APPLICATION OF NATURAL AND INTRODUCED TRACERS FOR OPTIMIZING VALUE-ADDED SEQUESTRATION TECHNOLOGIES

D.R. Cole and T. J. Phelps
(Collaborators: S. Fisher, J. G. Blencoe, J. Horita, J. C. Parker, A. V. Palumbo, and G. R. Moline)

INTRODUCTION

This project is one element (Task B.3) of an interdisciplinary public-private partnership, GEO-SEQ, that was established to develop and deliver the enabling technology and information needed to accelerate application of safe and cost-effective methods for geologic sequestration of carbon dioxide. Team members include researchers from LBNL, LLNL, Stanford University, the Texas Bureau of Economic Geology and the Alberta Research Council. The overall goal of the ORNL effort is to provide methods to interrogate the subsurface that will allow direct improvement of CO_2 sequestration during EOR, ECBM, EGR, or use of brine formations. This will be accomplished by utilizing the power of natural (isotopic) and applied gas tracers to decipher the fate and transport of CO_2 injected into the subsurface as well as other relevant processes. These methods have the potential to provide near-real-time information on process optimization. The resulting data will be used also to calibrate and validate the predictive models used for (a) estimating CO_2 residence time, reservoir storage capacity, and storage mechanisms, (b) testing injection scenarios for process optimization, and (c) assessing the potential leakage of CO_2 from the reservoir. This activity is being conducted in concert with the geophysical and inverse-modeling methods described in Tasks B.1 and B.2 and will provide a means for calibrating the transport model and as an aid to interpreting the time-series geophysical data. This work directly addresses a key objective of the overall GEO-SEQ project: to increase confidence in and the safety of geologic sequestration by identifying and demonstrating cost effective and innovative monitoring technologies to track migration of carbon dioxide and its reaction products in geologic formations.

RESULTS: APPLIED GAS TRACERS

Tracer studies have become an important technique for *in situ* subsurface characterization, allowing detailed interrogation of complex systems, which have components moving, mixing, and reacting. Simultaneous injection of multiple tracers at different concentrations and frequencies can lead to a maximum retrieval of information on subsurface conditions relevant to the fate and transport of CO_2. This approach has been used successfully to isolate and in many cases quantify specific processes affecting transport, including: diffusion into low permeability materials, sorption, partitioning into non-aqueous phase liquids, partitioning into trapped gas phases, and biodegradation.

COMPLETION OF FLOW SYSTEM

Pressure testing and construction of the flow-through system has been completed. Components of the system can be broken down into five main areas: injection, column, tracers, fluids, and data collection (Table 1, Fig. 1).

Table 1. Overview of flow-through system capabilities and design.

Injection
Multiple gas homogenization reservoirs (95 ml, 150 ml, 300 ml) allow for continuous sampling
Metered flow rates from 0.01 ml/min to 10 ml/min
Column
Constructed of corrosion resistant Monel (brine injection areas) and 2507 stainless steel with Swagelock valves and tubing
Working pressure range up to 344 bar (~5000 psi)
Working temperature up to 100°C
Temperature measurements by type T thermocouples
Pressure measurements using piezoelectric transducers (0–6000 psi)
Helium used to measure of substrate porosity
Tracers
Conservative tracers include stable isotopes, noble gases, nonreactive salts, and perfluorocarbons
Fluids
Ability to add hydrocarbons and/or brine conditions to column
System can operate with CO_2 as a gas, liquid, or supercritical fluid
Data Collection
System can be remotely operated via internet connection
Valco sample valve inject gaseous effluent directly into HP gas chromatograph with an electron capture detector
Data continuously monitored using Labview

