CO_2 FLOOD TESTS ON WHOLE CORE SAMPLES OF THE MT. SIMON SANDSTONE, ILLINOIS BASIN

W.K. O'Connor and G.E. Rush
Albany Research Center, Office of Fossil Energy, US DOE
1450 Queen Ave. SW, Albany, OR 97321
Phone: 541-967-5834 Fax: 541-967-5958
e-mail: oconnor@alrc.doe.gov; rush@alrc.doe.gov

Geological sequestration of CO_2, whether by enhanced oil recovery (EOR), coal-bed methane (CBM) recovery, or saline aquifer injection is a promising near-term sequestration methodology. While tremendous experience exists for EOR, and CBM recovery has been demonstrated in existing fields, saline aquifer injection studies have only recently been initiated. Studies evaluating the availability of saline aquifers suitable for CO_2 injection show great potential, however, the long-term fate of the CO_2 injected into these ancient aqueous systems is still uncertain. For the subject study, a series of laboratory-scale CO_2 flood tests were conducted on whole core samples of the Mt. Simon sandstone from the Illinois Basin. By conducting these tests on whole core samples rather than crushed core, an evaluation of the impact of the CO_2 flood on the rock mechanics properties as well as the geochemistry of the core and brine solution has been possible. This empirical data could provide a valuable resource for the validation of reservoir models under development for these engineered CO_2 systems.

INTRODUCTION

An enormous amount of information is currently available, and accumulates daily, on the geological sequestration of CO_2. Modeling is being utilized to predict plume migration, carbonate formation, and potential leakage over time. Field studies have increased in recent years, including the injection of CO_2 into depleted oil fields for enhanced oil recovery (EOR) using CO_2 as the displacement fluid. Normally, injected CO_2 is recovered in the process for recycle, but some portion of the CO_2 remains trapped in the formation and is sequestered. With the recent emphasis on CO_2 storage, these depleted oil fields are under investigation as storage sites for excess CO_2.

Injection of CO_2 into geological formations, such as deep non-potable sandstone and carbonate-hosted aquifers, is also under increased study as a potential sink for CO_2 storage. In this scenario, CO_2 may be stored in multiple forms, such as a gas, supercritical fluid, carbonic acid or some form of bicarbonate in solution, or even as precipitated carbonate minerals. It is likely that the stored CO_2 will exist in all of these forms to some extent. However, it is the long-term fate of the injected CO_2 in these ancient aquifer systems, salt domes, depleted oil fields, or other geological traps, that is uncertain. The injection of CO_2 acidifies the aquifer solution, changing the geochemical dynamics of the system, with obvious impact on the host rock. At depth, the increased pressure of the injected CO_2 can make it an aggressive solvent for species that may have been otherwise stable. These changes in geochemistry and mineralogy of the formation can play a significant role in its ability to contain the CO_2.

The Albany Research Center (ARC), part of the Office of Fossil Energy in the US DOE, and located in Albany, Oregon, has been working on CO_2 sequestration through mineralization over the past seven years. Initial studies focused on reaction optimization and process development, culminating in a feasibility study for an ex situ industrial process (*1*,*2*). This process utilized ultra-mafic rocks, in particular dunite (greater than 90% olivine), serpentinite, and wollastonite, as sources of basic cations for reaction with CO_2 to form mineral carbonates. The research included batch autoclave experiments to identify mineral-specific optimized carbonation conditions (*2*). As an example, the optimized carbonation conditions for the magnesium silicate olivine (Mg_2SiO_4) included a temperature of 185˚C, CO_2 partial pressure (P_{CO2}) of 155 atmospheres, in a carrier solution of 1 *M* NaCl and 0.64 *M* $NaHCO_3$. At these conditions, olivine ore ground through 400 mesh (38 microns) could be converted to the magnesium carbonate magnesite ($MgCO_3$) at a conversion efficiency of roughly 65% within a 1 hour reaction time. However, the great barrier to the ex situ process is two-fold: (1) the energy-intensive mineral pretreatment steps required, and (2) the material balance over the reaction. The energy requirements make the current mineral carbonation technology cost prohibitive, but the material balance, which is dependent on the mineral chemistry and reaction efficiency but independent of pretreatment demands and reaction kinetics, cannot be ignored. Using the process developed at ARC, up to 11 tons of olivine ore are required for each ton of coal burned to sequester the CO_2 released. This lead the ARC workers to consider an alternative application for the mineral carbonation technology, moving from an ex situ industrial process, to an in situ reservoir engineering process.

