

## Sequestration of Carbon Dioxide by Carbonation of Minerals at Supercritical Fluid Conditions

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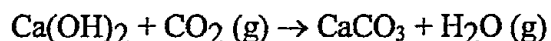
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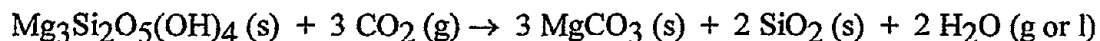
### Abstract

The increasing concentration of atmospheric carbon dioxide (CO<sub>2</sub>), generated by energy and process industries is receiving heightened international attention. Methods are being sought to reduce emissions and to remove from the environment CO<sub>2</sub> already produced. A sequestration strategy has been proposed whereby CO<sub>2</sub> can be disposed of through the carbonation of naturally occurring magnesium silicate minerals such as serpentine and olivine. The resulting non-toxic magnesium carbonate is thermodynamically stable, thereby offering permanent disposal of the CO<sub>2</sub> in safe form. Furthermore, sufficient high quality magnesium silicate deposits exist worldwide in order to easily handle the CO<sub>2</sub> resulting from the consumption of all of the world's coal and petroleum reserves.

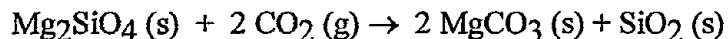
### Calcium Hydroxide



### Serpentine



### Olivine



We have performed carbonation reactions of several minerals, including silicates and hydroxides, at various conditions of CO<sub>2</sub> temperature and pressure. These studies allow us to evaluate the carbonating efficiency of liquid and supercritical fluid CO<sub>2</sub>, and at nominally anhydrous conditions. The hydroxides carbonate reacts very rapidly regardless of reaction conditions, while the preliminary results on the silicates show that the degree

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of carbonation is sensitively influenced not only by CO<sub>2</sub> conditions, but also by the presence of water. These observations are compared favorably to the results of thermodynamic calculations

Such laboratory-scale carbonation studies are useful for refining geochemical models and in designing large-scale treatment processes.

Keywords: global warming, carbon dioxide, sequestration, supercritical fluids

## Introduction

The United States as well as the other heavily industrialized countries consumes large amounts of energy that are predominantly derived from the combustion of fossil fuels. This energy has allowed a high quality of life and contributes to human productivity. However, with the rising CO<sub>2</sub> levels in the atmosphere many governments are beginning to question the future use of fossil energy. Carbon dioxide is a greenhouse gas and there is growing scientific consensus that the apparent increase in global average temperatures is attributable to the increased atmospheric level of CO<sub>2</sub> caused by the consumption of fossil fuels. Industrialized nations like United States, European Countries, Japan and the U.S.S.R. are the primary contributors to this emission. This relationship is characterized by a comparison of Mean Power Consumption Per Capita, (kW/person) and the Mean Gross Domestic Product Per Capita (\$/yr-person) , Figure 1, Ref 1. If this trend continues as other countries strive for higher standards of living, the effect will continue to increase. Therefore, even larger quantities of fossil fuel is consumed into the future the need to develop a technology to offset this greenhouse gas is apparent.

The United States annually produces about 5 Gigatons, Gt, of CO<sub>2</sub> of the present global annual output of 22 Gt. Since the beginning of the industrial age, the atmospheric CO<sub>2</sub> level has increased approximately 30% raising legitimate concerns about global climate change, Ref 2,3,4,5. In 1800 the atmospheric levels of CO<sub>2</sub> was 280 PPM while today it is about 370 PPM. In the last 50 years it has risen by 50 PPM. Ref 6.

## Objectives

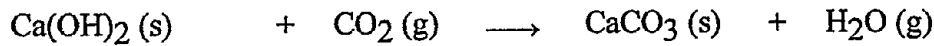
Various ideas have been proposed to reduce the CO<sub>2</sub> emissions while allowing continued consumption of fossil fuels Ref 7 and 8. These references describe two chemical processes to sequester CO<sub>2</sub> as carbonate minerals. The processes would combine CO<sub>2</sub> with divalent cations (principally Mg and/or Ca) derived from natural mineral deposits by direct carbonation at high pressure and high temperature in a slightly aqueous medium. Magnesium and calcium make up about 2.0 to 2.1 mole percent of the Earth crust, mostly bound to silicate minerals Ref 9. Magnesium silicate rocks like serpentinite and olivine deposits contain far more reactive material (MgO) per ton of ore (~40%) than calcium silicate rocks (~10% CaO). The magnesium silicates are also found in very large and rich deposits. We have therefore selected serpentinites as the material to focus on. Serpentine is found in high-grade serpentinite or an altered mineral form of peridotite. These magnesium-rich, ultramafic rocks are the best candidates for this sequestering process.