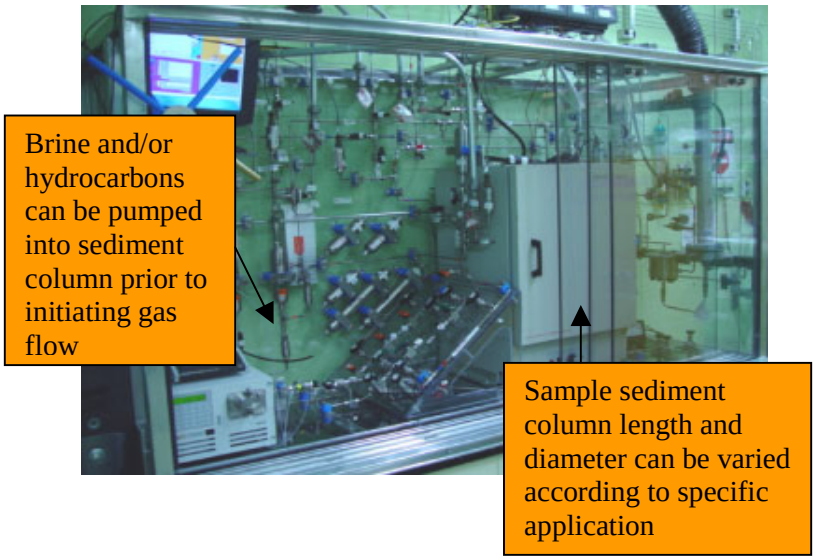

Fig. 1. Flow-through column apparatus.

The experimental plan for the laboratory flow-through column was designed to progress from simple to more complex systems: single phase (solid), dual phase (solid, brine), dual phase (solid, hydrocarbon), three phases (solid, brine, and hydrocarbon), and Frio core materials. Columns will be filled with solid material (clean quartz sand, carbonate, clay, and mixed reservoir solids) and each will be used for a succession of injections. Initial helium porosimetry measurements will be taken to obtain precise values for porosity. Brine and hydrocarbon saturations will be determined by repeating the He porosimetry after saturation and subtracting from the original pore volume. At every addition of some phase to the column, porosity will be re-determined. Thus, saturations will be known to great accuracy without having to disassemble the column to measure weight differences.

PERFLUOROCARBON TRACER METHOD DEVELOPMENT

The development of a PFT calibration standard dilution scheme was conducted. Because the PFT standards will exist in an aqueous and gaseous phase, calculations were done incorporating the density of the perfluorocarbons while taking into account the fact that PFTs are mostly insoluble in water. Therefore, methanol was incorporated into the scheme to aid in the solubility. Currently the perfluorocarbon standard curve ranges from 1.5 picograms to 5 nanograms conducted under injection volumes of 50 μL while the instrument detection limit had been determined at 1.5×10^{-14} g. Figure 2 shows the standard curve for all perfluorocarbons injected. Standard errors for injection replicates on the gas chromatograph have been >5%.

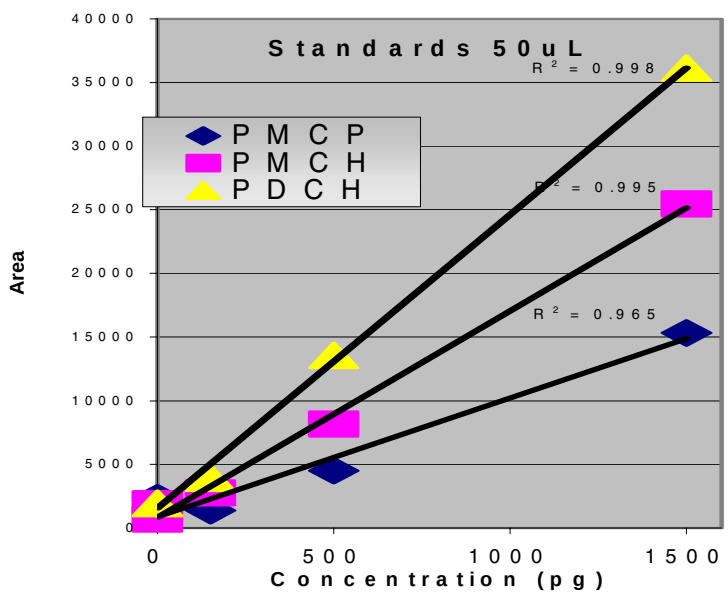

Fig. 2. Standard calibration curves (pg) for determination of PFTs.

