

SUBTASK 1.17–MEASUREMENT OF HYDROCARBON EVOLUTION FROM COAL AND PETROLEUM RESERVOIRS UNDER CARBON DIOXIDE FLOODS

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ABSTRACT

The project developed, built, and tested three apparatuses for studying different interactions of carbon dioxide with geologic materials. In Year 1, an online instrument was constructed by coupling a high-pressure carbon dioxide extraction system with a flame ionization detector that can yield a real-time profile and quantitative measurements of hydrocarbons removed from materials such as coal and petroleum reservoir rock. In Years 2 and 3, one instrument was built to measure the excess sorption of carbon dioxide in geologic materials such as coal and showed that measurable uptake of carbon dioxide into the coal matrix is rapid. The final apparatus was built to expose geologic materials to carbon dioxide for long periods of time (weeks to months) under the range of pressures and temperatures relevant to carbon dioxide sequestration. The apparatus allows as many as twenty gram-sized samples of geologic materials to be exposed simultaneously and can also include exposures with geologic brines. The system was used to demonstrate complete conversion of magnesium silicate to magnesium carbonate in less than 4 weeks when exposed to clean water or brine, compared to no measurable conversion of dry magnesium carbonate.

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EXECUTIVE SUMMARY

The project developed, built, and tested three laboratory systems for studying different interactions of carbon dioxide with geologic materials. In Year 1, an online instrument was constructed by coupling a high-pressure carbon dioxide extraction system with a flame ionization detector (FID) that can yield real-time hydrocarbon production profiles (extraction rates) under a range of pressures up to 400 bar (ca. 6000 psi) and temperatures up to 250°C. Since the FID responds very similarly for any hydrocarbon based on the mass of CH units in the material, the mass of hydrocarbon and the rate of its release can be determined. In an off-line mode, the hydrocarbons can be collected for analysis, if desired. The instrument can only use small samples (100 mg) and uses relatively high ratios of carbon dioxide to sample, thus yielding the maximum amount of hydrocarbon production possible under the given temperature and pressure conditions.

In Years 2 and 3, one instrument was built to measure the excess sorption of carbon dioxide in geologic materials such as coal and showed that measurable uptake of carbon dioxide into the coal matrix is rapid. The instrument was configured so that the effect of exposure time on carbon dioxide sorption could be measured. It was found that any measurable sorption of carbon dioxide to test coals occurred rapidly; i.e., within a few minutes. Because of the unavoidable Joules-Thompson (J-T) cooling that occurs when the carbon dioxide is introduced into the sample cell, a few minutes is required to reequilibrate the system temperatures with each test pressure step. Therefore, no shorter sorption rates can be determined. Carbon dioxide sorption profiles were obtained for test coals that agree well with the literature. Although not part of the present project, we plan to perform minor modifications so that the instrument can also be used to determine solubility behavior in geologic brines related to deep-well carbon disposal.

The final apparatus built in Years 2 and 3 was built to expose geologic materials to carbon dioxide for long periods of time (weeks to months) under the range of pressures and temperatures relevant to carbon dioxide sequestration (pressures to 400 bar, and temperatures up to 150°C). The apparatus allows as many as twenty gram-sized samples of geologic materials to be exposed simultaneously and can also include exposures of geologic brines, as well as mixed systems containing brines and test minerals. The system was used to demonstrate complete conversion of magnesium silicate to magnesium carbonate in less than 4 weeks when exposed to clean water or brine, compared to no measurable conversion of dry magnesium carbonate. The system is currently being used to expose various materials related to carbon dioxide sequestration in support of projects under separate funding.

