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Abstract

The process developed for carbon dioxide sequestration utilizes a slurry of water mixed with olivine - forsterite end member (Mg_2SiO_4), which is reacted with supercritical CO_2 to produce magnesite ($MgCO_3$). Carbon dioxide is dissolved in water, to form carbonic acid, which likely dissociates to H^+ and HCO_3^-. The H^+ hydrolyzes the silicate mineral, freeing the cation (Mg^{2+}), which reacts with the HCO_3^- to form the solid carbonate. Results of the baseline tests, conducted on ground products of the natural mineral, have demonstrated that the kinetics of the reaction are slow at ambient temperature (22˚C) and subcritical CO_2 pressures (below 7.4 MPa). However, at elevated temperature and pressure, coupled with continuous stirring of the slurry and gas dispersion within the water column, significant conversion to the carbonate occurs. Extent of reaction is roughly 90% within 24 hours, at 185˚C and partial pressure of CO_2 (P_{CO2}) of 11.6 MPa. Current studies suggest that reaction kinetics can be improved by pretreatment of the mineral, catalysis of the reaction, and/or solution modification. Subsequent tests are intended to examine these options, as well as other mineral groups.

Introduction

Carbon dioxide gas generated by the combustion of fossil fuels is considered the most significant of the greenhouse gases, with CO_2 emissions estimated at 6 Pg C/year from fossil fuels alone by Freund and Ormerod, (1). Means to reduce the CO_2 emissions from the energy and/or process industries has become increasingly emphasized as a primary environmental concern. This can be achieved by efficiency improvements in fossil-fuel-fired power plants, use of alternative energy technologies, sequestration of CO_2, or some combination of these methods. Mineral carbonation, in which the CO_2 is reacted with minerals to form solid carbonates, is truly a permanent sequestration method, because the mineral carbonates are stable over geologic time periods.

Prior discussion of CO_2 disposal in solid form has appeared in the literature, as described by Lackner et al (2-3). The focus of these discussions has been an aqueous process using hydrochloric acid to leach serpentine and produce magnesium chloride. This reaction was well developed by the Tennessee Valley Authority by Houston (4) and U.S. Bureau of Mines by Gee (5) during World War II as part of an alternative process for the production of magnesium metal. Further steps in the mineral carbonation method include the production of magnesium hydroxide and recovery of the hydrochloric acid in a second unit operation, followed by reaction of the magnesium hydroxide with CO_2 to form magnesite ($MgCO_3$). The complexity of this process lead the authors to consider alternative mineral carbonation processes, which resulted in an investigation of the direct carbonic acid route, a new method for which DOE has filed a report of invention by O'Connor et al (6). Carbon dioxide is dissolved in a slurry of water and mineral reactant, such as forsterite (Mg_2SiO_4). The dissolved CO_2 forms carbonic acid, which likely dissociates to H^+ and HCO_3^-, with the H^+ hydrolyzing the silicate mineral, freeing the cation (Mg^{2+}). The Mg^{2+} then reacts with the HCO_3^- to form the solid carbonate mineral magnesite. The theorized reaction equation follows.

$$Mg_2SiO_4 + 2CO_2 + 2H_2O \qquad 2MgCO_3 + H_4SiO_4$$

Forsterite Carbon dioxide Water Magnesite Silicic acid

Although this method dramatically simplifies the mineral carbonation process flowsheet by combining the mineral dissolution and carbonation reactions in a single unit operation (figure 1), the vast amount of mineral reactant necessary for any ex-situ process is significant. Assuming a mean magnesium oxide (MgO) content of the major magnesium silicate ore minerals of 400 g/kg, the amount of the silicate mineral necessary to carbonate 100% of the CO_2 emissions from a single 500 MJ/s coal-fired power plant was estimated. Based on this concentration, the stoichiometry of the carbonation reaction, and assumptions regarding the ore recovery (95%) and efficiency of the carbonation reaction (80%), a single 500 MJ/s power plant, generating approximately 9 Gg/day CO_2, would require approximately 20 Gg/day of magnesium silicate ore. Several ultramafic complexes in North America are reported by Goff et al (7) to contain sufficient quantity of magnesium silicate mineral to provide raw materials for the mineral carbonation of all annual CO_2 emissions for many years. However, the scale of these mining operations, with significant mining and milling costs, and associated trace element contaminants, causes concern over the environmental impacts and economics of any ex-situ sequestration process. In spite of these drawbacks, the work conducted at ARC is intended to provide basic understanding of the reaction mechanics, and meaningful engineering data in order to estimate industrial-scale operating costs.