PRELIMINARY GAS TRACER ANALYSES

Preliminary testing of single PFTs and evaluation of the dynamic flow system were conducted. Perfluoromethyl cyclopentane (PMCP) was chosen as the initial tracer for preliminary injection testing. 1mL of the 0.1 μg standard was injected through a 70°C-heated gas-tight syringe and allowed to homogenize overnight. System evaluation indicated a source of potential tracer dilution through the condensation trap located on the system, therefore the system was modified. Additional proceeding tests were conducted using perfluorodimethyl cyclohexane (PDCH) because of its distinct isomeric peak signatures that are distinct from nitrogen peaks. A 10-ml headspace sample of the 0.1 μg PDCH standard was drawn using a gas-tight syringe that was heated to 70°C and injected under vacuum into the simulator for homogenization in gas homogenization reservoir (GHR). The system was then pressurized to the selected experimental pressure of 700 psi with an ambient temperature of 19°C. Samples were allowed to homogenize overnight to ensure though mixing with the nitrogen carrier gas. An equal pressure gradient was maintained both upstream and downstream of the sediment flow-column. Upstream pressure was maintained by the use of an HPLC pump (Varian Instruments) with a built-in pressure transducer, while downstream pressures were regulated the use of a backpressure regulator. An experimental flow rate of 3ml/min was established using the HPLC to direct tracers from the GHRs into the sediment flow-column through a series of valves.

A Hewlett-Packard 5890 gas chromatograph (Agilent Technologies, Wilmington, DE) was used to quantify peak separation of PDCH. GC parameters included the use of an $ALOH_2$ column (50 m length, 0.53 mm ID), 51 ml/min split vent, 2.6 ml/min septum purge, 11.5 ml/min column flow, 250°C detector temperature, and injector temperature of 90°C. Oven parameters followed a temperature ramp program by setting the initial temperature to 120°C and raised 50°C (per 40 seconds) to reach a final temperature of 170°C. Samples were retrieved 7 minutes through a 10-inlet valco gas-sampling valve containing a 250 μL sample loop. Sample times were based upon retention times of perfluorocarbon standard curves.

RESULTS

The initial injection of PDCH into one of the 300mL GHRs was 2ng, thus 7pg/mL of PFT was allowed to homogenize within the GHR. Upon exiting the flow through column filled with Ottawa sand, PFT sample concentrations were determined based upon the standard curve to be 0.1pg (Fig. 3), corresponding to our predictions. The resulting concentration approached the instrument detection limit, but was approximately 10 above the baseline.

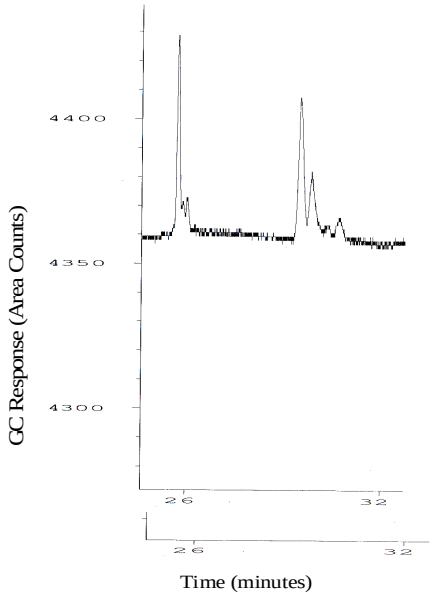

Fig. 3. GC Response for PDCH determined from preliminary PFT injections on flow-through system sampled from gas sample valve.

Results from our preliminary experiments on the Geo-Sequestration Simulator have demonstrated a working system that is reproducible, sensitive to low levels of detection, and is capable of distinguishing physical and geochemical parameters effecting long-term sequestration of CO_2.