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INTRODUCTION AND BACKGROUND

Carbon dioxide floods are used to increase the production of liquid and gas hydrocarbon products from petroleum reservoirs (1). The potential for sequestering carbon dioxide in petroleum reservoirs and in coal beds with the associated production of hydrocarbon gas is also being considered (2). Determining the effect of carbon dioxide conditions (essentially temperature, pressure, and flow rate) and the effect of sample characteristics (including type of source material, particle size, and permeability) on hydrocarbon production typically requires large “bomb” type systems which are slow to operate. Collection and analysis of the products is a problem, since such systems do not easily allow the quantitation of gas and liquid hydrocarbon products. The Energy & Environmental Research Center (EERC) is developing laboratory-scale methods to determine the evolution of hydrocarbons from coal and petroleum reservoir rock under carbon dioxide floods performed at relevant geologic conditions. These methods can be used to determine the effect of carbon dioxide temperature and pressure on hydrocarbon evolution from coal and reservoir rock, but can not be used to determine the fate of carbon dioxide.

In addition to methods for measuring hydrocarbon evolution during carbon dioxide floods under geologically relevant conditions, inexpensive and reliable laboratory tests are needed to study the long-term fate of carbon dioxide in geologic reservoirs, whether the carbon dioxide is used to increase hydrocarbon production (e.g., as in tertiary oil recovery) or introduced into geologic formations for carbon dioxide sequestration. The fate of carbon dioxide is highly dependent on the temperature and pressure in the formation, as well as on the type of formation (e.g., coal, petroleum reservoir rock, mineralogy of the formation, brine salt concentrations) (2). At present, insufficient laboratory studies have been performed to allow the ultimate fate of carbon dioxide under these wide ranges of conditions to be predicted.

The present method for studying carbon dioxide fate in geologic formations is based on doing short-term sorption isotherm measurements under different pressure conditions at a set temperature. In short, the method does not allow a large number of samples to be evaluated, and sorption rate (kinetics) data are not normally available. In addition to the lack of knowledge about carbon dioxide sorption phenomena, potentially important mineralization processes are largely unstudied under geologic conditions of carbon dioxide storage. The development of a simple method to investigate the fate of carbon dioxide over long time periods (months to several years) would greatly help to understand the stability of geological carbon dioxide sequestration.

The purpose of the project was to develop, build, and test instrumentation to address three important areas in carbon dioxide use and sequestration; i.e., hydrocarbon production under carbon dioxide floods, chemisorption of carbon dioxide to geologic materials such as coal, and long-term reactions of geologic materials exposed to carbon dioxide.

EXPERIMENTAL

The apparatus for determining hydrocarbon evolution is shown in Figure 1. High-pressure carbon dioxide is supplied by a syringe pump into a preheating coil placed inside of the gas chromatography (GC) oven. The carbon dioxide then passes through the sample cell containing the sample (e.g., coal, petroleum reservoir rock, oil sands). The effluent from the sample cell then passes through a flow restrictor and into the flame ionization detector (FID) for hydrocarbon quantitation. Typical sample size is 100 mg. Carbon dioxide is provided at the desired pressure by the syringe pump, and the flow rate is controlled by the restrictor placed between the outlet of the sample cell and the FID. Typical carbon dioxide flow rate is 50 $\mu\text{L}/\text{minute}$ measured as liquid carbon dioxide in the pump. The apparatus can be run for several hours on one fill of the pump, but typical run times are 1 hour since nearly all hydrocarbon evolution occurs during this time frame.

The apparatus for determining carbon dioxide sorption to geologic materials (e.g., coal) is shown in Figure 2. Both the reference cell and sample cells and associated plumbing are placed in a constant-temperature water bath. Both cells were carefully calibrated for volume (included associated plumbing). To perform a sorption study, the sample is placed in the sample cell and its volume determined by first pressurizing the reference cell with an inert gas (e.g., nitrogen), then opening the valve between the reference and sample cell and determining the pressure in the cells after a short equilibration period (a few minutes). Since the volume of the reference and sample cells are accurately known and the initial and final pressures in the cells are known, the volume of the sample is then determined by simple pressure/volume calculations.