Materials

Several magnesium silicate minerals are suitable for the ex-situ carbonation reaction, including serpentine [$Mg_3(Si_2O_5)(OH)_4$], enstatite ($MgSiO_3$), and olivine, which actually represents a mineral group encompassing the solid-solution series between magnesium-rich (forsterite, Mg_2SiO_4) and iron-rich (fayalite, Fe_2SiO_4) end members. Each of these minerals occur in ultramafic complexes, several of which were well documented in North America by the International Geological Program (8). Serpentine is actually an alteration product of olivine and other magnesium silicates, and occurs in huge deposits on both the east and west coasts, but is quite rare in the mid-continent of North America. Enstatite generally occurs in similar geologic sequences to serpentine, but in lower abundance. Olivine, particularly the forsterite end member, is also found in huge deposits on both coasts, with those located in North Carolina described in great detail by Hunter (9). In fact, forsterite is the much more abundant end-member of the olivine solid solution series, although perhaps not as abundant as serpentine. For the purpose of the initial test series, simplification of the reaction sequence was desired. This meant selecting a magnesium silicate mineral of high purity, low water content, and high MgO concentration. Because serpentine is a hydrated mineral and contains a lower molar concentration of MgO than olivine, olivine was selected for the initial series of direct carbonation tests conducted at ARC. Olivine has been mined for most of the past century as a refractory material used for furnace and kiln linings. Olivine sand is used extensively in the metal foundry industry for sand mold castings. A large quantity of this foundry-grade olivine was available at ARC, and was thus selected for the initial phase of experimental tests.

In order to simplify the reaction route even further, a sample of synthetic forsterite of ultra high purity was purchased for comparison to the natural mineral. Samples of the natural and synthetic mineral underwent chemical analysis to determine the bulk chemistry of each material. The results from the chemical analyses are included in table 1. Magnesium oxide concentration was clearly much higher in the synthetic material, at 578 g/kg, compared to 497 g/kg in the natural olivine sample. The primary reason for the lower MgO concentration in the natural mineral is iron oxide that occurs in substitution for the MgO. The natural mineral contained 60 g/kg FeO, with an additional 26 g/kg Fe_2O_3. The iron oxide concentration is to be expected in the natural mineral, but because it has been shown to also form the carbonate, it appears to have no detrimental effect on the carbonation reaction.

To confirm the phase composition of both the natural and synthetic mineral samples, X-ray diffraction (XRD) analyses were also conducted. The XRD results are reported in table 2. The presence of enstatite in the head sample of the natural olivine is not unusual. It is to be expected that a source of natural olivine will contain several magnesium silicate minerals, including forsterite and enstatite. Because XRD is a qualitative analysis, where the concentration of the various species is determined by the peak intensity and the operators interpretation of the diffraction pattern, only relative abundances of the individual species can be determined. The relative abundances for the mineral species identified are classified by an overlapping scale: Primary phase 400-1000 g/kg ; Secondary phase 200-600 g/kg; Minor phase 50-300 g/kg; and Trace phase 10-100 g/kg. However, these determinations can be improved significantly by comparing the diffraction patterns for the samples to those made from standards of extremely pure mineral concentrates. This standardized practice was used for all XRD determinations.

Evident from the XRD analyses is the fact that the synthetic forsterite material was not actually pure forsterite, but contained significant concentrations of quartz (SiO_2) and periclase (MgO). Although the chemical analyses of the synthetic material confirm that it is composed of nearly the exact molar concentrations of MgO and SiO_2 in forsterite, the presence of these other compounds are evidence of unreacted starter materials used in the synthetic manufacturing process. A series of leach tests were conducted to determine the concentration of free MgO in the synthetic material. A solution of 3 molar ammonium chloride at 70˚C was used to leach the free MgO, without leaching the MgO from the silicate. Based on the bulk chemistry, XRD analyses, molar ratio of MgO to SiO_2 in forsterite (2:1), and these leach tests, it is estimated that the synthetic material contains approximately 820 g/kg forsterite, 110 g/kg periclase, and 70 g/kg quartz. This is important because the periclase was found to be much more soluble than the forsterite, and readily reacts with the carbonic acid to form the carbonate. This must be taken into account when comparing the reaction rates and extent of reaction between the natural and synthetic materials.