RESULTS: NATURAL ISOTOPE TRACERS

Naturally-occurring elements, such as the stable isotopes of the light elements (O, H, C, S, N), noble gases and their isotopes (He, Ne, Ar, Kr, Xe), and radioactive isotopes (e.g., tritium, ^{14}C, ^{36}Cl, ^{125}I, ^{129}I, ^{131}I), have been used extensively to determine the sources of fluid and gas species and their mechanisms of migration, assess the extent of fluid/rock interactions, and quantify the residence times of fluids in the subsurface. These naturally occurring constituents and their isotopic compositions have the advantage of being readily available in most systems. In particular, by accounting for how $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios in CO_2 vary during the injection process, we can (a) understand complex natural geochemical processes involving CO_2 in the subsurface, and (b) assess and monitor quantitatively both short- and long-term consequences of subsurface CO_2 injection and sequestration, and possible leakage from the system.

ISOTOPE AND GAS CHEMISTRY AT THE LOST HILLS, CA CO_2 INJECTION SITE

We have now completed gas and isotope (carbon; oxygen) analyses of samples obtained from the Chevron Lost Hills, CA CO_2 injection test. Samples were taken this past year on 2/14/02, 6/12/02 and 10/8/02. The gas chemistries from these samples are plotted together with results we had obtained previously from earlier samplings on CO_2–CH_4–ΣC_2-C_6 ternaries show in Fig. 4. By way of review, gases sampled prior to injection were dominated by CH_4 (~60%) with lesser amounts of CO_2 (~30%) and subordinate amounts of C_2-C_6 (~10%). The $\delta^{13}C$ (PDB) values for CH_4 in pre-injection and all return gases were very similar, ranging from –36 to –42%, with an average of –40.4% (±1.5% 1 σ). The initial injection CO_2 had a $\delta^{13}C$ (PDB) value of about –31% and $\delta^{18}O$ (VSMOW) values of between –1 and –2 %. The brine has a $\delta^{18}O$ value of about –1% VSMOW. The most extensive CO_2 injection was conducted at the end of 2002, with lesser magnitude injections occurring during the end of 2001 and the