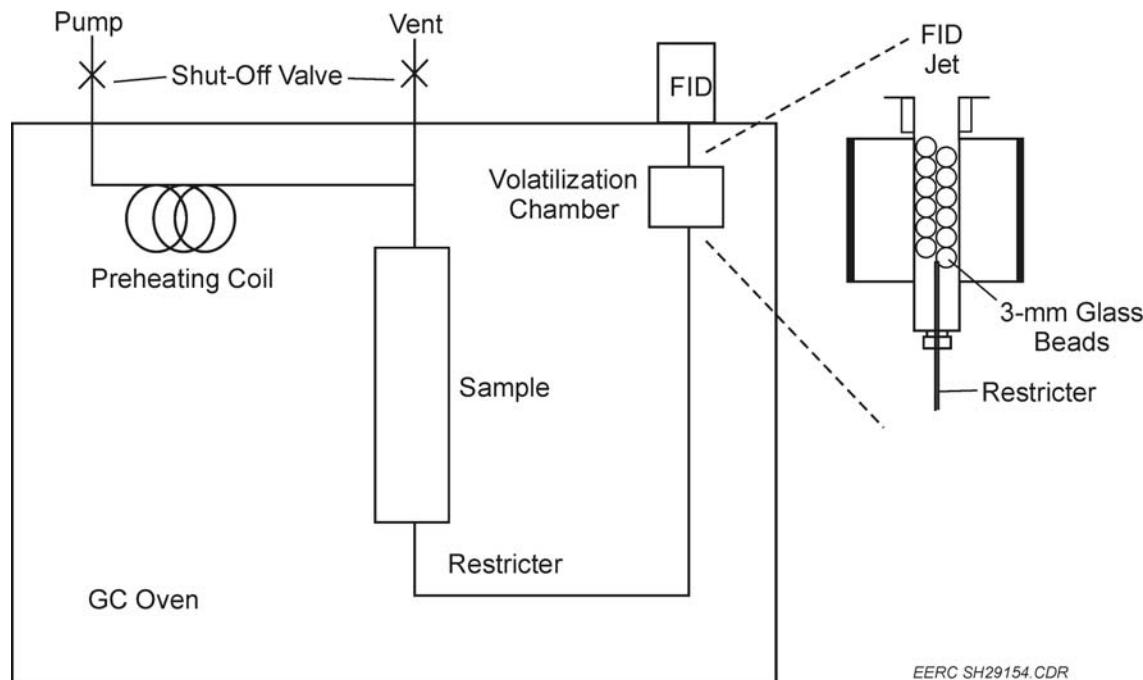
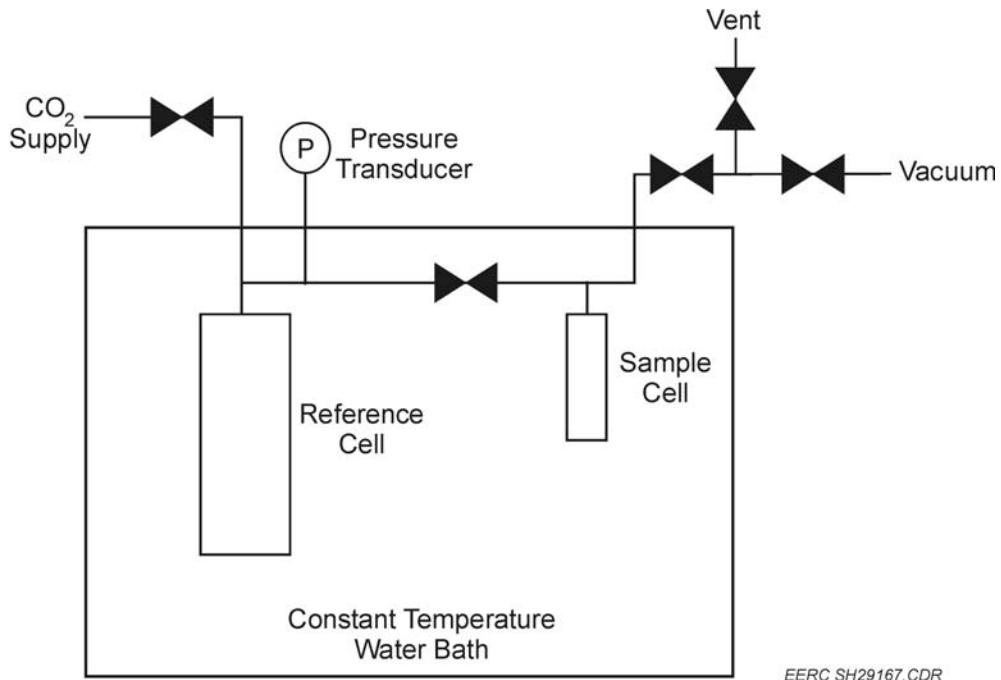