Experimental Methods

The proof-of-concept tests utilized an autoclave, or high pressure vessel, with continuous agitation/stirring. This stirred-tank-reactor, or STR, was placed in a custom-fitted furnace for temperature control. Process parameters, such as temperature and pressure, were monitored and recorded continuously. The STR was prepared for operation by the following procedure:

1) 100 g of olivine weighed and placed in the STR;
2) 400 ml of distilled water poured into the STR;
3) the STR sealed, evacuated, weighed (tare weight), and placed into an ice bath;
4) liquid CO_2 introduced into the STR;
5) the STR placed back on the scale, weight of CO_2 determined
6) pressure bled off while STR on scale until the proper weight of CO_2 remained;
7) STR heated to final process temperature and pressure.

The proper weight of CO_2 was calculated in advance by using the compressibility factor for CO_2 at the desired test conditions, and the solubility of CO_2 in water at those same conditions. Estimates for these parameters (at the pressure and temperature necessary for these tests) were extrapolated from the available literature initially. Adjustments to these estimates were made following each test, until the current figures were derived. These figures have proven quite accurate: conditions - 12.9 MPa, 185˚C; CO_2 compressibility factor, z = 0.7402; CO_2 solubility in water = 30 g/kg. Water vapor pressure at 185˚C is ~1.6 MPa, thus the final target pressure of 12.9 MPa was reduced by this amount to calculate the vapor pressure of CO_2 in the system. Total mass of CO_2 necessary to produce the final operating conditions was determined to be approximately 286 g. An example calculation follows.

Targets:	200˚C; 12.7 MPa
Additions:	100 g olivine, $\rho = 3.32\ g/cm^3 \therefore v = 30.12\ cm^3$ 400 cm^3 water
STR volume:	2,054.7 cm^3
Solids & water:	430.1 cm^3
Net free volume:	1,624.6 cm^3

Water vapor pressure @ 200˚C: 1.6 MPa

Final target pressure (CO_2): 12.7 MPa - 1.6 MPa = 11.1 MPa

The compressibility factor must be used to calculate the final CO_2 partial pressure because the CO_2 no longer behaves as an ideal gas at supercritical conditions. Thus, the compressibility factor equation of state was used to calculate the final partial pressure of CO_2:
Solving the equation for the molar volume resulted in 3.83 mol/L CO_2. Because the measured free volume was 1.6246 liters, the total gram-moles of CO_2 necessary to fill this volume at the specified conditions was 6.22 moles, or 273.7 g CO_2. Assuming 30 g/kg solubility of CO_2 in water at these conditions, an additional weight of 12 g CO_2 was added to produce the desired pressure at the final operating temperature. Thus, the target CO_2 addition was determined to be 285.7 g. Heating the vessel resulted in actual measured parameters of 12.9 MPa at 186˚C.

$$P\hat{V} = zRT$$

where
$P =$ pressure, $11.1\ MPa$
$\hat{V} =$ molar volume, mol / L
$z =$ compressibility factor, 0.7402
$R =$ gas constant, $8.314\ m^3 \cdot Pa / mol \cdot K$
$T =$ temperature, $473.2\ K$

Experimental Results

A test series following this procedure was conducted, with the test summaries reported in table 3. This test series used nearly identical test conditions: 100 g of feed material; 400 ml distilled water; roughly 186˚C; and 12.9 MPa. Thus, a series of baseline tests of 3, 6, 12, 24, and 48 hour duration was completed. The extent of reaction for these tests clearly indicates that although the reaction rates are relatively slow, the process resulted in successful carbonation of the head material (naturally occurring olivine or synthetic forsterite). Chemical analyses of the solid products are included in table 4. The concentration of CO_2 in these products, and the total weight of each product, were used to determine the actual extent of reaction.

X-ray diffraction (XRD) analyses were conducted on the products to determine actual phase composition of the materials. These results are included in table 5. The identification of magnesite in the process products confirms the success of the process. The presence of enstatite in both the feed and products for the tests using the natural olivine is of interest. It is to be expected that a source of natural olivine will contain several magnesium silicate minerals, including forsterite and enstatite. However, the enstatite identified in the process products is not believed to merely represent remnants of enstatite from the feed material. The experimental results suggest that enstatite is an intermediate alteration product of forsterite, prior to complete carbonation of the silicate mineral. The XRD results show that the relative enstatite concentration increased slightly in the process products, from a trace phase in the olivine head, to a trace-to-minor phase in the products. Additional studies have been conducted that tend to confirm that the enstatite in the products is primarily an alteration product. A simplified set of reactions, which are believed to better depict the actual reaction path, follow.