BACKGROUND

Injection technology is well known. EOR injection of CO_2 into marginally productive fields, as well as natural gas injection for storage in trapped geological formations until needed is now widely practiced. Toxic and municipal wastes have been injected into geological formations for disposal. But what is the long-term fate of the injected CO_2? Celia (*3*) points out that in mature sedimentary basins, such as those in North America that underwent intense exploration for and production of hydrocarbons, the number and density of wells is extremely high, and a plume of injected CO_2 is likely to encounter many wells that have to be identified and monitored. He also mentions diffuse leakage across aquitard and concentrated leakage along faults and fractures as other possible ways that CO_2 might find its way to non-target strata or the surface. Bradshaw (4) makes a very good argument that injected CO_2 into depleted petroleum systems will stay put, sighting natural CO_2 accumulations that have been trapped for millions of years. He also points out that any leakage will be identified very early into the injection process where remediation or cessation will limit leakage. Lindeberg (*4*) concedes that CO_2 disposed into gas and oil reservoirs is usually considered as a safe and permanent storage option, but goes on to mention that aquifers do not have a similar proven sealing capacity.

Aquifers are generally either termed unconfined, where the water table is exposed to the atmosphere through the zone of aeration, or less common confined, which as the name implies, the aquifer is isolated between relatively impermeable layers. Most aquifers are unconfined and recharged by movement of water from the surface or vertically. Target aquifers for CO_2 injection will most likely be *confined* with waters thousands to millions of year old, and flows of just a few meters a year. These waters tend to be oxygen deficient and contain minerals from the host rock and confining formations and are termed brackish to salty depending on the ionic and salt concentrations. These deep brackish to salty non-potable aquifers are the targets for CO_2 injection.

Aquifers are rarely if ever isolated, thus, recharge, flow, and discharge, how ever slow, will likely increase with CO_2 injection. The laws of hydrology dictate that a fluid will compress only slightly, if at all, suggesting that the formation will either experience a quick pressure increase, or displacement of the formation waters, to surface or surrounding strata, will occur. Vertical or horizontal flow through jointing or faults in the host rock or aquitard can lead to migration of fluids or gasses into unwanted strata. It should also be noted that faults also form geological traps by off-setting or pinching out formations, there by stopping flow across the fault. It is likely that a deep water bearing formation will accept some increase in pressure over the existing hydrostatic head or water column pressure, much like the pressure vessel of a water well system. Just how much pressure will depend on the fracture strength of the confining formation.

Prior studies conducted at ARC investigated the impact of a CO_2 flood on block samples or cores of rock types ranging from sandstone, dunite, to basalt. In a majority of these tests, a measurable increase in porosity suggested that alteration of the sample had occurred over the 2000 hour test duration. Rush (*5*) observed that cation/anion dissolution was largely dependent on solution pH, with acidic conditions favoring anion (Si) dissolution, while alkaline conditions favored cation (Mg) dissolution. Thus, the porosity increase was attributed to dissolution of pre-existing secondary minerals and/or the host rock itself by the aggressive supercritical CO_2/brine mixture. Ennis-King (*6*) discusses similar changes in permeability due to two competing processes. At the displacement front where CO_2 is dissolving into formation waters, lowering the pH, secondary minerals will dissolve, increasing permeability and creating a flow channel. However, the increase in flow will likely entrain and deposit fine particles of clay, sand, etc., which can impede flow. In the field, this dissolution phenomenon might yield greater storage capacity within the target horizon, or could lead to increased potential for leakage beyond the confining layers. The latter could point to an application of the ex situ mineral carbonation studies to geological sequestration, namely, the addition of a reactive mineral matrix to strategic sites within the aquifer to mitigate unwanted migration of the CO_2 plume. The volume increase that accompanies the precipitation of solid mineral carbonates could provide the mechanism to engineer geological seals. Strategies to minimize CO_2 migration beyond the natural reservoir seals should be identified prior to full-scale implementation.