Another advantage of this mineral is that it is widely distributed throughout the world. In the United States, attractive deposits run up and down the eastern and western borders of the country. Serpentine minerals (chrysotile, lizardite and antigorite) are the common hydration products of ultramafic rocks, dunite and peridotite. Different serpentinites contain different concentration of these serpentine minerals, with lizardite forming the largest fraction on average. Lizardite is a layer silicate with the ideal chemical formula of  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . It is calculated that 1 kilogram of chrysotile can absorb 0.48kg of  $\text{CO}_2$ . Olivine or forsterite is also found in ultramafic formations. The magnesium end member of olivine has the chemical formula of  $\text{Mg}_2\text{SiO}_4$ .

### Methodology

At the initial stages of this research we calculated the properties of  $\text{CO}_2$  and the thermodynamic implications of the carbonation reaction as a function of temperature and pressure.

The Change in Gibbs Free Energy with Temperature at Constant Pressure:



The change in free energy, as a function of *both temperature and pressure*, can be found using

$$\begin{aligned} \Delta G_{T,P} &= \Delta G_T^0 + RT \ln \frac{(a_{\text{CaCO}_3})(a_{\text{H}_2\text{O}})}{(a_{\text{Ca(OH)}_2})(a_{\text{CO}_2})} \\ &= \Delta G_T^0 + RT [\ln a_{\text{CaCO}_3}] + RT [\ln a_{\text{H}_2\text{O}}] \\ &\quad - RT [\ln a_{\text{Ca(OH)}_2}] - RT [\ln a_{\text{CO}_2}] \end{aligned} \quad (1)$$

where

$$\Delta G_T^0 = \left( \Delta H_{298,1 \text{ bar}} + \int_{298}^T \Delta C_p dT \right) - T \left( \Delta S_{298,1 \text{ bar}} + \int_{298}^T \frac{\Delta C_p}{T} dT \right) \quad (2)$$

The change in free energy of a pure substance is given by

$$dG_i = V_i \cdot dP - S_i \cdot dT \quad (3)$$

so that the free energy change effected by an increase in pressure from 1 bar to pressure P, at constant temperature is

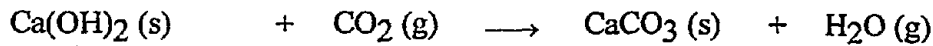
$$dG_i = V_i \cdot dP \quad (4)$$

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Integration of Eq. (4) gives

$$G_i - G_i^0 = \int^P V_i \cdot dP \quad (5)$$

The compressibility of solids is small, so that the increased pressure does not appreciably change the volume. Therefore,  $V \cong V^0$ , and we can write Eq. (5) is

$$G_i - G_i^0 = V_i^0 (P - 1) \quad (6)$$

But  $G_i - G_i^0 = RT \ln a_i$ , so that

$$RT \ln a_i = V_i^0 (P - 1) \quad (7)$$

Inserting Eq. (7) into Eq. (1), we have

$$\begin{aligned} \Delta G_{T,P} &= \Delta G_T^0 + V_{\text{CaCO}_3}^0 (P - 1) + RT [\ln a_{\text{H}_2\text{O}}] \\ &\quad - V_{\text{Ca(OH)}_2}^0 (P - 1) - [\ln a_{\text{CO}_2}] \\ &= \Delta G_T^0 + (P - 1) (V_{\text{CaCO}_3}^0 - V_{\text{Ca(OH)}_2}^0) \\ &\quad + RT [\ln a_{\text{H}_2\text{O}}] - RT [\ln a_{\text{CO}_2}] \end{aligned} \quad (8)$$