The direct carbonation with carbonic acid/aqueous CO_2 process is believed to follow these reaction paths. Magnesium oxide is leached from the forsterite, followed by reaction of the magnesium (in solution) with the CO_2 (dissolved in solution) to form the magnesium carbonate, magnesite. Analysis of the process products shows that the forsterite is altered to the intermediate magnesium silicate phase, enstatite, but with continued dissolution, additional carbonation occurs until only magnesite and free silica remain.

$$Mg_2SiO_4 + CO_2 \qquad MgSiO_3 + MgCO_3$$

Forsterite   Carbon dioxide   Enstatite   Magnesite

$$MgSiO_3 + CO_2 \qquad MgCO_3 + SiO_2$$

Enstatite   Carbon dioxide   Magnesite   Silica

Solution chemistries for the carbonation tests are reported in table 6. These results are not of the in-situ solutions, but of samples collected after return of the system to ambient conditions. Still, several trends are obvious. Solutions from the two tests using the synthetic material (SC-15 and SC-18) are clearly different from those of the natural olivine. However, these differences may be due as much to changes in the feed materials as to actual reaction conditions. Comparison of the solutions from the tests conducted on the natural olivine are perhaps more useful. Carbon dioxide concentration increased by about one third in the solution from test SC-25 (only test including gas dispersion in the water column). Solution pH also increased for test SC-25, from less than 6.0 for all prior tests on the olivine, to a neutral pH. Magnesium concentrations are nearly constant for all tests on the natural olivine, at roughly 60 mg/l, while Si concentration decreased dramatically for test SC-25, from well over 400 mg/l to less than 200 mg/l. This decrease may be due to the nearly complete extent of reaction for test SC-25. Silicon was no longer being dissolved from the silicate mineral, and the Si already dissolved may have formed a silica gel. This is still under investigation. In fact, the extent of reaction for test SC-25, neutral pH, and lower Si concentration may indicate the system was reaching equilibrium. Additional tests have been conducted repeating the extent of reaction observed from test SC-25, although results were not complete in time for this report.

Discussion

The experimental results indicate that the reaction is extremely slow or non-existent at ambient and elevated temperatures, as long as the partial pressure of CO_2 is maintained below its critical point, 7.4 MPa. For example, a test conducted at 150˚C and 5.2 MPa, designed to more closely simulate in-situ conditions, resulted in 10% conversion to the carbonate after 144 hours. However, once temperature and pressure were raised to supercritical CO_2 conditions, above 31˚C and 7.4 MPa, the rate of conversion to the carbonate was increased significantly. Increasing the process temperature and CO_2 partial pressure improves reaction kinetics.

The final test included in table 3, SC-25, was conducted in a new autoclave with a pressure rating of 34.4 MPa at 400˚C. The new system includes a CO_2 gas booster pump, mass flow meter, and automated vessel heating/cooling functions. In addition, the new system utilizes a gas dispersion agitator within the vessel, which resulted in nearly doubling the extent of reaction for the 24 hour tests, from 52% for tests SC-3 and SC-4 to 91.5% for test SC-25. Test conditions were identical for all three tests, other than the use of the gas dispersion agitator. Dissolution of the olivine is thought to be surface controlled, thus the improved extent of reaction is attributed to increased surface area contact between the carbonic acid/aqueous CO_2 and the solids, caused by the gas dispersion.

The higher pressure/temperature rating of the new autoclave permits operation at simultaneous supercritical water (374.1˚C, 22.1 MPa) and supercritical CO_2 conditions. Recent tests have included a 1 hour pretreatment interval at 385˚C and 27.5 MPa. It was anticipated that subjecting the olivine solids to supercritical water conditions would improve the dissolution rate, and ultimately increase the rate of the carbonation reaction. Following the 1 hour pretreatment interval, the vessel was cooled to 185˚C, and CO_2 was injected to a pressure of 12.9 MPa, to duplicate the test conditions from test SC-25. The extent of reaction based on CO_2 analyses of the solid products was approximately 95%, and the reaction appeared to reach this level within 18 hours, cutting 25% from the total reaction time from test SC-25. No significant pressure drop was recorded after about 18 hours, indicating that the carbonation reaction had essentially ceased. This tends to support the assertion made previously that the system was reaching equilibrium at the end of test SC-25. This observation was based on an extent of reaction curve derived from the delta P data recorded from each test. Additional tests of shorter duration are necessary to confirm the extent of reaction curves, but these preliminary results suggest that the reaction rate can be improved by additional modification of the test conditions. Subsequent tests will be conducted at increasing temperatures and CO_2 partial pressures, up to simultaneous supercritical water and supercritical CO_2 conditions.