Figure 1. Schematic of the instrument to determine hydrocarbon evolution from carbon dioxide floods.



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Figure 2. Schematic of the apparatus for determining carbon dioxide sorption isotherms.

To determine carbon dioxide sorption to sample materials such as coal [3], the sample volume is first determined as described above. Then, both the sample and reference cells are evacuated, and the valve between them is shut. Carbon dioxide is introduced into the reference cell from a carbon dioxide cylinder to the desired pressure (e.g., a few bar). The valve to the carbon dioxide supply is shut, and the cell is left to equilibrate for a few minutes and the pressure noted. The valve between the sample cell is opened and the system allowed to equilibrate. After the desired exposure time of the carbon dioxide to the sample, the pressure is noted. Excess carbon dioxide sorption to the sample is then determined by pressure/volume calculations including adjusting for the compressibility of the carbon dioxide. The “missing” moles of carbon dioxide that result from these calculations represent the moles of carbon dioxide sorbed to the test sample. The entire process is repeated at sequentially higher pressures to obtain the sorption curve data.

The apparatus constructed for long-term exposures of carbon dioxide to geologic materials is shown in Figure 3. Our original intent was to construct several smaller vessels that each would be separately pressurized. However, discussions with members of the PCOR (Plains CO₂ Reduction) Partnership group (both the U.S. Department of Energy [DOE] funded group at the EERC and their commercial partners) led to a change in the design for two reasons. First, it became apparent that a system that could expose several samples to carbon dioxide under *identical* temperature and pressure conditions was more useful than several separate devices. Second, the most desired experiments included the study of saltwater brine in contact with related minerals and carbon dioxide, thus requiring that the samples be placed in glass rather than stainless steel because of the corrosion of stainless steel caused by chloride in the brines. Therefore, the design was modified so that one large pressure vessel contains twenty individual



Figure 3. Apparatus for long-term exposure of twenty samples to carbon dioxide. The rack of sample vials on the left is placed into the pressure vessel, which is then attached to the carbon dioxide supply and placed in an oven.

glass sample vials (4 mL each), as shown in Figure 3. Each vial is capped with a lid in which there has been made a small pin hole to allow carbon dioxide to enter and exit the cell during pressurization and depressurization cycles. The assembled apparatus is placed in an oven at the desired temperature. Carbon dioxide can be provided by a gas cylinder (up to ca. 70 bar) or by a syringe pump (up to 400 bar). Pressure is constantly monitored by a pressure transducer.

RESULTS AND DISCUSSION

The use of the online carbon dioxide flood/FID apparatus shown in Figure 1 to determine the elution profiles and mass of hydrocarbon eluted from petroleum reservoir rock is shown in Figure 4. The dramatic differences in hydrocarbon elution rate and quantity recovered from replicate 100-mg samples is clearly demonstrated. First, the higher pressure (150 bar) gave substantially more hydrocarbon product than 75 bar. The effect of extraction temperature was also dramatic. It should be noted that, while the 140°C (150 bar) conditions gave the most