MINERAL SLURRY INJECTION STRATEGIES

For the subject research, several methodologies for improving reservoir seal integrity by mineral slurry injection, for the minimization of CO_2 mobility beyond the natural hydrodynamic barriers, are theorized. These theoretical methods may include (1) co-injection with the CO_2 in the main injection well; (2) fracture-filling to inhibit excessive porosity/permeability; (3) emplacement of a slurry wall or grout curtain between the CO_2 flood and known fault zones or facies changes; and (4) fracture healing in the overlying aquitard or seal. These methods are depicted schematically in a hypothetical geologic cross section in Figure 1.

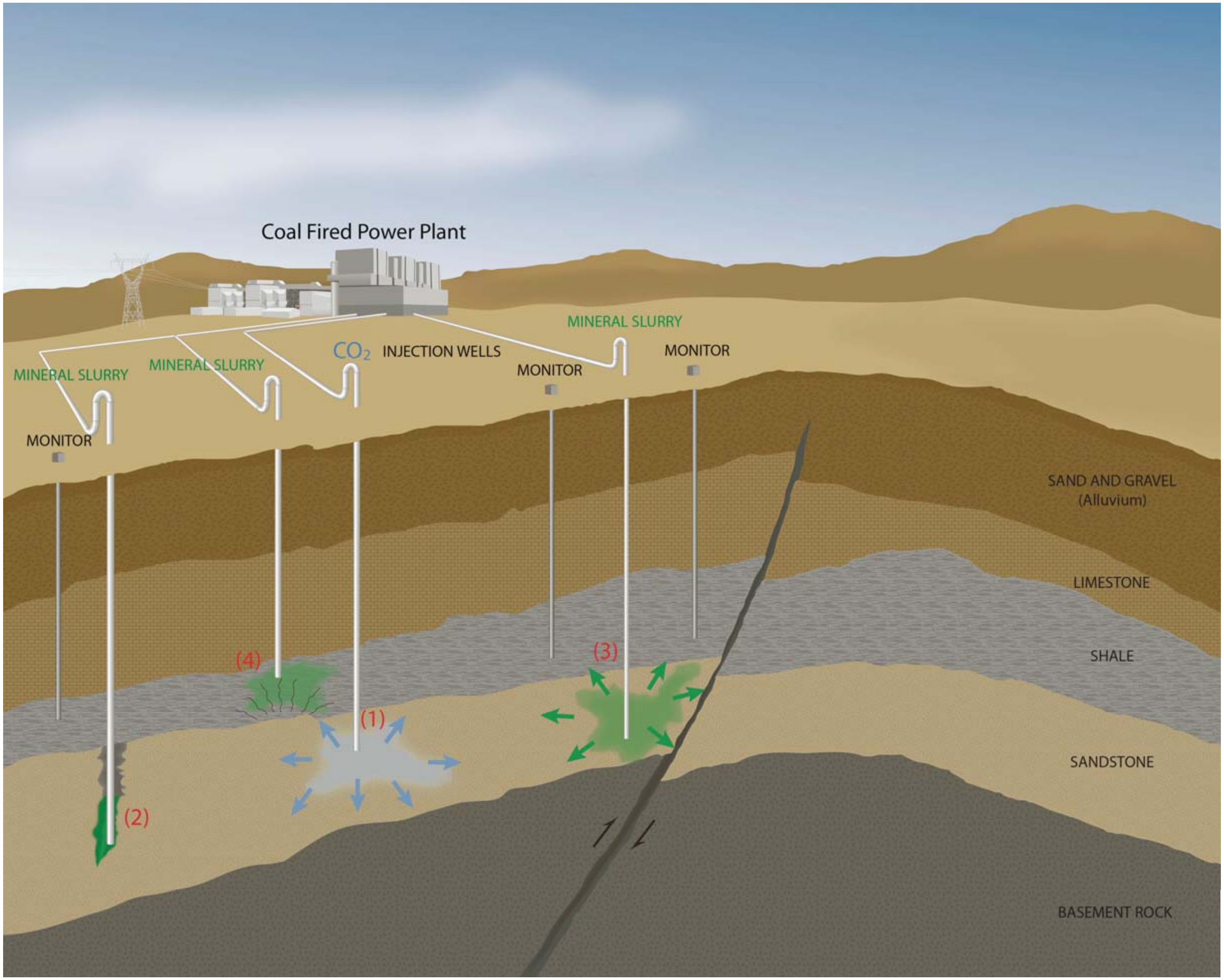

Figure 1. Hypothetical geologic cross section showing potential strategies for mineral slurry injection.

These strategies represent a potential application of the mineral carbonation studies conducted at ARC toward saline aquifer storage of CO_2. Knowledge of the specific mineral dissolution rates and P-T conditions necessary for carbonate precipitation, derived from the ARC data and appropriate literature, can be mated with knowledge of the reservoir engineering parameters, such as injection rate, reservoir threshold pressure, pressure drop from the point of injection, and injection well spacing. It may be feasible to calculate the appropriate concentration for mineral reactant to be co-injected with the CO_2, such that carbonate and other secondary mineral precipitation would commence once cation concentrations exceed saturation. It is conceivable that an engineered *carbonate-curtain* could be generated to produce a self-sealing CO_2 reservoir, with the boundaries of each plume falling at the limits of each injection well. Candidate materials for co-injection could include the ultramafic minerals investigated at ARC, or industrial solid wastes, such as coal fly ash, cement kiln dust, or electric arc furnace dust. Precipitation of secondary minerals, particularly the carbonates, could help seal any breach in the aquifer horizon due to volume expansion and the incumbent changes to the system P-T conditions.