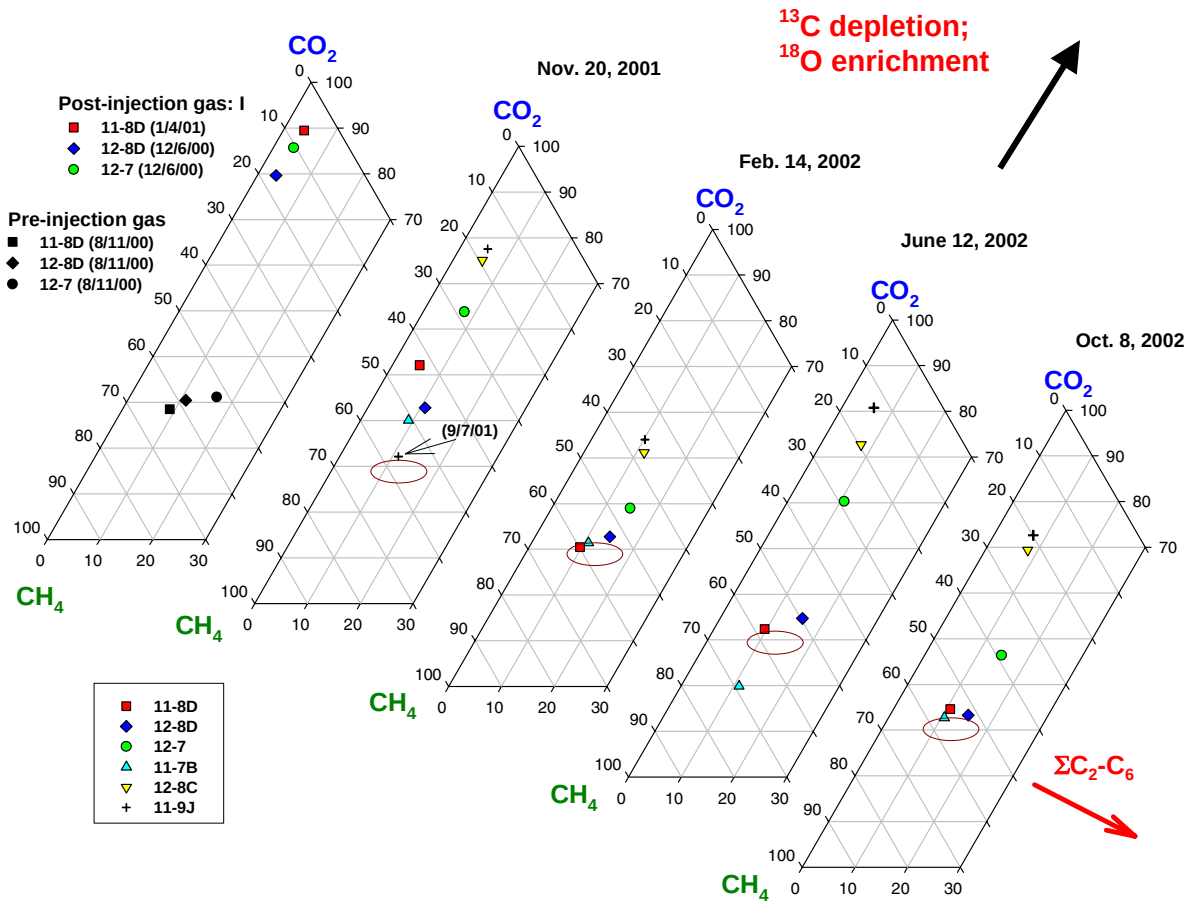

Fig. 4 Lost Hills gas chemistry plotted in CO_2-CH_4-ΣC_2-C_6 ternary space as a function of sample date.

summer of 2002 (June–August). A major water flood was conducted prior to CO_2 injection (Jan. 2000–August 2000) and also in early 2002.

Based on data presented in Fig.4, it is clear that the contribution by injectate CO_2 becomes far less pronounced with an increase in time starting from our earliest post-injection samplings (12/6/00; 1/4/01). In fact, after the 11/20/01 sampling time, three of the wells, 11-8D, 12-8D and 11-7B, exhibit gas compositions very similar to those for wells sampled prior to the initiation of the CO_2 injection test (9/19/00) which we presume represents the "baseline" reservoir chemistry. The caveat here, however, is that this part of the Lost Hills reservoir had been undergoing water injection as far back as 1/7/00, some 8 months prior to the CO_2 test. Thus, the gas and isotope chemistry of reservoir gas will never be known for this area because of the long history of perturbation.

Samples obtained from Lost Hills, CA on Feb. 14, 2002 coincide with an extensive period of water injection that started in mid-November of 2001. The contribution of injectate CO_2 appears to be considerably less than the previous sample time of 2/14/02 as well as subsequent samplings (6/12/02 and

10/8/02). These latter two sample times occurred during periods of modest CO_2 injection. The contribution by injectate CO_2 became somewhat less pronounced with an increase in time since the June 12th sampling for some wells (11-9J, 11-7B, 12-7). Gas chemistries for wells 11-8D, 12-8D and 11-7B sampled in October, 2002 plot very close to the gas compositions determined for wells sampled prior to the initiation of the CO_2 injection test (9/19/00), i.e. the "reservoir" signature. The gas chemistry for well 11-7B plots within the range of compositions thought to represent the indigenous reservoir system, but with considerably more CO_2 than it exhibited in the more CH_4-rich June sample. The reason for this shift to more CO_2 is not immediately apparent since the CO_2 injection activity ended on Sept. 15, 2002. Despite the fact that CO_2 injection had been stopped roughly three weeks prior to the Oct. sampling, there is still a significant contribution of injectate to three of the six wells sampled. Interestingly, these three wells are located at approximately opposite corners of the four 2.5 acre pattern—i.e., wells 11-9J and 12-8C are in the SW quadrant, and well 12-7 is located in the NE corner. The implication of this observation is being assessed in the context of both the nature of the injection (i.e. which injection wells were used and for how long), and the known fault structure in the area.