Table I gives the molar volumes of the solid phases. Inserting their values into Eq. (8) gives

$$\begin{aligned} (P - 1) \Delta V_{\text{solids}} &= (P - 1) [36.9 - 33.2] \\ &= (P - 1) [3.7] \end{aligned} \quad (9)$$

In our experiments, the  $\text{CO}_2$  is provided in large stoichiometric excess, which acts not only as a chemical reactant but a transport media for the removal of the  $\text{H}_2\text{O}$ . Therefore, to a first approximation, we assume that

$$a_{\text{H}_2\text{O}} = 0 \quad (10)$$

For the  $\text{CO}_2$  phase, the activity can be expressed as

$$a_{\text{CO}_2} = \left( \frac{f_{\text{CO}_2}}{f_{\text{CO}_2}^0} \right) \quad (11)$$

where  $f_{\text{CO}_2}$ ,  $f_{\text{CO}_2}^0$  are the fugacity, or thermodynamic pressure, of  $\text{CO}_2$  at T and P and the defined standard state conditions of T and  $P^0$ , respectively. We make the assumption that at T = T and  $P^0 = 1$  bar,  $f_{\text{CO}_2}^0 = 1$ , so that

$$a_i = f_i \quad (12)$$

Further,

$$f_i^{T,P} = \gamma_i^{T,P} \cdot P_{\text{CO}_2} \quad (13)$$

Eqs. (9) and (13) into (8) gives

$$\Delta G_{T,P} = \Delta G_T^0 + 3.7 (P - 1) - RT \ln (\gamma_{\text{CO}_2} \cdot P_{\text{CO}_2}) \quad (14)$$

Empirical expressions for  $\gamma_{\text{CO}_2}^{T,P}$ , as a function of reduced temperature,  $1.5 \leq T_r \leq 35$  and reduced pressure,  $0 \leq P_r \leq 20$ , have been given by Ref 10.

For  $12 < T_r < 35$ :

$$\begin{aligned} \gamma_{\text{CO}_2}^{T,P} = & 1 + 0.014986 P_r - 0.0007015 T_r P_r + 0.00001024 T_r^2 P_r + 0.00010787 P_r^2 \\ & - 0.000006007 T_r P_r^2 + 0.000000087 T_r^2 P_r^2 \end{aligned}$$

For  $3 < T_r < 12$ :

$$\begin{aligned} \gamma_{\text{CO}_2}^{T,P} = & 1 + .0124 P_r + .000254 T_r P_r - 0.00005104 T_r^2 P_r + 0.0011089 P_r^2 \\ & - 0.0001998 T_r P_r^2 + 0.000009393 T_r P_r^2 \end{aligned}$$

For  $1.5 < T_r < 3$ :

$$\begin{aligned} \gamma_{\text{CO}_2}^{T,P} = & 1 - 0.2242 P_r + 0.14667 T_r P_r - 0.02276 T_r^2 P_r + 0.008899 P_r^2 \\ & - 0.005119 T_r P_r^2 + 0.000786 T_r^2 P_r^2 \end{aligned} \quad (15)$$

The fugacity of  $\text{CO}_2$  is taken from the equation of state given by, Ref 11 and is applicable for  $-57^\circ\text{C} < T < 150^\circ\text{C}$  and  $0 \text{ psig} < P < 45,000 \text{ psig}$ .

Similar calculations were performed on the Serpentine and Olivine reactions. Respectively, figures 2, 3, and 4 show the Gibbs free energy change ( $\Delta G$ ) for calcium



hydroxide, serpentine, and olivine upon carbonation. The carbonation reactions are all seen to be exothermic and are thermodynamically favored at ambient conditions.

An approximately 1.5 gram sample aliquot of the hydroxide or mineral is placed in a uniformly heated sealed container. The pressure is brought above the critical pressure of CO<sub>2</sub>. The use of supercritical fluids as solvents stems from their unique combination of liquid-like properties of solubility and density and their gas-like properties of high diffusivity. To a first approximation, the solvent power of a fluid is related to its density. The high, liquid-like densities of supercritical fluids therefore allow for high solubility. Figure 5 shows the pressure-temperature-density surface for pure CO<sub>2</sub>. The critical point for pure CO<sub>2</sub> (31°C and 1072 psig) is shown in Figure 5 as a solid circle. The low, gas-like viscosity, Figure 6, of supercritical CO<sub>2</sub> allows for easy penetration into porous and micro-porous matrices. In addition, the supercritical fluids possess high, gas-like diffusivities, providing for highly effective mass transport.

