

CARBON DIOXIDE STORAGE AS MINERAL CARBONATES

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INTRODUCTION

The sequestration of greenhouse gas emissions in the 21st century, in particular carbon dioxide (CO₂), will have a profound influence on the environmental impact of electric power systems within the United States and abroad. Within the U. S., nearly one-third of all anthropogenic or human-caused CO₂ emissions are generated by electric power systems estimated at 6 GtC/year (1). Large economic benefits will continue for the U.S., when and how CO₂ sequestration technologies will be implemented, thus, securing inexpensive and plentiful sources of fossil-fuel-based electric power.

As participants in the Mineral Carbonation Study Program within the United States Department of Energy (DOE), the Mineral Carbonation Research Cluster has focused its carbon sequestration efforts on developing a long-term mitigation strategy. Our approach employs reacting abundant magnesium-rich silicate minerals in an exothermic reaction with CO₂ forming thermodynamically stable and environmentally benign mineral carbonate products. Drawing on mineral carbonation to reduce CO₂ emissions has a myriad of potential advantages. Mineral carbonation mimics the natural weathering of rock. Mineral carbonates, the principal product of the process, are known to be stable over geological time periods (millions of years). For this reason, mineral sequestration ensures permanent fixation rather than temporary storage of CO₂ guaranteeing no legacy issues for future generations. Readily accessible deposits of magnesium silicate minerals exist as ultramafic complexes along the eastern and western coastal regions of North America (2,3). Globally, these natural raw materials for binding CO₂ exist in grand quantities. Therefore, readily accessible deposits/outcrops exist worldwide in quantities that far exceed even the most optimistic estimates of coal reserves. Finally, the overall mineral carbonation process is exothermic and hence, has the potential to become economically feasible.

The aim of DOE's Mineral Carbonation Program is to generate a valuable knowledge base that can lead to development of cost-competitive mineral CO₂ sequestration methods. In achieving this goal, mechanisms, kinetics, and heat requirements of various CO₂ mineral reactions must be understood well enough to identify feasible reaction pathways and to permit engineering process development. A secondary and equally significant target is to acquire knowledge essential to understanding the reactions of CO₂ with underground minerals, in support of the U.S. DOE's geological sequestration programs where CO₂ may be injected into deep saline formations, or depleted oil or gas reservoirs. Knowledge of the reaction characteristics of CO₂ with various minerals at elevated pressures and temperatures such as those found deep underground would help predict the long-term effects of such practices.

Experiments investigating the reactivities of olivine and serpentine in aqueous and bicarbonate aqueous solutions under supercritical CO₂ pressures were conducted to help determine effects of particle size, P_{CO2}, temperature, and solution chemistry. Here we summarize published continuous-stirred-tank-reactor (CSTR) results (4,5) for reactions of ultramafic minerals with supercritical CO₂ and, for comparison, with a lignite fly ash.

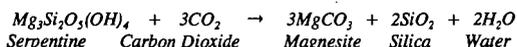
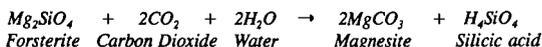
MATERIALS AND METHODS

All mineral carbonation reactions were performed in Hastelloy C-276 autoclaves. Tests were conducted at subcritical (P_{CO2} = 51 atmospheres) and supercritical CO₂ (P_{CO2} = 80, 126, and 136 atmospheres) pressures; reaction temperatures of 155°, 185°, and 230°C and residence times ranging from 3 to 144 hours. In a typical experiment, finely ground minerals and water (15-20% solids concentration) were charged into the CSTR. The CSTR was immediately sealed, purged with

gaseous CO₂, weighed (tare weight), and submerged into an ice bath. Liquid CO₂ was carefully injected through the side port of the autoclave while heating to a pre-calculated process temperature and pressure. The mineral/water/liquid CO₂ mixture was sufficiently agitated during heat up to prevent any settling of magnesium-enriched solids. A modified CSTR system to include a CO₂ gas booster pump and pressure switch was latter designed and operated under relatively constant CO₂ pressures. The addition of the gas booster pump permitted successful operation at an operating pressure of 126 atmospheres (P_{CO2} = 115 atmospheres).