Yet to be investigated are the (1) effects of inorganic and/or organic catalysts on the reaction rate; (2) solution modifications to increase CO_2 concentration in solution; (3) mineral pretreatment; and (4) alternative minerals, such as serpentine . These investigations are to be conducted in the coming months. Significant improvement is clearly necessary to achieve reaction rates that could prove feasible for an industrial ex-situ carbonation process. However, knowledge gained from these tests concerning reaction mechanisms, solution chemistry, and reaction kinetics associated with ex-situ or in-situ mineral carbonation should prove valuable for numerous other CO_2 sequestration technologies.

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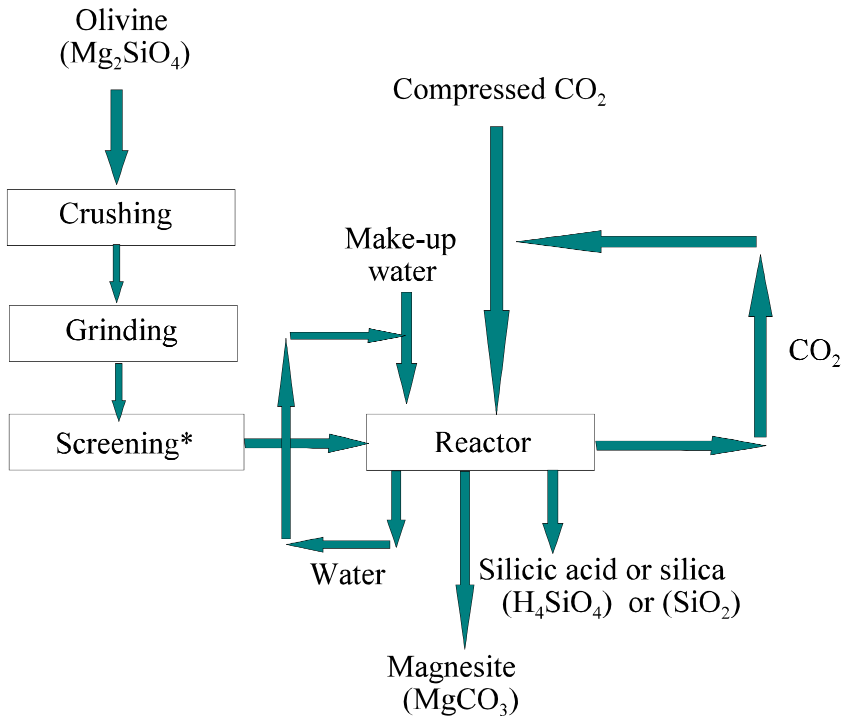

*Several size fractions used for proof-of-concept tests:
150 x 270 mesh (106 x 53 µm)
270 x 400 mesh (53 x 37 µm)
minus 400 mesh (-37 µm)

Figure 1.- Process flow diagram for the direct carbonation by carbonic acid/aqueous CO_2 process.

Table 1.- Chemical composition of the head sample materials (g/kg).

Oxide	Olivine (forsterite)	Synthetic forsterite
Al_2O_3	2.08	2.64
CaO	0.70	6.61
Cr_2O_3	0.44	0.12
FeO	59.66	0.09
Fe_2O_3	25.58	0.00
MgO	496.77	578.45
K_2O	0.07	0.19
SiO_2	413.57	379.29
Na_2O	0.99	1.01
Volatiles[1]	4.01	1.23
Total	1003.87	969.63

[1] Volatile constituents listed below

C, CO_2	<3.00	NA
C, fixed	0.21	0.63
C, total	0.21	0.63
H_2O[2]	3.80	0.60
Total	4.01	1.23

[2] Includes water of dehydration (free moisture) and chemically-bonded (interstitial) water.

Table 2.- X-ray diffraction analyses for the feed materials.

Material	Primary phase	Secondary phase	Minor phase	Trace phase
Olivine head	forsterite Mg_2SiO_4	ND	ND	enstatite $MgSiO_3$
Synthetic forsterite	forsterite	quartz SiO_2 periclase MgO	ND	ND

Primary phase: 400-1000 g/kg Secondary phase: 200-600 g/kg Minor phase: 50-300 g/kg
Trace phase: 10-100 g/kg ND: not detected

Table 3.- Test summaries for proof-of-concept tests.