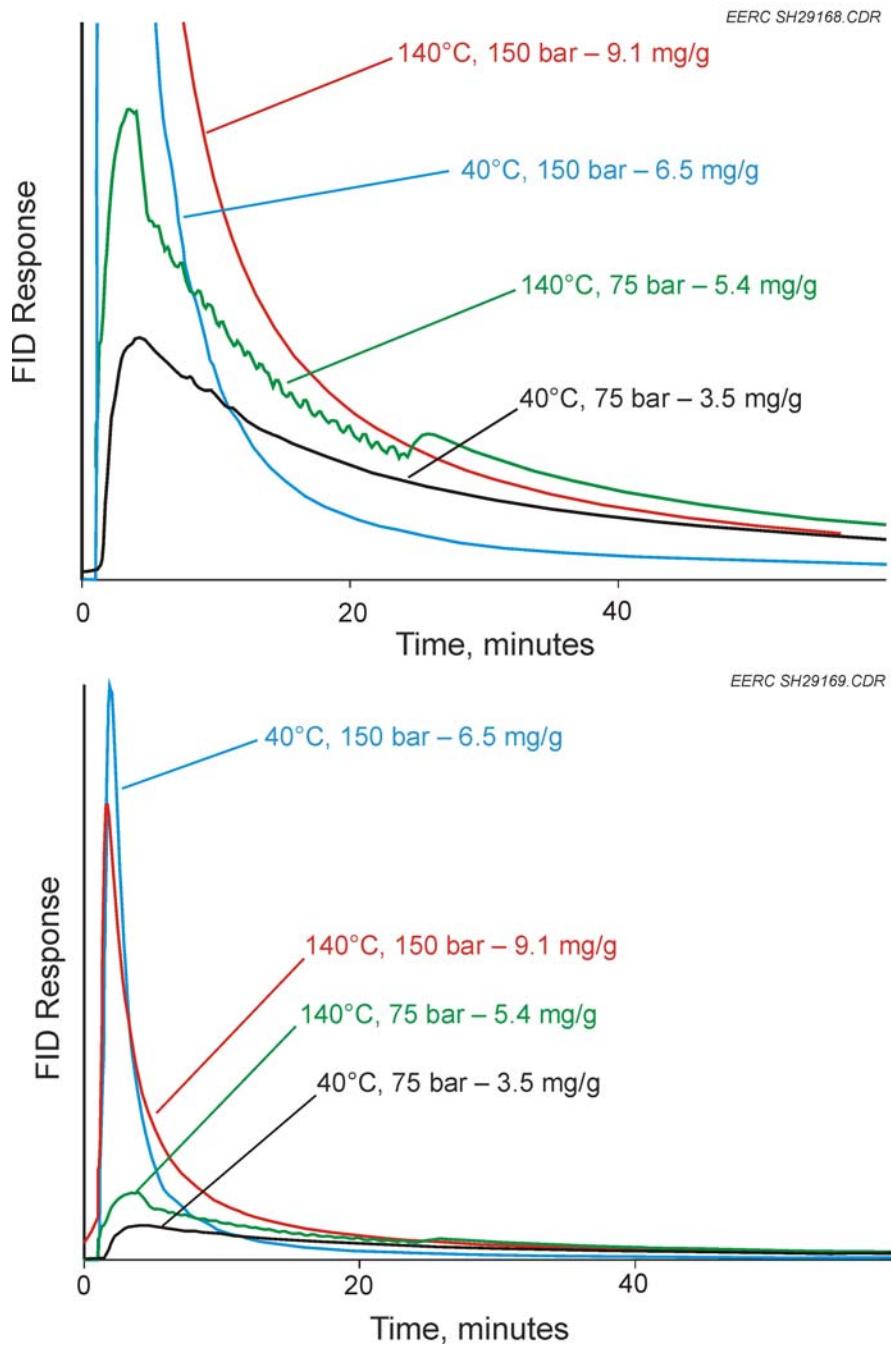


Figure 4. Real-time determination of hydrocarbon evolution from petroleum reservoir rock with carbon dioxide flushes under different pressure and temperature conditions. The bottom trace shows an expanded Y axis to allow the elution profiles at longer times to be more easily observed.