The carbon isotope compositions of CO_2 are plotted as a function of time in Fig. 5. The $\delta^{13}C$ (PDB) values for pre-injection CO_2 ranged from 15.6 to 18.5% whereas the return CO_2 gases from the first sampling effort (12/6/00 and 1/4/01) exhibited a narrow range of values, –27.5 to –29.9%, very similar to the injectate value of –31%. Chemically, return gases from this first sampling effort were very rich in CO_2 and clearly have carbon isotope values very close to the injection CO_2. Carbon isotope values determined for samples obtained during intervals of CO_2 injection are more depleted in ^{13}C compared to samples obtained during or just after water injection. This is consistent with an increased contribution of injectate CO_2, which has a very negative carbon isotope signal (~ –31%) compared to the "reservoir" CO_2. For example, CO_2 obtained June 12th had much lower $\delta^{13}C$ values for wells 11-9J and 12-7 compared to the Feb. 14 sampling, but a somewhat modest shift to a more depleted value for well 12-8C. In fact, the carbon isotope compositions of these three wells mimic those observed from the Nov. 20, 2001 sampling which also was conducted during a period of CO_2 injection. At no time, however, have the gas chemistries ever exhibited as rich a CO_2 content, nor as negative a carbon isotope value as were observed in the very first samples obtained at the end of the first (and most major) CO_2 injection period (9/00–12/00). Because 12-7 and 11-9J/12-8C are located at opposite corners of the four 2.5 acre well pattern, separated by major faults, it is clear that increase in CO_2 concentration (along with more negative carbon isotopes) is probably a consequence of communication with the closest injector wells, 12-7W and 11-8WA, respectively. Tracking the changes in chemistry and stable isotopes are complicated by the fact that the durations and capacities of separate injections of water and CO_2 have been varied through time, as was which set of the wells was used during a particular injection test.