RESULTS & DISCUSSION

The conceptual process for sequestering CO₂ as mineral carbonates was initially proposed by O'Connor, et. al. (4,5) utilizing olivine, water, and supercritical carbon dioxide. In this method, injected CO₂ is dissolved in a slurry of water and mineral reactant, such as olivine. The CO₂ reacts with the olivine/water mixture forming carbonic acid, which dissociates into hydrogen cations and bicarbonate anions. Reaction of carbonic acid with the solid mineral consumes most of the hydrogen cations and liberates equivalent amounts of magnesium cations. These Mg²⁺ cations react with the HCO₃⁻ to form magnesite (MgCO₃). Under supercritical CO₂ pressures, carbonic acid is continuously being generated, consumed, and regenerated. The reaction sequence is concluded: 1) when the reactive surface of the mineral particle is depleted or 2) becomes inactive by mass transfer resistance (i.e., formation of a foreign oxide coating on the surface of mineral reactant particle). The acid-base chemistry for Mg₂SiO₄ and Mg₃Si₂O₅(OH)₄ are given below:



Olivine [forsterite end member (Mg₂SiO₄)] and serpentine [Mg₃Si₂O₅(OH)₄] were identified as being solid mineral reactants for the direct carbonation reaction (4-7). A foundry-grade olivine (identified as ARC olivine), a natural olivine (Twin Sisters, Washington purchased from WARD'S Natural Science Establishment, Inc.) and a synthetic forsterite sample (Alfa Aesar, a Johnston Matthey Company) were selected based on their desired characteristics of high purity, high MgO concentration and low water content. Chemical analyses of the ARC and WARD'S natural olivine, synthetic forsterite, and Cedar Hills quarry serpentine feed samples are included in Table 1. The magnesium oxide concentration was noticeably higher in the synthetic feed material (57.8 wt %) in comparison to both the ARC olivine (49.7 wt %) and WARD'S olivine samples (51.8 wt %). The basis for the lower MgO concentration in these natural feed minerals was attributed to iron substitution for magnesium within the solid solution series. X-ray diffraction data and patterns identified forsterite (Mg₂SiO₄) as the primary phase for both natural olivine feed samples. XRD also confirmed a trace constituent, enstatite (MgSiO₃), for each of the natural olivine samples. This finding was fully anticipated for the raw materials.

Olivine carbonation results from the preliminary series of tests performed at ARC are included in Table 2. Initial results revealed the mineral carbonation reaction is extremely slow at ambient temperatures and pressures. For example, test MC-14 conducted at 150°C and 750 psi (P_{CO2} = 51 atms.) resulted in only a 17.6% conversion of olivine to magnesite after 144 hours. However, increasing both process temperature and CO₂ partial pressure helped to improve upon the kinetics of the carbonation reaction. This was demonstrated during the series of tests at different time intervals (3, 6, 12, 24, and 48 hours) under identical conditions (T = 185°C and P_{CO2} = 115 atmospheres in distilled water) using again the ARC olivine feed sample. Collectively, carbonation tests conducted within the series under relatively short reaction times (3, 6, and 12 hours) gave minor to moderate conversions of Mg₂SiO₄ to MgCO₃. Under longer residence times (24 and 48 hours), the conversion of silicate to carbonate increased with time-on-stream, achieving 51.8% and 56.1% of its stoichiometric maximum in 24 hours and 48 hours respectively. In substituting the synthetic forsterite for the solid reactant, olivine, within the series, significant improvement in terms of carbonation activity was attained. As shown in Table 2, the synthetic forsterite (MC-3) achieved carbonation to 76% of its stoichiometric maximum in just 3 hours, again at 185°C and 1,850 psig. While the chemical analysis of the synthetic material confirmed nearly exact molar concentrations of MgO and SiO₂ as compared to the natural counterparts, the presence of free periclase (MgO) and its subsequent reactivity with carbonic acid resulted in accelerating the mineral carbonation activity within the CSTR. A series of leach tests were later performed to help quantify the free MgO concentration present in the synthetic forsterite material. Results estimated the synthetic material to contain approximately 11 wt % MgO. Although preliminary in nature, these results tend to suggest MgO acts as a promoting agent within the carbonation reaction.