product hydrocarbon, the initial extraction rate was somewhat slower than the 40°C (150 bar) conditions. However, the ultimate quantity extracted at 140°C (150 bar) was 9.1 mg, which was substantially higher than the 6.5 mg extracted at 40°C (150 bar). At the lower (75 bar) pressure, the recovery of hydrocarbon was also higher at 140°C (5.4 mg) than at 40°C (3.5 mg). These results are contrary to conventional wisdom which states that lower temperatures (and, therefore, higher carbon dioxide densities at a given pressure) are always better at extracting hydrocarbons. The results in Figure 4 clearly show the importance of understanding temperature and pressure effects for carbon dioxide floods.

Despite the inherent problems with quantitative reproducibility when integrating the FID traces such as those shown in Figure 4, the reproducibility of the method is quite good. For example, eight replicate extractions of a different source rock at 90°C (112 bar) gave hydrocarbon recoveries of 6.7 ± 0.5 wt%, which is quite good reproducibility, especially when considering that the sample reservoir rock was unlikely to be completely homogeneous.

The use of the sorption isotherm apparatus shown in Figure 2 to measure excess carbon dioxide sorption to coal is shown in Figure 5. Excess sorption (i.e., the amount of carbon dioxide that is chemisorbed to the coal bed and, presumably, would be sequestered in coal for long-term disposal) increases at different carbon dioxide pressures, as would be expected. The sorption isotherm curve shown in Figure 5 was generated with sequentially higher pressures. The reflexive curve (not shown) that results when the pressure is dropped sequentially basically retraces the isotherm shown in Figure 5, thus demonstrating that the chemisorbed carbon dioxide

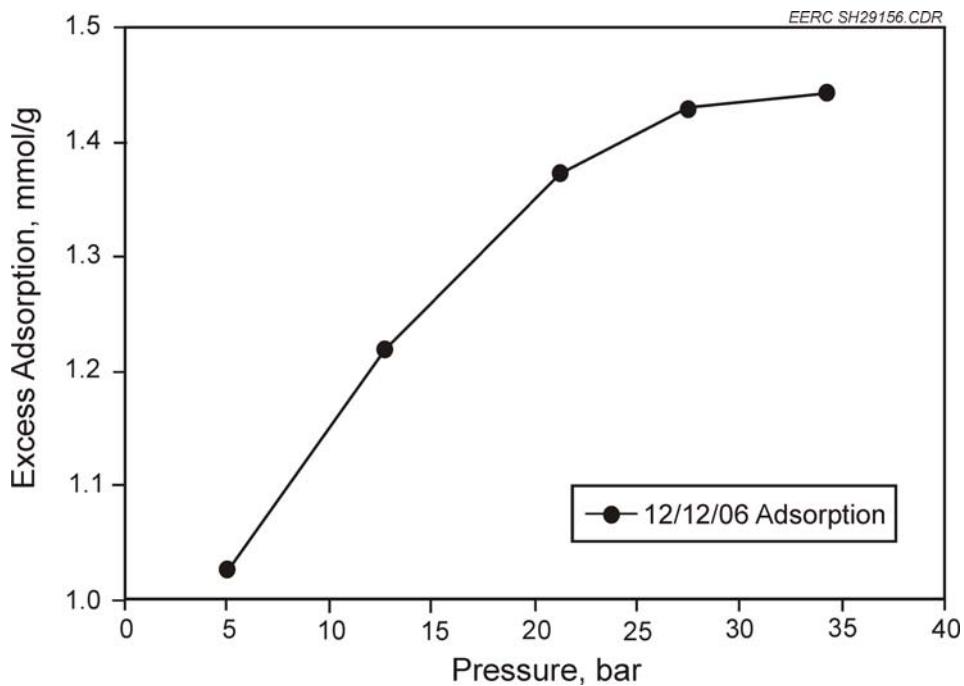


Figure 5. Sorption isotherm for carbon dioxide on Pocahontas coal determined using the apparatus shown in Figure 2.