It can be seen that relatively small changes in temperature or pressure near the critical point can result in large changes in CO<sub>2</sub> density. It is this tunability of density, and thus tunability of solvent power, which is the most attractive attribute of supercritical fluids. The conditions used for our experiments ranged from 1000 to 7000 psig and 50 °C to 140°C for serpentine, olivine and calcium hydroxide.

The supercritical extraction system is manufactured by ISCO, Inc. (Lincoln, Nebraska) and consists of three units: a Model 260 D syringe pump, a model SFX-2-10 extractor and a heated, constant-flow restrictor or variable restrictor, pictured in Figure 8. During the experiments the CO<sub>2</sub> system was operated in one of two modes. In the static mode, following the introduction of the high pressure CO<sub>2</sub>, no additional CO<sub>2</sub> was introduced other than that needed to maintain the fixed pressure. In the dynamic mode, CO<sub>2</sub> was continually swept over the sample material. This had the effect of carrying off any water that was either evolved from the sample during the carbonation reaction or water that was initially introduced with the sample to initiate the carbonation reaction. X-ray diffraction (XRD) analyses were carried out with a Siemens D500 system equipped with incident- and diffracted-beam Sollerslits and a Si(Li) solid-state detector. The XRD system is easily capable of resolving 1-wt% content levels. XRD powder samples were prepared as front-packed mounts

Reagents used in these experiment were obtained as described below. Supercritical fluid extraction-grade CO<sub>2</sub> is supplied with a helium-headspace cylinder. The CO<sub>2</sub> was obtained from Scott Specialty Gas Company,(Longmont CO). The gas purity is SFE extraction grade. Calcium hydroxide was purchased from Fischer Scientific, Fair Lawn, NJ. Some of the serpentine was furnished by Ref 12, W. O'Connor of the ARC(Albany Research Center). This serpentine was heat pretreated at 630°C prior to carbonation attempts. Additional serpentine was collected by F. Goff and subsequently calcined at 630°C for three hours by D. Byler, both of the Earth and Environmental Sciences Division at Los Alamos National Laboratory. The olivine was donated by the American Minerals Inc. King of Prussia, PA

## Observations

Initial studies were performed on the simple system of calcium hydroxide as opposed to the more complex mineral silicate material. The studies were based on the carbonation of the calcium hydroxide forming calcium carbonate. Temperature, pressure and time values were varied to study the thermodynamics and kinetics of the system. As shown in Figure 9, the samples run at 50°C and 3000 psig were fully carbonated, 95% to 100%, within 60 minutes. The runs at 140°C and 3000 psig achieved approximately 40% carbonation in the same time period but appeared to have reached the maximum carbonation achievable under those conditions.

The calcium hydroxide system was also used to compare the gravimetric carbonation analysis to the XRD data. A variety of reaction conditions were used. As presented in Table 2, for the most part, the data show good agreement between the two methods. However, in the two cases a significant difference was found which we attribute to incomplete drying of the sample prior to its weight determination after the carbonation reaction. For this reason only select samples were chosen for XRD analysis and the gravimetric data is used to determine carbonation yields.

A final experiment performed with calcium hydroxide was used to study the reproducibility of the reaction system. The conditions that were selected were 1750 psig, 50°C and a reaction time of 5 minutes. Five samples were treated to determine statistical factors. Results are presented in Table 3. The average carbonation for the five samples was 100% with a standard deviation of 0.0105 and a percent relative standard deviation of 1.07%.