Test	Test time, h	Temp., ˚C	Pressure, MPa	Head material	Particle size, µm[1]	Stoich. conversion, %
SC-3	24	188	12.9-11.9	olivine	106 x 75	52
SC-4	24	185	12.9-12.2	olivine	53 x 37	52
SC-10	6	186	12.9-12.4	olivine	53 x 37	3.5
SC-11	48	186	12.9-6.9	olivine	53 x 37	56
SC-12	3	186	12.9-10.2	olivine	53 x 37	0.9
SC-13	12	186	12.9-12.6	olivine	53 x 37	18.6
SC-15	3	186	12.9-10.8	syn. forsterite	minus 45	70
SC-16	3	186	12.9-12.7	olivine	minus 37	1
SC-18	3	186	12.9-11.9	syn. forsterite	minus 45	70
SC-25[2]	24	185	12.9	olivine	minus 37	91.5

[1] Particle size refers to the particle diameter of the head material, in micrometers.
[2] Test SC-25 conducted in new reactor, including gas dispersion.

Table 4.- Chemical composition of the solid process products (g/kg).

Oxide	SC-3 product	SC-4 product	SC-10 product	SC-11 product	SC-12 product	SC-13 product	SC-15 product	SC-16 product	SC-18 product	SC-25 product
Al_2O_3	1.55	1.71	1.58	1.49	2.27	2.59	2.04	2.42	1.63	1.71
CaO	1.24	1.55	2.24	1.55	1.29	1.37	4.91	2.27	4.00	2.30
FeO	60.58	59.54	67.65	59.80	83.98	68.68	0.57	72.28	<0.10	52.71
MgO	441.76	416.75	463.43	405.08	526.77	483.43	376.74	510.10	370.07	355.00
SiO_2	327.86	332.14	315.00	325.71	405.00	375.00	278.57	398.57	276.43	268.00
Volatiles[1]	183.40	177.33	12.80	198.60	3.52	65.80	329.07	5.90	317.65	332.14
Total	1016.39	989.02	862.70	992.23	1022.83	996.87	991.90	991.54	969.78	1011.86

[1] Volatile constituents listed below.

CO_2	183.00	177.00	12.50	198.00	3.30	65.80	325.00	5.80	317.00	323.00
C, org.	0.40	0.33	0.30	0.60	0.22	0.00	4.07	0.10	0.65	9.14
Total	183.40	177.33	12.80	198.60	3.52	65.80	329.07	5.90	317.65	332.14

Table 5- X-ray diffraction analyses for the solid products.

Test	Primary phase	Secondary phase	Minor phase	Trace phase
SC-3	magnesite ($MgCO_3$)	forsterite (Mg_2SiO_4)	enstatite ($MgSiO_3$)	ND
SC-4	ND	magnesite forsterite	ND	enstatite
SC-10	forsterite	ND	enstatite	magnesite
SC-11	magnesite	forsterite	ND	enstatite
SC-12	forsterite	ND	enstatite	ND
SC-13	forsterite	magnesite	ND	enstatite
SC-15	magnesite	ND	forsterite quartz (SiO_2)	amorphous
SC-18	magnesite	ND	forsterite quartz (SiO_2)	amorphous
SC-25	magnesite ferroan magnesite [$(Mg,Fe)CO_3$]	ND	ND	forsterite enstatite

Primary phase: 400-1000 g/kg Secondary phase: 200-600 g/kg Minor phase: 50-300 g/kg
Trace phase: 10-100 g/kg ND: not detected

Table 6.- Leach liquor chemistry from the direct carbonation tests (mg/L).

Element	SC-3 solution	SC-4 solution	SC-10 solution	SC-11 solution	SC-12 solution	SC-13 solution	SC-15 solution	SC-18 solution	SC-25 solution
CO_2	400	360	440	430	260	520	2190	2490	660
Iron	2.2	1.7	1.0	1.5	0.6	3.0	<0.1	<0.1	<0.1
Magnesium	62.2	56.3	55.6	48.1	62.9	82.4	440	584	66.5
Silicon	563	586	527	472	291	570	84	242	168
pH	5.7	5.1		5.9	5.8	5.7	7.2	6.7	7.0
Test time, h	24	24	6	48	3	12	3	3	24
CO_2, molal[1]	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.06	0.02
CO_2, molal[2]	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68	0.68

[1] Molality of leach solution at ambient conditions, after removal from STR.

[2] Estimated in-situ molality based on CO_2 solubility at 185˚C and 1,850 psi (127 atm).