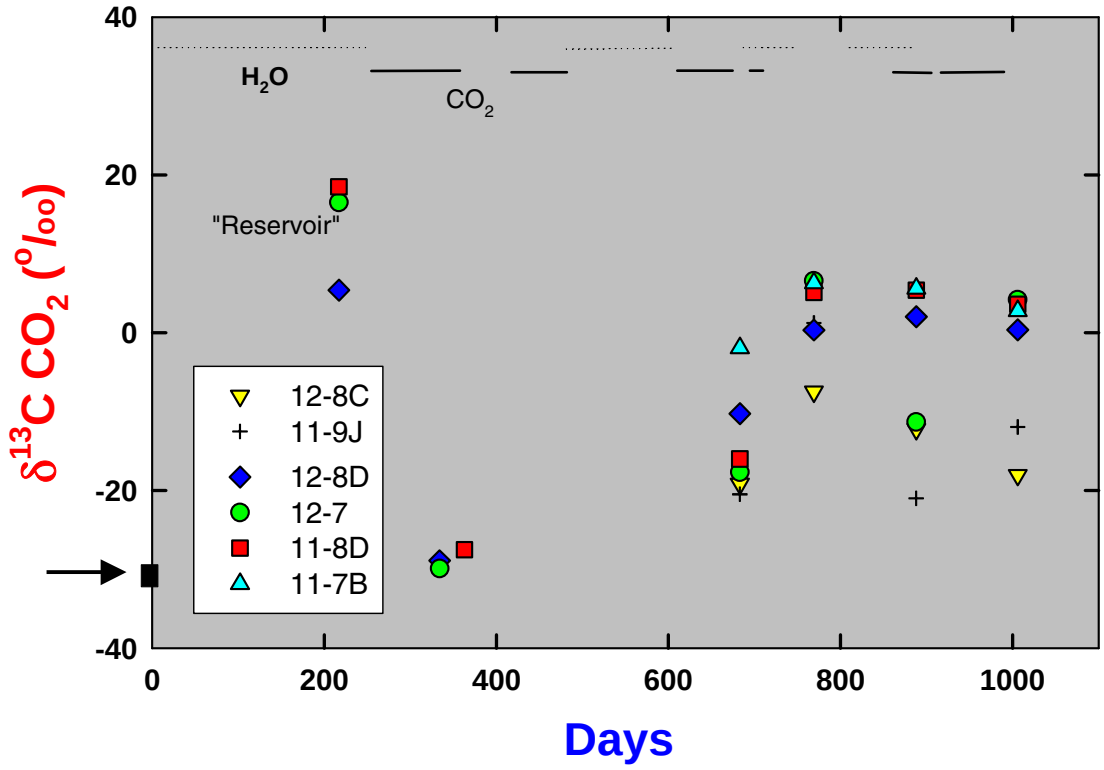

Fig. 5 Carbon isotope compositions of CO_2 plotted against time for the Lost Hills system. The injectate CO_2 has a $\delta^{13}C$ value of roughly –31%.

The $\delta^{18}O$ compositions of the pre-injection CO_2 ranged from about 16 to 24% (average ~20.9%), whereas the return CO_2 gases from the first sampling effort were somewhat more enriched, ranging from approximately 29 to 34%. Since these samples are dominated by injectate CO_2 (78–90%), this constitutes nearly a ~30% increase in $\delta^{18}O$ from the injection value of –1.1%. Subsequent CO_2 samples exhibit $\delta^{18}O$ values that have remained relatively constant over time, varying between 36 and 40%. Simple mixing of an isotopically light injectate and the heavy "reservoir" CO_2 cannot explain the even heavier $\delta^{18}O$ values measured in the three return wells. It is likely that the enrichment in ^{18}O is due to kinetically fast exchange of CO_2 with water encountered during migration. The values we observe (36 to 40%) would be expected if the CO_2 equilibrated with reservoir brines (–1%) at temperatures between ~40 and 60°C.

SUMMARY

(1) Gas and isotope chemistry of the CO_2 clearly demonstrates that increases in CO_2 and more depleted ^{13}C values correlate with periods of CO_2 injection.

(2) During water flood events, the CO_2 gas contents decrease and the ^{13}C values in CO_2 return to more "reservoir-like" in magnitude.

(3) Certain wells communicate with the injection wells far more readily than others, which may be controlled, in part, by faults that strike NE-SW.

(4) Oxygen isotope values in CO_2 demonstrate that the gas has equilibrated with reservoir brine in the temperature range of ~40 to 60°C.

REFERENCES

Hayduk, W., and H. Laudie, 1974. Prediction of diffusion coefficients or non-electrolysis in dilute aqueous solutions. AIChE J. 20:611–615.

Sanford, W. E., R. G. Shropshire, and D. K. Solomon, 1996. Dissolved gas tracers in ground water: Simplified injection, sampling, and analysis. Water Resour. Res. 32:1635–1642.

Wilke, C. R., and C. Y. Lee, 1955. Estimation of diffusion coefficients for gases and vapors. Ind. Eng. Chem. 47:1253–1257.

PRESENTATIONS AND PUBLICATIONS

L. S. Fisher, D. R. Cole, J. G. Blencoe, G. R. Moline, J. C. Parker, and T. J. Phelps (2003). High-pressure flow-through column for assessing subsurface carbon sequestartion. 2nd Annual Conference on Carbon Sequestration.

D. R. Cole, J. Horita, M. C. van Soest, B. M. Kennedy, and M. F. Morea (2003). Gas chemistry and isotope monitoring during the Lost Hills, CA CO2 injection test. 2nd Annual Conference on Carbon Sequestration.