The experiments that were done with the serpentine were promising. We used calcined and as received serpentine. The calcining as performed at 630°C for three hours. XRD data showed that the end product following carbonation at 7000 psig, 140°C and 5.5 hours in the static mode and 1.5 hours in dynamic mode was 38.8% by weight magnesite ( $\text{MgCO}_3$ ). Assuming that the starting serpentinite was 40 weight percent MgO and that upon heat pretreatment 10% of the starting sample weight was lost due to the evolution of water, a value of 38.8% weight percent magnesite for the product material corresponds to a fractional carbonation of 52% of the starting MgO in the serpentinite. This was compared with the as received serpentine where under identical conditions only 5.2% of the material was carbonated. This value corresponds to a fractional carbonation of only 6.4% of the MgO in the starting serpentinite. The same conditions were attempted on the as received serpentine but using only the dynamic mode for 14 hours. Results again showed that no significant carbonation had occurred. Additional runs were performed at lower temperatures and pressures with a less than or equivalent carbonation as seen above.

Final experiments were performed on olivine. As received material was tested in this study. Reaction conditions were 7000 psig, 140 °C and the same time as discussed in the

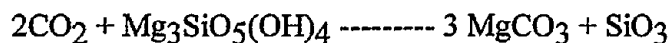
initial serpentine section. Results have shown carbonation yield, 3.1%, that are lower than the 5.2% obtained in the serpentine reaction.

## Discussion

Other experiments were run with the calcium hydroxide system at the stated conditions above and at 85 °C and 100 °C. In general the percent carbonation results were between the previous two selected temperatures. The ISCO reaction system flow was very difficult to control. The system first used a fixed restrictor to control flow. This type of restrictor would plug during a run and flow times and volumes were not consistent. The system was modified by using a variable restrictor that allowed for the manual control of the flow during a run. This modified system was still somewhat problematic and the reaction times and flows of the CO<sub>2</sub> with the hydroxide would vary. The data presented was reviewed and only experiments that had a 20% agreement between the run time and total flow volume were used. The other data had a high degree of variability and was not used to study the thermodynamics of the system. The data presented in the Table 2 used data where both XRD and gravimetric comparisons and the amount of time or flow did not affect a single sample analysis.

Thermodynamically the reaction has a larger free energy at higher temperatures, as shown on Figure 2. Based on this data carbonation should be larger with an increase in this variable; however, the results are contradictory to this hypothesis.

The heat treatment of serpentine to 600 °C resulted in a loss of 2 moles of water, . Results have shown that runs completed on the calcined serpentine shown low to no carbonation. However, if an addition of water was added to the system directly prior to reaction the largest yield was obtained, 43%. The calcining process both chemically changes the starting material and thoroughly disrupts its layered crystal structure exposing much larger surface areas. This effect would facilitate the carbonation and yield of magnesite. It appears that water being present in the system initiates the carbonation reaction. This was shown in the data present earlier were a comparison of 43% to 5.2% is made for a sample with water and a sample without water. This affect has been suggest by, W.K O'Connor of the ARC (Albany Research Center). They used an aqueous system of sodium bicarbonate and sodium chloride to act as a CO<sub>2</sub> carrier. The chloride has been speculated to activate the mineral. It may also be involved in the removal of carbonic acid as it is generated during the experiment. The system has been theorized to have the slurry react with supercritical carbon dioxide to form the magnesium carbonate. The carbon dioxide is dissolved in the water to form carbonic acid, which dissociates to a hydronium ion and a bicarbonate ion. The acid reacts with the mineral to liberate the magnesium. A sodium bicarbonate was added to buffer the system. By achieving this reaction with the mineral more hydroxyl sites should be available to be carbonated.



The calcinations step, although showing a better yield, is an added step one would like to omit due to added cost to the process in situ.

The olivine material yielded the poorest results for carbonation. Thermodynamic calculations support these findings and can be directly related to the absence of the hydroxyl groups in the chemical structure,  $\text{Mg}_2\text{SiO}_4$ .