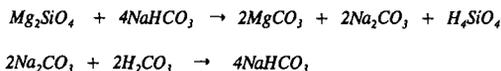
Duplicate experiments at NETL at higher process temperature and pressure (T = 230°C, P_{CO2} = 120 atm in distilled water) conditions coupled with using a minus 325 mesh raw material (WARD'S olivine feed) and a gas dispersion tube within the CSTR provided new evidence into the efficiency of the mineral carbonation reaction. Duplicate CO₂ analysis showed 28.9 weight percent of the recovered solid product as being identified as magnesium carbonate. The extent of reaction was experimentally determined to be over 80% of its stoichiometric maximum after 24 hours.

A major limitation of the CSTR mineral carbonation units at ARC and NETL was its lack of ability to introduce additional CO₂ to the reaction vessel as the carbonation reaction progressed. Hence, for longer test times, the P_{CO₂} decreased with increased extent of reaction, which perhaps retarded the reaction. A modified CTSR system to include a CO₂ gas booster pump and pressure switch was designed and operated at ARC at a operating pressure of 126 atmospheres. This development lead to a major improvement in rate and extent of reaction, as illustrated by the olivine and serpentine carbonation tests shown in tables 2 and 3 respectively. Under the modified system, test MC-25 showed a 91.5% rate of conversion for a finely ground olivine (-325 mesh) mineral to MgCO₃. In view of this finding, the effects of particle size, temperature, and P_{CO₂} on the olivine carbonation reaction were systematically examined.

Particle size of the silicate mineral was recognized as a key element in aiding the acceleration of the mineral dissolution reaction. This effect can be easily viewed by comparing % conversions of tests MC-4, MC-25, and MC-31 shown in Table 2. Under test conditions (T = 185°C, P_{CO₂} = 115 atm. in distilled water), test MC-25 produced over a 90% conversion of Mg₂SiO₄ to MgCO₃ employing a minus 37 micron natural olivine feed. In contrast, tests MC-31 and MC-4 achieved mineral carbonation conversions of 10.6% and 51.8% respectively in 24 hours utilizing the identical feed ARC olivine with the exception of the feed particles sizes being 150 x 106 microns for test MC-31 and 106 x 75 microns for test MC-4.

Another series of completed experiments aided in defining the temperature and CO₂ partial pressure requirements for the olivine carbonation reaction. At 115°C and P_{CO₂} = 80 atmospheres, test MC-42 showed no reaction had occurred after 6 hours. However, significant conversion to carbonate (68.2%) resulted in test MC-43 by increasing the process temperature to 185°C while holding CO₂ pressure identical to that in test MC-42. The extent of reaction, as exemplified in test MC-40, was enhanced further to ~85% by increasing the CO₂ process pressure to 115 atmospheres while holding the process temperature constant.

An improvement in mineral carbonation efficiency was established in modifying the solution chemistry of the liquid reactant, water. The final series of tests was conducted in a bicarbonate aqueous solution, 0.5 M NaHCO₃, 1 M NaCl, which dramatically enhanced the overall reaction rate. Sodium bicarbonate was established as a more effective CO₂ carrier, generating product solutions of nearly 20g/liter CO₂, compared to 0.5-1.0 g/liter CO₂ in tests using distilled water. The modified solution was found to be very stable, with nearly constant pre- and post-test pH values (~7.8), and relatively constant CO₂ concentrations. The following equations represent a possible reaction sequence in the bicarbonate aqueous solution.