does not remain in the coal as the pressure is dropped; therefore, pressure must be maintained for carbon dioxide to be permanently stored on this coal. An additional purpose of this apparatus was to be able to observe sorption of carbon dioxide in real time from the minute to day time frames. However, the observable sorption occurred rapidly (in a few minutes) while the temperature was being stabilized after the effect of pressurization heating and depressurization cooling that occurs based on the Joules-Thompson (J-T) effect. No observable sorption occurred when the system was left for several hours. These results showed that chemisorption of carbon dioxide to the test coals occurred in just the few minutes it took for the temperature of the apparatus to come to temperature equilibrium after each pressurization or depressurization step.

With modifications, the instrument should be able to measure solubilities of carbon dioxide in geologic brines and brine–mineral mixes. These modifications are planned to be made under separate commercial funding.

The long-term exposure apparatus shown in Figure 3 has been tested for up to 1 month with several different liquid and solid samples. Table 1 shows the conversion of magnesium silicate to magnesium carbonate under carbon dioxide flood as determined by gravimetric

Table 1. Conversion of Magnesium Silicate to Magnesium Carbonate under Carbon Dioxide Flood

	Weight, g Mg_2SiO_4	Moles Mg_2SiO_4	Theoretical Weight Change, g	Actual Weight Change, g	Percent Conversion
1 Week, 80°C, 4000 psi					
$Mg_2SiO_4 + H_2O$	0.36421	0.00260	0.22898	0.12055	53
	0.47766	0.00341	0.30030	0.20625	69
$Mg_2SiO_4 + Brine$	0.28273	0.00202	0.17775	0.16522	93
	0.51621	0.00369	0.32454	0.26698	82
2 Weeks, 80°C, 4000 psi					
$Mg_2SiO_4 + H_2O$	0.65291	0.00466	0.41048	0.40347	98
	0.47779	0.00341	0.30039	0.32271	107
$Mg_2SiO_4 + Brine$	0.57187	0.00408	0.35953	0.36409	101
	0.53551	0.00383	0.33668	0.29767	88
	0.49942	0.00357	0.31399	0.30098	96
	0.55668	0.00398	0.34998	0.34426	98
4 Weeks, 80°C, 4000 psi					
$Mg_2SiO_4 + H_2O$	0.60018	0.00429	0.37733	0.36864	98
	0.48730	0.00348	0.30637	0.34103	111
$Mg_2SiO_4 + Brine$	0.48791	0.00349	0.30675	0.34445	112
	0.61643	0.00440	0.38755	0.42238	109
	0.51560	0.00368	0.32416	0.41772	129

measurement. As shown in Table 1, the conversion is significant after only 1 week and appears essentially completed at the end of 2 weeks. It should also be noted also that dry magnesium silicate showed no conversion.

It should be noted that the mass measurement is somewhat inaccurate for wet samples since some error is introduced in the pressurization and depressurization steps. However, the mass measurements are useful to ca. 10% error. Additional proof of the conversion was obtained by x-ray fluorescence (XRF) which clearly demonstrated 100% conversion to magnesium carbonate. At present, the apparatus is being used to study carbon dioxide reactions with various geological samples in support of both PCOR and commercial client projects.

CONCLUSIONS

This project designed, developed, built, and tested three instruments to investigate interactions of carbon dioxide with geological materials. The instruments can measure (on lab-scale samples) a range of important behaviors under geologically relevant conditions with gas, liquid, and supercritical carbon dioxide including hydrocarbon evolution under carbon dioxide floods, excess sorption of carbon dioxide to materials such as coal, and the long-term reactions of carbon dioxide with both wet and dry geological materials relevant to carbon dioxide sequestration. The instruments are all either presently being applied to PCOR and commercial client projects under separate funding or their use has been requested and funding verbally committed to additional studies.

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