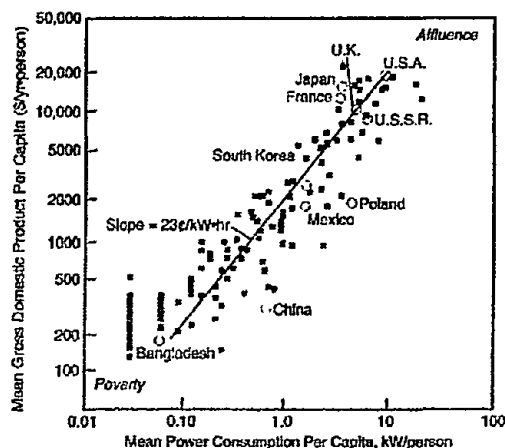
## Conclusions

The carbonation reaction of carbon dioxide with calcium hydroxide shows the highest level of carbonation. The minerals used, serpentine and olivine, showed a lower level of carbonation in comparison, with the serpentine achieving up to a 43% weight fraction of manesite in the end product, which corresponds to an approximately 60% conversion of the  $\text{MgO}$  in the starting serpentine to a carbonate. A continued effort of the simple system, calcium hydroxide, will be completed to further understand the discrepancy between the thermodynamic data and the experimental results. The study will also be expanded to understand the kinetics of the system. This will facilitate the optimization of conditions for the mineral reactions. The affects of water as an initiator also need to be expanded to understand its role as a product and in the equilibrium shift of the chemical reaction.

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**Figure 1 Per capita GDP versus per capita annual energy usage.**  
Data are taken from Hoffert and Potter, 1997, as they derived them from Hammond, 1990.

Equations	Ca(OH) <sub>2</sub>	CaCO <sub>3</sub>
$\rho \left( \frac{\text{g}}{\text{cm}^3} \right)$	2.24 <sup>a</sup>	2.71 <sup>a</sup>
$\text{MW} \left( \frac{\text{g}}{\text{mole}} \right)$	74.095 <sup>b</sup>	100.089 <sup>b</sup>
$V_0 \left( \frac{\text{cm}^3}{\text{mole}} \right)$	33.056 <sup>b</sup>	36.934 <sup>b</sup>
$\Delta H_{298}^\circ \left( \frac{\text{kJ}}{\text{mole}} \right)$	-986.085 <sup>b</sup>	-1207.370 <sup>b</sup>
$\Delta S_{298}^\circ \left( \frac{\text{kJ}}{\text{K} \cdot \text{mole}} \right)$	83.39 <sup>b</sup>	91.71 <sup>b</sup>
Coefficients for heat capacity equation – For Ca(OH) <sub>2</sub> : $C_p(T) = a + b \times 10^{-2} \cdot T + c \times 10^3 \cdot T^{-1/2} \left( \frac{\text{J}}{\text{K} \cdot \text{mole}} \right)$ For CaCO <sub>3</sub> : $C_p(T) = a + b \times 10^{-2} \cdot T + c \times 10^6 \cdot T^{-2} \left( \frac{\text{J}}{\text{K} \cdot \text{mole}} \right)$	$a = 186.67$ <sup>b</sup>	$a = 99.715$ <sup>b</sup>
	$b = -2.1911$ <sup>b</sup>	$b = 2.6920$ <sup>b</sup>
	$c = -1.5998$ <sup>b</sup>	$c = -2.1576$ <sup>b</sup>

$a$  – calculated from  $\left( \frac{\text{MW}}{\rho} \right)$

$b$  – R.A. Robie, B.S. Hemingway and J.R. Fisher, Thermodynamic Properties of Minerals and Related Substances at 298.125 K and 1 bar (10<sup>5</sup> Pascals) Pressure and at Higher Temperature (USGS, Washington, DC, 1979).