The four strategies depicted in Figure 1 could have both positive and negative impacts on CO_2 injection. Co-injection with the CO_2 stream (strategy #1 in Figure 1) could have the positive effects described above, enveloping the CO_2 plume with a natural carbonate barrier, but could also result in premature carbonate precipitation at the primary injection well, inhibiting CO_2 injection capacity. Secondary injection of the mineral reactants (strategies 2-3 in Figure 1) would avoid premature carbonate precipitation at the primary injection well, but would require an array of secondary injection wells placed around the primary CO_2 injection well. This would increase costs, but the array could be engineered such that a slurry wall of mineral reactants could be emplaced about the CO_2 injection plume. Depths of the secondary wells could target the natural barrier horizons that occur stratigraphically above and below the CO_2 injection horizon, for vertical isolation of the CO_2 plume. Horizontal isolation could be accomplished by emplacing the mineral slurry wall at the appropriate well spacing or zones of natural facies changes, fractures, or faults within the target horizon.

BASIS FOR GEOCHEMICAL STUDIES

Examination of the available geochemistry literature provides a framework for developing kinetic models for gas-water-rock reactions in high partial pressure CO_2 (P_{CO2}) systems. Lasaga (*7,8*) provided a definitive geochemical examination of the kinetics of water-rock interactions and chemical weathering rate laws in two landmark papers. Examples of host rock alteration in natural CO_2-bearing aqueous systems were provided by Eurybiades (*9*) and Bischoff (*10*), who described gas-water-rock alteration of dolomite and rhyolite, respectively, at varying temperatures and P_{CO2}. The application of the empirical data resulting from the ARC experimental program, in tandem with the latest field and modeling studies, could provide a unique perspective on the impact of CO_2 injection on resident mineral alteration, aqueous fluid geochemistry, and reservoir characteristics such as porosity, permeability, and ultimately, CO_2 capacity and mobility.