NaHCO₃ is consumed by the mineral silicate, along with being regenerated by reaction with carbonic acid, which is also continuously regenerated due to the high P_{CO₂} in the system.

A Cedar Hills serpentine sample obtained from the Pennsylvania/Maryland state line district was selected for serpentine carbonation testing. XRD determinations established antigorite as the primary constituent for the serpentine feed sample with minor elements of chrysotile, magnetite, and kaolinite. Initial carbonation tests (T = 185°C, and P_{CO₂} = 115 atms.) performed for 24 hours with serpentine resulted in a much lower extent of reaction (34%) compared with identical tests conducted with the ARC olivine feed (51%). The removal of (both physically adsorption and chemically bound) inherent water present in the serpentine feed sample via heat treatment was envisioned to produce a more reactive sample. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were completed on the Cedar Hills feed sample to determine treatment temperature(s). DTA revealed three separate points of inflection, occurring at 160°C, 375°C (evolution of water of crystallization); and 614°C (evolution of constitutional water). For that reason, heat pretreatments were performed at 650°C for 2 hours.

It was also acknowledged that oxidation of the minor constituent magnetite present in the serpentine feed sample during heat treatment could potentially form a passive layer of hematite on the mineral surface, inhibiting the carbonation reaction. Thus, heat treatments on the serpentine feed sample were conducted in both air and CO₂. Chemical analysis of the air-treated products identified hematite being present, while magnetite oxidation to hematite was limited during treatments in CO₂. XRD analysis also confirms heat-treated serpentine samples were partially transformed to forsterite.

Table 3 shows both the serpentine carbonation conditions and results obtained in the series of tests performed at ARC. Tests conducted in distilled water for 24 hours showed marginal improvement in the serpentine carbonation reaction with the air-treated sample (57%) in comparison to the untreated serpentine sample (34%). Test MC-37 utilizing an air-treated serpentine feed sample showed a moderate improvement in extent of reaction (63.5%) for the serpentine carbonation test conducted in a bicarbonate aqueous solution (0.5 M NaHCO₃). The effect of gaseous atmosphere (CO₂ versus air) during heat treatments of serpentine was found significant for the carbonation tests conducted in the carbonation starting solution, 0.5 M NaHCO₃, 1 M NaCl. Extent of reaction increased to over 83% for the serpentine heat-treated in CO₂ compared to 41% for the serpentine treated in air. Both results were achieved in identical carbonation tests (T = 185°C; P_{CO₂} = 115 atms) conducted for 6 hours. In contrast, test MC-44 conducted under identical conditions utilizing

an untreated serpentine feed sample showed only minor conversion of serpentine to magnesite (6.8%) after 6 hours.

Finally, studies at NETL demonstrated a lignite fly ash (16% CaO + MgO) could also be used to produce a carbonated product as identified by XRD. Recent work by Anthony et. al. (8) has shown carbonation to be rapid at FBC operating conditions for dry ashes above 400°C. Hydration of the ash promotes the carbonation reaction below this temperature. Fly ash is seen as an excellent candidate to be used solely or in conjunction with mineral silicates for sequestering CO₂ within the mineral carbonation process. Future work at NETL will utilize a Coal Combustion By-product (CCB) database system for identifying best candidates to be used in the Mineral Carbonation Study Program.

CONCLUSIONS

DOE-sponsored carbon sequestration research at NETL, ARC, LANL, and ASU is addressing important issues related to the mineral sequestration of CO₂. Experimental investigations confirm magnesium silicates, olivine and serpentine, are equally amenable to the mineral carbonation process, even though serpentine requires heat treatment. Experimental data are being sought to help facilitate and develop kinetic models that can be employed to identify large-scale, cost-effective mineral sequestration strategies and to evaluate its physical, chemical, and environmental effects on the terrestrial and underground environments.

