4.4	427	0.49
3	4	11 030	9	10	303	15	4.4	427	0.49
4	31	11 360	72	72	2117	15	30.7	427	0.43
5	69	13 080	184	187	552	19	10.3	55	0.06
6	85	13 080	220	231	3971	15	57.7	250	0.26
7	28	13 080	75	76	492	14	6.9	91	0.09

^a As-fired coal heat value based on primary coal used in each region. ^b Total CO₂ emissions based on coal consumption and carbon content by region; CO₂ sequestered assumes sequestration of 100% of emissions. ^c Carbonation cost per ton of ore, derived from feasibility study (15).

power plant for which the sequestration operation was designed.

Although the feasibility study was based on olivine, it is possible to use the sensitivity graphs included with the study and other information to estimate the cost for other minerals with mineral-specific cost adjustments. The adjustments ignore capital costs for processing equipment and the cost of capturing and transporting the CO₂; thus, the costs are lower than would be expected from a more detailed analysis.

The results of these calculations are presented in Table 4. The basis for this table is sequestration of all the CO₂ produced by coal-fired power plants within 200 miles of the

center of the ore body in each region identified in Figure 2 (14).

If the energy required for the mineral-carbonation process is supplied by the same coal-fired power plants generating the CO₂ to be sequestered, the CO₂ generated by the process can be calculated and subtracted from the total CO₂ sequestered to calculate net CO₂ avoided (Table 5). Carbonation costs increase accordingly, to roughly \$80 and \$112 per ton of CO₂ avoided for the olivine ores and the wollastonite ore, respectively. Carbonation costs for the antigorite and lizardite serpentine ores increase to roughly \$300 and \$500 per ton of CO₂ avoided.

TABLE 5. Energy Consumption for the Mineral-Carbonation Process, with Derived CO₂ Avoided

region	energy, GW·h (1000 s)	CO ₂ seq, Mt ^a	energy consumption, GW·h/Mt CO ₂ seq			CO ₂ avoided, Mt		carbonation cost, \$/t CO ₂ avoided	
			std ^b	act. ^c	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	220	231	180	829	1009	187	<0	309	NC
7	75	76	190	239	429	62	43	112	110

^a Total CO₂ emissions based on coal consumption and carbon content by region; CO₂ sequestered assumes sequestration of 100% of calculated emissions. ^b Energy consumption for complete sequestration operation, including standard (std) pretreatment and carbonation reaction. ^c Energy for activated (act.) pretreatment (mechanical or thermal) (from Table 2).

A wet magnetic-separation step was demonstrated to produce a marketable magnetic concentrate from serpentine ores. This product would result in modest savings of an estimated \$0.01/kW·h for the carbonation cost of the serpentine ores, but would not offset the excessive energy consumption required for the heat-activation step, nor, without heat activation, the unfavorable CO₂ balance resulting from low reactivity of the ores.

The minimum ore requirement can be calculated for an ideal process using R_{CO_2} . Like the second law of thermodynamics, the minimum requirement is true only for an ideal process; a real process would require more ore. R_{CO_2} is independent of the process used to sequester CO₂ and assumes all of the Mg, Ca, and Fe²⁺ react to form their respective carbonates. In the best-case scenario (Twin Sisters olivine), the mass of ore required is 1.6 times the mass of CO₂ sequestered; for the other ores, R_{CO_2} is greater than 2. However, it may be more appropriate to compare the mass of mineral required to sequester the CO₂ to the mass of coal required to produce that same CO₂. Burning 1 ton of carbon produces 3.66 tons of CO₂. Again, in the best-case scenario and assuming coal is 10% ash, ~5.3 tons (3.66 × 1.6 × 0.9) of olivine has to be mined for each ton of coal. The ratios range from 6.5:1 to 8.9:1 for serpentine and ~8.9:1 for wollastonite. The scale of mining and milling the mineral reactant alone presents significant environmental and economic cost.

Alternative Resources. The following industrial byproducts have been suggested as alternative mineral resources for ex situ carbonation: asbestos-mining tailings; electric-arc-furnace (EAF) dust; steel-making slag; cement-kiln dust; waste concrete; coal fly ash.

Some of these (asbestos-mining tailings, EAF dust, cement-kiln dust, and coal fly ash) are already appropriately sized, eliminating much of the cost associated with size reduction of mined ore. The quantities of many of these resources are not well defined, but they are small (Mt) when compared to the amount of CO₂ to be sequestered (Gt/yr). Their use would most likely be in niche applications where a hazardous waste could be remediated by carbonation or where a company could sequester enough CO₂ to meet emission targets or potentially sell CO₂ credits.