Perhaps even more critical than mineralogical alteration in high P_{CO2} systems engineered within the reservoir host rock itself is the gas-water-rock reactions within the aquitards that seal the saline aquifer. Marty (*11*) presented encouraging evidence for natural aquifer isolation over geologic timeframes. The proposed research must extend this examination to the high P_{CO2} engineered environments and their impact on the natural seals. Again, the literature provides the means to develop the appropriate experimental methodology and apparatus to derive a modified geochemical kinetic profile for gas-water-rock reaction mechanisms in an engineered high P_{CO2} system. Cheng (*12*) provides the fundamentals of multilayered aquifer systems, while Laurent (*13*) and Gunter (*14*) describe the development of laboratory-scale models and empirical data collection of simulated geological systems, respectively.

The unique perspective of the subject research is the utilization of whole core samples in custom-fabricated pressure isolation systems to examine the migration of the CO_2 flood through the core (Figures 2). This methodology will also permit the acquisition of rock mechanics data, such as porosity, permeability, comprehensive strength, etc., and the impact of the CO_2 flood on these physical characteristics of the core.

METHODOLOGY

CO_2 Flood Tests

The CO_2 flood tests were conducted using high-pressure core holders to permit P_{CO2} of up to 1500 psig, at 35˚C. Split core of the Mt. Simon sandstone from the Illinois Basin were supplied by the Illinois State Geological Survey (ISGS), and made up the primary test specimens for the investigation. The 4-inch diameter core, covering a depth range of roughly 4000-4150 ft, was re-cored perpendicular to the formation bedding plane. Thus, when the nominal 1.375-inch diameter test cores are oriented horizontally in the high pressure core holder, the CO_2 flood flowed through the core at the natural orientation of the formation bedding plane (Figure 3). Brine solution was formulated to simulate that reported within the Illinois Basin (Table 1), in an effort to duplicate the natural system as closely as possible.

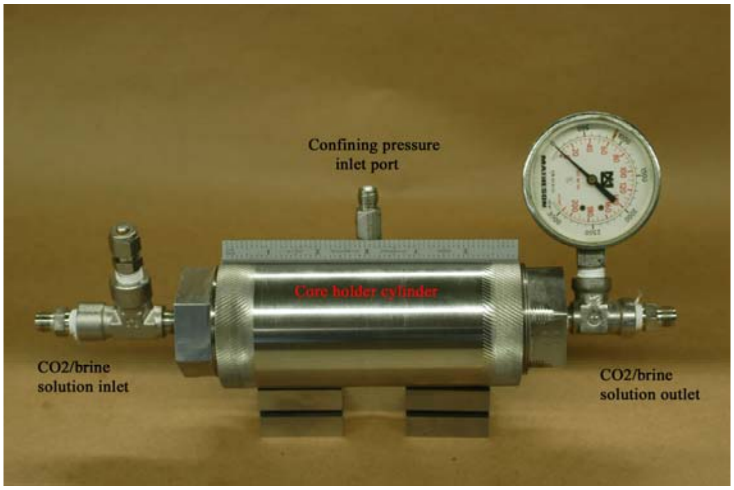

Figure 2. High pressure core holder.