**Table 1, Thermodynamic Properties of Ca(OH)<sub>2</sub> System**

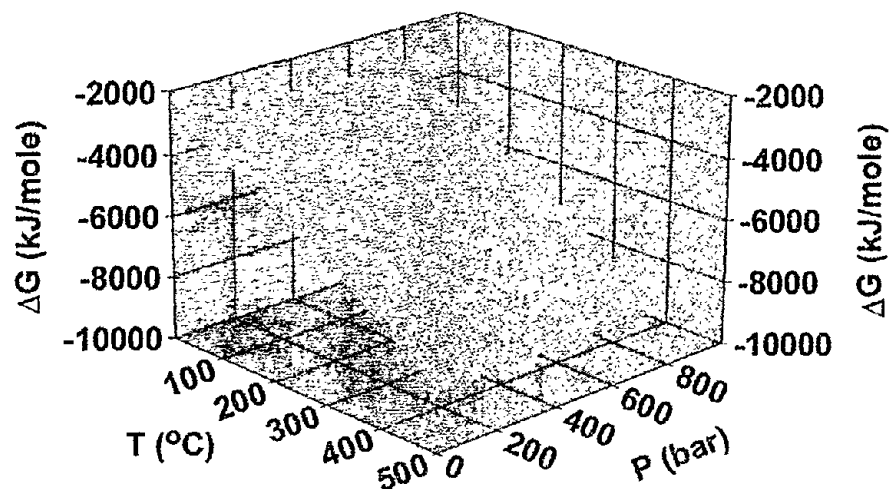


Figure 2. Free energy of the reaction  $\text{Ca}(\text{OH})_2 (\text{s}) + \text{CO}_2 (\text{g}) \rightarrow \text{CaCO}_3 (\text{s}) + \text{H}_2\text{O} (\text{g})$ , as a function of temperature and  $\text{CO}_2$  pressure

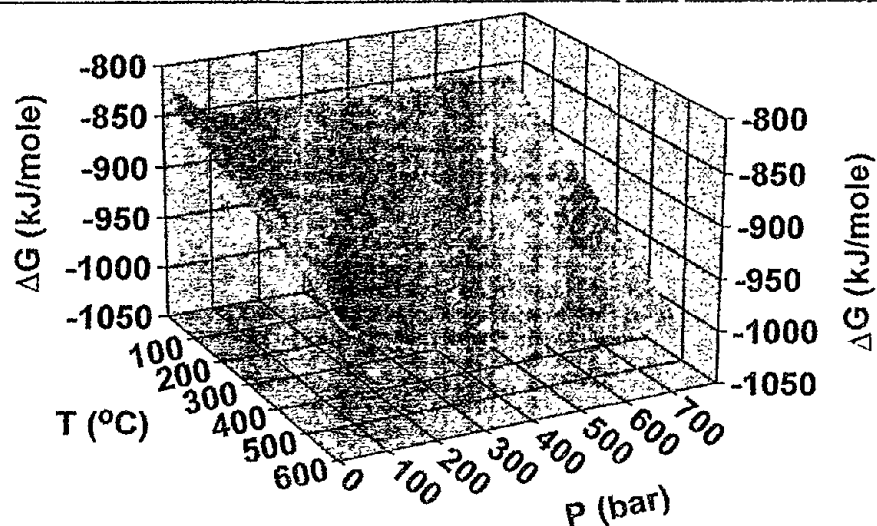


Figure 3. Free Energy of the reaction  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 (\text{s}) + 3 \text{CO}_2 (\text{g}) \rightarrow 3 \text{MgCO}_3 (\text{s}) + 2 \text{SiO}_2 (\text{s}) + 2 \text{H}_2\text{O} (\text{g})$  as function of temperature and pressure

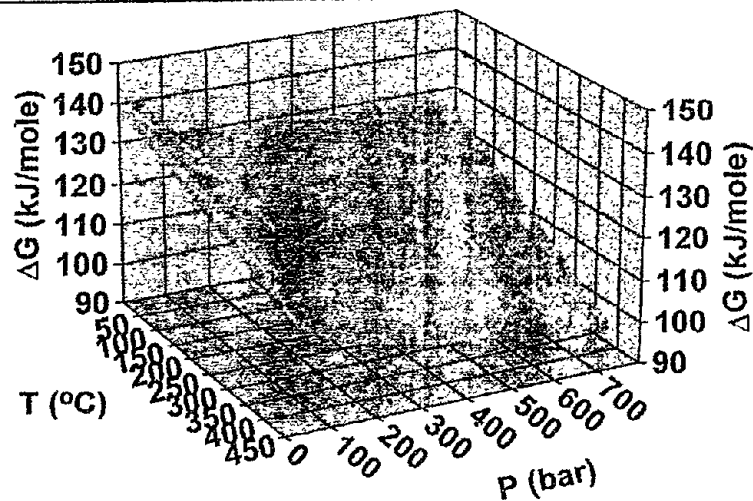


Figure 4. Free Energy of the reaction  $\text{Mg}_3\text{SiO}_4 (\text{s}) + 2 \text{CO}_2 (\text{g}) \rightarrow 2 \text{MgCO}_3 (\text{s}) + \text{SiO}_2 (\text{s})$  as function of temperature and pressure.