Asbestos Mining Tailings. Chrysotile, an asbestiform mineral included in the serpentine group, has the same chemical formula but a crystallographic structure different from those of antigorite and lizardite, the two primary serpentine minerals studied in this research. In most deposits, chrysotile is only a small percentage of the serpentine, and where serpentine is mined for chrysotile asbestos, the tailings typically contain significant residual asbestos and may be classified as hazardous. These tailings would be ideal feed for mineral carbonation, because not only has size reduction already taken place, but when chrysotile is carbonated, the

asbestiform nature of the mineral is destroyed. Carbonation of these tailings could both remediate a hazardous waste and sequester CO₂.

The United States has an estimated 5–8 Mt of tailings from asbestos mining, located primarily in Vermont and California, that could be used for carbon sequestration. Assuming an R_{CO_2} of 2.2 and 100% conversion, these resources could sequester 2–4 Mt of CO₂. Asbestos tailings in Canada are a significantly larger potential resource, with an estimated 40 Mt in Baie, New Foundland; 25 Mt in Cassiar, British Columbia; and 90 Mt in Quebec. With the same assumptions as above, these resources could sequester 18, 11, and 41 Mt of CO₂, respectively.

EAF Dust and Steel-Making Slags. Steel-making operations produce significant quantities of CO₂, but they also produce dusts and slags that could potentially be used as carbonation feeds. EAF dust contains significant quantities of MgO, CaO, and FeO compounds that readily form carbonates, and its small particle size would facilitate a rapid reaction rate. However, the quantity of material available is unclear, and the EAF dust may contain significant quantities of metals that in an aqueous process could go into solution, creating a potential water pollution problem.

Steel-making slag is compositionally similar to EAF dust. For a small cost, the slag could be granulated, but further size reduction would likely be necessary for carbonation.

Cement-Kiln Dust and Waste Concrete. The nonhydrated dust from cement kilns would be an ideal candidate for carbonation. Its small particle size and oxide form make it more reactive than silicates. An estimated 5 Mt is produced each year, but some is used as soil-liming agent. Assuming all 5 Mt were available for carbonation, the dust is 85% CaO, the R_{CO_2} is 1.5, and 100% conversion, this resource could sequester ~3 Mt CO₂, less than half the annual CO₂ emissions from a 1-GW, coal-fired power plant. Cement kilns are major CO₂ producers, but the CO₂ produced by cement making exceeds the amount that could be sequestered from the dust. Again, it might be possible to sequester enough to reduce emissions and sell CO₂ credits.

Waste concrete has a composition similar to that of cement-kiln dust, but it would have a higher R_{CO_2} due to hydration and the inclusion of aggregate. Transportation and size-reduction costs probably make its use cost-prohibitive.

Coal Fly Ash. The ash content of coal is highly variable, and its composition varies from <1 to >20% minerals that could be carbonated. Wyoming subbituminous coal contains ~6% ash, while Texas lignite contains more than 50% ash.

A typical anthracite contains 11% ash with an analysis of 0.6% CaO and 0.3% MgO. The ash from burning this coal could carbonate less than 0.03% of the CO₂ produced from burning the coal. The numbers differ for different coals, but in all cases, the result is the same: an insignificant amount of CO₂ could be sequestered using the ash from the burned

coal. In addition, much of the ash is already sold to the cement industry as pozzolan.

Significance of Results. Ex situ carbon sequestration by mineral carbonation has the potential to safely sequester CO₂ as carbonate minerals. Because carbonates are naturally occurring minerals that are stable over geologic periods of time, the mineral-carbonation product is safe and stable, resulting in negligible release of CO₂ to the environment. Appropriate mineral resources near the coasts of the contiguous United States exist in sufficient quantities to sequester all of the CO₂ produced by coal-fired power plants in those regions.

However, ex situ sequestration creates its own environmental legacy, due to the massive mineral requirements and associated scale of mining. Assuming complete conversion, more than 5 times as much ore as coal must be mined to sequester all of the CO₂ generated by burning that coal; an actual industrial process would require more ore. The size of the mining operation is a significant economic and environmental problem for any ex situ process.

While it may not be a complete solution in itself, ex situ mineral carbonation could be part of an integrated approach to carbon sequestration that combines remediation of hazardous wastes such as asbestos tailings and use of readily available fine industrial wastes such as EAF and cement-kiln dusts to meet CO₂ emission goals.

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