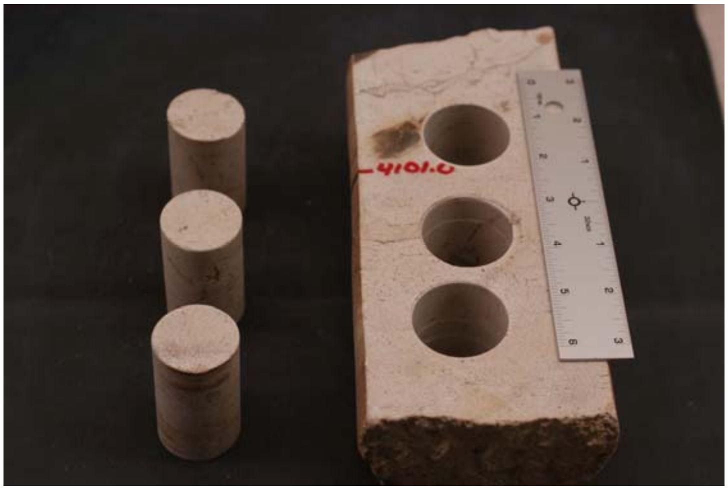

Figure 3. Mt. Simon sandstone core.

Porosity was measured using a helium porosimeter, and

Table 1. Illinois Basin brine chemistry (mg/L).

Ca	Fe	Mg	K	Si	Na	Cl	CO_2	HCO_3	F
3670	18.6	1280	141	10.8	23400	49600	70	50	83.3

permeability measured using a gas-liquid permeameter with a nitrogen flood. Permeability was measured at two inlet pressures, roughly 125 and 1500 psig, respectively. Permeabilities were relatively constant at the two pressures, with all but four of the samples indicating higher permeabilities at the lower inlet pressure. It is possible that higher turbulence within the sample at the higher pressure lead to the reduced permeabilities, although this is speculation at this point. The porosity and permeability measurements were intended to provide a baseline for the core samples prior to the CO_2 flood tests. Post test measurements were made to evaluate the impact of the CO_2 flood on these physical characteristics of the core. Crushing and shear strengths were also measured pre- and post-test for similar purposes.

A closed-loop system was for the CO_2 flood tests (Figure 4). Autoclaves were placed upstream and downstream from the core holders, with the brine solution re-circulated through the system continuously over the 1,500 hour test duration. Solution samples were drawn at 500 hour intervals. Bulk chemical and X-ray diffraction (XRD) analyses were acquired for the core prior to the tests, and were repeated upon their completion, again to evaluate the impact of the CO_2 flood on the geochemistry of the core. These samples of the Mt. Simon can be described essentially as a quartz sandstone consisting of over 95 wt pct SiO_2. The cement matrix consists of a mixture of feldspar, clay, and mica, which could provide some of the cations necessary for carbonate formation. However, the total molar concentration for the Ca, Fe^{2+}, and Mg is quite low, at less than 0.1 g-moles per 100 grams of sample. This suggests that a reactive mineral matrix must be added to improve the potential for carbonate formation.