DISCLAIMER

Reference in this report to any specific product, process, or service is to facilitate understanding and does not imply its endorsement or favoring by the United States Department of Energy.

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Table 1. Chemical composition of reactant minerals, wt %

Oxide	ARC Olivine	WARD'S Olivine	Alfa Aesar Forsterite	Cedar Hills serpentine
Al ₂ O ₃	0.208	0.148	0.264	0.156
CaO	0.070	0.130	0.661	0.028
Cr ₂ O ₃	0.044	N/A	0.012	0.037
FeO	5.966	N/A	0.009	4.333
Fe ₂ O ₃	2.558	9.059	0.000	2.629
MgO	49.677	51.789	57.845	45.843
K ₂ O	0.007	0.02	0.019	<0.002
SiO ₂	41.357	38.205	37.929	37.500
Na ₂ O	0.099	0.00	0.101	<0.002
Volatiles ¹	0.401	0.70	0.123	11.500
Total	100.387	100.051	96.963	102.026

¹ Volatile constituents include: fixed carbon, mineral carbon, water

N/A - not available

Table 2 – Olivine Carbonation Tests – Test Summary

Test	Particle size, microns	Time, Hrs	Temp., C	PCO ₂ , atm	Carbonation Starting Solution	Product Solids CO ₂ , wt pct	Percent Stoichiometric Conversion
MC-3	-44	3	185	115	Distilled H ₂ O	32.50	76.0
MC-4	106 x 75	24	185	115	Distilled H ₂ O	18.30	51.8
MC-10	53 x 37	6	185	115	Distilled H ₂ O	1.25	3.5
MC-11	53 x 37	48	185	115	Distilled H ₂ O	19.80	56.1
MC-12	53 x 37	3	185	115	Distilled H ₂ O	0.33	0.9
MC-13	53 x 37	12	185	115	Distilled H ₂ O	6.58	18.6
MC-14	53 x 37	144	150	51	Distilled H ₂ O	6.21	17.6
MC-25 ¹	-37	24	185	115	Distilled H ₂ O	32.30	91.5
MC-31	150 x 106	24	185	115	Distilled H ₂ O	3.74	10.6
MC-40	-37	6	185	115	0.5 M NaHCO ₃ , 1 M NaCl	29.80	84.4
MC-42	-37	6	115	80	0.5 M NaHCO ₃ , 1 M NaCl	0.00	0.0
MC-43	-37	6	185	80	0.5 M NaHCO ₃ , 1 M NaCl	24.09	68.2

¹ Test MC-25 and all subsequent tests conducted in modified CSTR facility with gas dispersion

Table 3 – Serpentine Carbonation Tests – Test Summary

Test	Particle Size microns	Heat Pretreatment ¹	Time, Hrs	Temperature	PCO ₂ atmospheres	Carbonation Starting Solution	Product Solids CO ₂ , wt pct	Percent Stoichiometric Conversion
MC-32	-37		24	185	115	Distilled H ₂ O	11.40	34.2
MC-33	-37		24	185	115	Distilled H ₂ O	11.50	34.5
MC-34	-37	in air	24	185	115	Distilled H ₂ O	22.30	57.0
MC-37	-37	in air	24	185	115	0.5 M NaHCO ₃	22.60	63.5
MC-38	-37	in air	24	185	115	0.5 M NaHCO ₃ , 1 M NaCl	24.70	69.4
MC-39	-37	in CO ₂	6	185	115	0.5 M NaHCO ₃ , 1 M NaCl	28.20	83.2
MC-41	-37	in CO ₂	24	185	115	Distilled H ₂ O	20.17	59.5
MC-44	-37	in air	6	185	115	0.5 M NaHCO ₃ , 1 M NaCl	2.28	6.8
MC-45	-37	in air	6	185	115	0.5 M NaHCO ₃ , 1 M NaCl	14.45	40.6

¹ Heat treatments conducted for 2 hours at 600-650°C