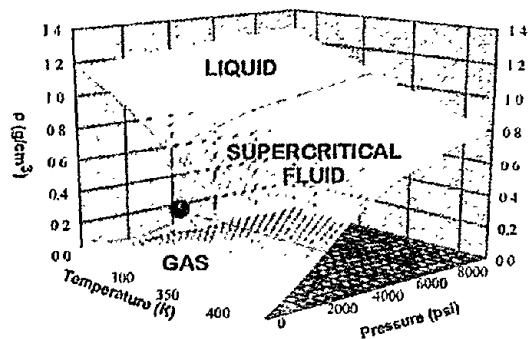


Figure 5. Density,  $\rho$ , as a function of temperature and pressure for pure  $\text{CO}_2$ .

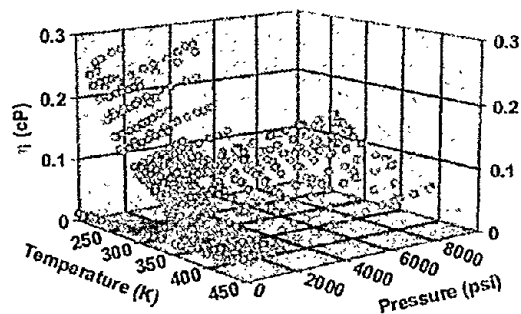
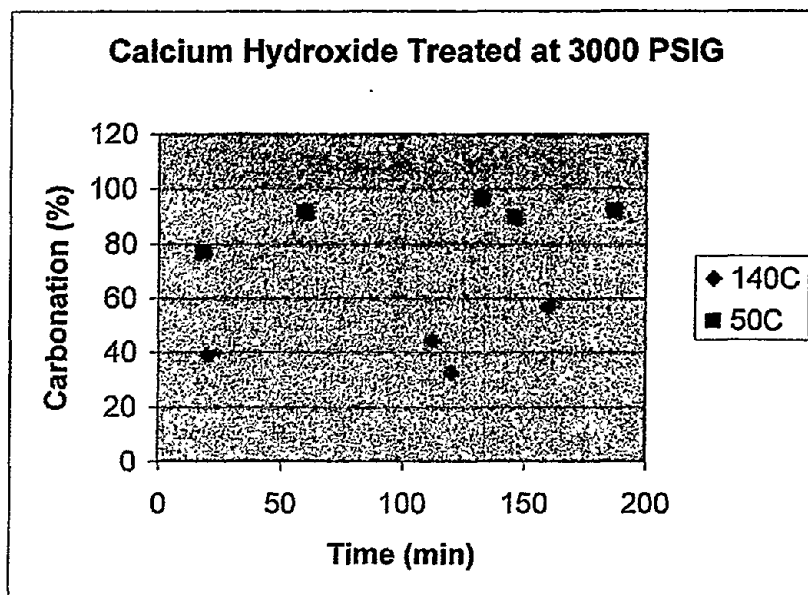


Figure 6. Viscosity,  $\eta$ , as a function of temperature and pressure for pure  $\text{CO}_2$





**Figure 8, ISCO extraction system**



**Figure 9, Carbonation yields for varying temperature and time at 3000 psig.**

Sample	Gravimetric	Amount of Calcite	Difference
1	36.4	33.3	3.1
2	32.2	36.5	-4.3
3	52.3	48.9	3.4
4	68.3	50.4	17.9
5	95.5	67.6	27.9
6	73.3	78.1	-4.8
7	91.9	96.5	-4.6

**Table 2: Comparison of Gravimetric Results to XRD Results**

Initial Weight	Maximum Carbonation	Final Weight	% Carbonation
1.5076	2.0360	1.9812	0.9731
1.5193	2.0518	2.0285	0.9886
1.5996	2.1603	2.2041	1.0203
1.5996	2.1603	2.1988	1.0178
1.5201	2.0529	2.028	0.9879
		Average	0.9805
		Std Dev	0.0105
		%RSD	1.067

**Table 3: Precision of Carbonation of  $\text{Ca}(\text{OH})_2$**