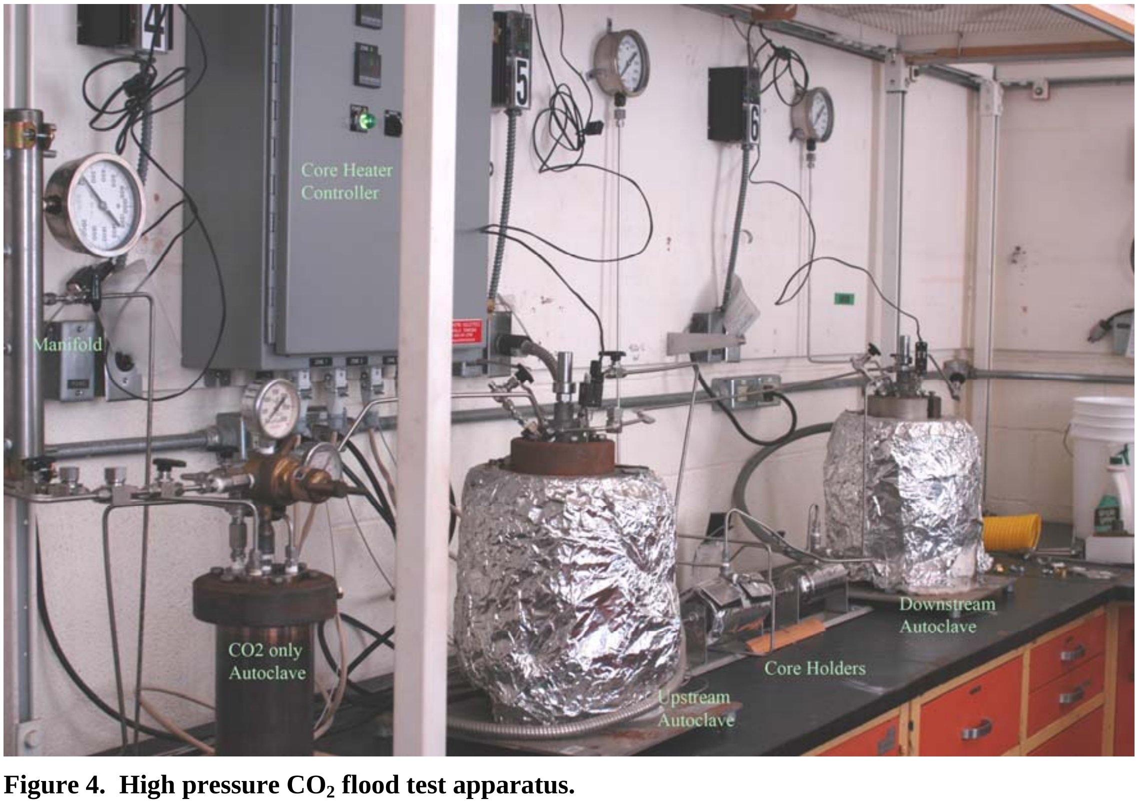

Figure 4. High pressure CO_2 flood test apparatus.

EXPERIMENTAL RESULTS AND DISCUSSION

Mt. Simon Sandstone Core Physical Characteristics

Porosity and permeability measurements were evaluated relative to depth of the core (Figure 5). The results showed that even over a relatively short depth interval, in this case about 150 ft, variations in porosity and permeability can be significant. While porosities varied over a relatively narrow range of roughly 8-12% over this depth interval, measured permeabilities changed dramatically at about the 4100 ft depth interval, from less than 10 to over 300 mD. Physical examination of the core revealed that grain size increased significantly at this depth. Chemical analyses revealed that the chemically-bonded water content of the cores from the 4100 ft depth and lower had double the water content than those from the shallower depths. This may be indicative of higher cement content between the coarser quartz grains, providing greater cross-sectional area for passage of the nitrogen flood gas. The laboratory observations corroborated core logs provided by the ISGS, which describe the core from the shallower depths as a fine grained, weakly-bedded, bioturbated structureless sandstone, while the core from the 4100 ft depth and lower was described as a cross-bedded sandstone.

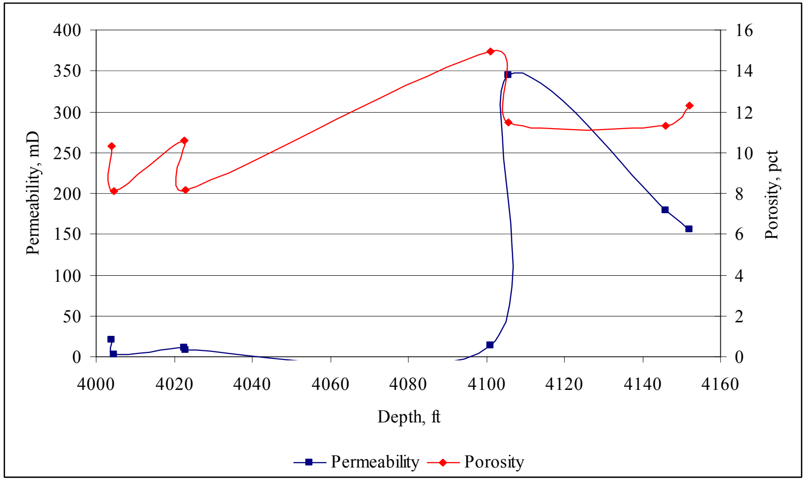

Figure 5. Porosity and permeability versus depth.

The physical characteristics of the core indicate that the CO_2 injection point at this site within the Mt. Simon sandstone should be beneath the 4100 ft depth interval, where higher permeability would not inhibit CO_2 injection. They also suggest that the section of the Mt. Simon overlying the injection zone could act as an internal aquitard for CO_2 migration beyond the target horizon. Thus, a likely target zone for mineral slurry injection would be this overlying low permeability zone within the Mt. Simon formation, at least at this particular site in the Illinois Basin.

Test conditions for the CO_2 flood tests included: Illinois Basin brine solution; temperature = 35˚C, P_{CO2} = 1,400 psig; and 1,500 hour duration. The impact of the CO_2 flood on the physical properties of the Mt. Simon core samples, namely porosity, permeability, and compressive strength, ranged from modest to dramatic (Table 2).

Table 2. Pre- and post-CO_2 flood test physical properties of the Mt. Simon core samples.

Core depth	Porosity, pct			Permeability, mD			Compressive strength, kpsi		
	Pre	Post	Δ, %	Pre	Post	Δ, %	Pre	Post	Δ, %
4101.0	7.9	8.3	4.7	8.9	8.0	-10.1	na	na	nc
4105.5	11.5	13.0	13.0	344.5	351.4	2.0	12.2	4.8	-61.0
4106.0	13.3	na	nc	288.9	na	nc	10.8	4.2	-61.6

Porosity and permeability did not change significantly following the CO_2 flood tests. However, compressive strength for the core samples decreased by roughly 60%. This dramatic reduction in compressive strength measured for the core could be an indication of reduced reservoir integrity due to exposure to the supercritical CO_2. Additional data is necessary to verify these initial findings, but a breakdown of the sandstone cement by dissolution with the CO_2 could become problematic in an engineered CO_2 reservoir. Reduction in injection capacity, premature retirement of the injection well, or loss of seals could result from a breakdown of the sandstone host rock.

OBSERVATIONS AND CONCLUSIONS

Test procedures included daily venting of the CO_2 from the downstream autoclave in the system to reduce pressure by about 500 psig. This would drive approximately 125 ml of brine solution through the cores while the two outer autoclaves re-equilibrated at the reduced pressure. Carbon dioxide was then re-injected into the upstream autoclave to bring the system pressure back up to 1,400 psig. Lag time for the downstream autoclave to reach 1,400 psig increased as the tests progressed, indicating some blockage to flow through the cores. This could be due to physical erosion of the core, debris blocking the solution pathways, and/or swelling of the cements in the sandstone core.

Solids analysis showed no significant change in the bulk chemistry of the core. No carbonate minerals were identified by X-ray diffraction (XRD). Solution chemistry trends showed increased Ca concentration over time, an indication of calcite cement dissolution. Little dissolution of the quartz sandstone matrix appeared to occur over this time frame, based on the limited increase in Si concentration over time.

The slight increases in porosity may be due to the dissolution of pre-existing secondary minerals and/or the cement matrix, while there was essentially no change in permeability of the cores. The structural impacts appear to have been the greatest, with approximately a 60% reduction in compressive strength. This could be an indication of reduced core integrity over time at high P_{CO2} conditions.

Future work will include additional tests to determine the reproducibility of the subject results. Tests may also be modified to include ultramafic mineral additions to the brine solution, to increase the cation potential available for carbonate formation, injection of a brine/CO_2/mineral slurry directly into the cores, and flow rate measurement through the cores.

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