Monitoring CO$_2$ Storage in Brine Formations: Lessons Learned from the Frio Field Test One Year Post Injection

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ABSTRACT

The Frio Brine pilot is a closely monitored, small-volume (1,600 tons), short-duration experiment using injection of CO$_2$ into a high-permeability brine-bearing sandstone of the Frio Formation east of Houston, Texas, to test the feasibility of using this technique as a method to reduce atmospheric buildup of greenhouse gases. For the experiment, pure CO$_2$ was injected for 10 days 1500 m below surface. Because the injection period was brief and the formation was on the flank of a steeply dipping structural compartment, a year since injection takes us well into the postinjection phase of monitoring. Key findings are relevant to the design of the next experiments:

(1) Understanding site hydrogeology is critical for designing a successful project .

(2) Numerical simulation of flow is essential to guided site selection, well design, and tool selection.

(3) Successful geochemical techniques include detection of CO$_2$ breakthrough at the observation well, evolution of formation waters as CO$_2$ interacted with rock and brine, and recovery of tracers to quantify CO$_2$ saturation.

(4) Field measurements of saturation using time-lapse neutron logging, cross-well seismic, and vertical seismic profiling (VSP) were successful in measuring CO$_2$ plume evolution.

(5) Models and conceptualization suggest that significant CO$_2$ is trapped post injection as relative permeability to gas decreases over time (two-phase trapping); measurements confirm the correctness of this process.

(6) An innovative sampling devise, the U-tube, provided high-frequency, minimally altered, samples of two-phase fluids in the wellbore during injection .

(7) Complex and rapidly changing surface environments and interference among test elements create challenging conditions to monitor for CO$_2$ leakage in groundwater and soil. Geochemical monitoring in the sandstone above the injection interval provided better signal.

BIOGRAPHICAL SKETCH

Susan D. Hovorka is a Research Scientist at the Bureau of Economic Geology, Jackson School of Geosciences, The University of Texas at Austin. She is the chief scientist of the Gulf Coast Carbon Center (**www.gulfcoastcarbon.org**), an academic-industry consortium seeking an economic basis on which to move forward on carbon sequestration. Currently she is leading a team in a Frio Brine field pilot CO$_2$ injection to assess the cost, safety, and effectiveness of geologic sequestration as a mechanism for reducing atmospheric greenhouse gas emissions. She is also actively facilitating exchange between applied scientists and citizens, with a focus on precollege students and teachers.

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INTRODUCTION

Field demonstration is widely recognized as an important element in developing a national program for geologic storage of CO_2. As the first test of closely monitored CO_2 injection in brine in the United States, the Frio Brine Pilot experiment was funded by the Department of Energy (DOE) National Energy Technology Laboratory (NETL) under the leadership of the Bureau of Economic Geology (BEG) at the Jackson School of Geosciences, The University of Texas at Austin, with major collaboration from GEO-SEQ, a national lab consortium led by Lawrence Berkeley National Laboratory (LBNL).

The Frio Brine Pilot has four goals: (1) demonstrate to the public and other stakeholders that CO_2 can be injected into a brine formation without adverse health, safety, or environmental effects, (2) measure subsurface distribution of injected CO_2 using diverse monitoring technologies, (3) test the validity of conceptual, hydrologic, and geochemical models, and (4) develop experience necessary for development of the next generation of larger scale CO_2 injection experiments. In this paper, we review the results of the study with the emphasis on achieving the fourth goal, providing recommendations relevant to the next generation of field tests.

METHODOLOGY

The injection site was selected in 2003 after characterization of 21 representative saline formations in the onshore United States (Hovorka and others, 2000). Sandstones of the Oligocene Frio Formation are an ultimate target for large-volume storage because they are part of a thick, regionally extensive sandstone trend that underlies a concentration of industrial sources and power plants along the Gulf Coast of the United States. However, the specific site selected was optimized for a small demonstration, and the injection well is not suitable for, nor was it ever intended to be, a full-scale injection project. The experimental site is in a historical oil field, where site access, use of an idle well as an observation well, wireline well logs, 3-D seismic, and production data were donated by the operator, Texas American Resources.

Detailed characterization was conducted using traditional reservoir assessment tools. This effort included use of seismic and log analysis to define facies, structure, and diagenetic evolution and estimation of petrophysical and geochemical properties using core from analogous facies in Chambers County to build a quantitative reservoir model. From this characterization, a numerical model was created using LBNL TOUGH2 code. Geologically constrained numerical models of injection and monitoring scenarios were prepared and used to optimize the experimental design, well locations and completion, and monitoring tool selection. The Frio "C" sandstone, a 23-m-thick brine-bearing interval above oil production was selected as the injection target. The well pad was improved, a new injection well was completed to near Class I standards, and the existing oil production well was plugged back and recompleted as an observation well in the injection zone. Additional site-specific geologic and petrophysical characterization was completed using new core and log suites collected in the new injection well, and baseline cross-well and vertical seismic profile (VSP) surveys. In addition, a two-well pumping test using an introduced an fluorescent tracer was conducted to determine hydrologic properties under single-phase (brine only) conditions. All of these data were used to revise the flow model, which was then used as a predictive tool to determine the final design of the experiment.

The injection was conducted under a Class V experimental well authorization under the jurisdiction of the Texas Commission on Environmental Quality (TCEQ) Underground Injection Control (UIC) Division. Sandia Technologies, LLC, an experienced injection well engineering firm provided field services and assured that the injection was compliant and supported the research elements. At the request of TCEQ, the research team prepared a report to accompany the Class V application that detailed information relevant to this injection that is normally put into a Class I application. . The research team also conducted a public notification campaign as part of

our public outreach program. We also completed an Environmental Assessment required to obtain Federal funding under the National Environmental Policy Act. These documents are available for review online (www.gulfcoastcarbon.org). From October 4 to 14, 2004, the Frio Brine Pilot team injected 1,600 tons of CO_2 at a constant rate of 3 kg/s, except for pauses used as pressure fall-off tests. Well-head pressure was variable, around 800 psi. Gas was delivered as cold liquid at pressure, heated to gas at 50 to 70 degrees F, and became supercritical fluid as it descended down tubing.

The subsurface CO_2 plume was measured and monitored using a diverse suite of technologies in three intervals: the injection zone, the area above the injection zone, and the shallow near-surface environment. Each monitoring strategy used a preinjection and one or more postinjection measurements. Wireline logging, pressure and temperature measurement, and geochemical sampling were also conducted during injection.

In-zone objectives were to measure changes in CO_2 saturation through time, in cross section, and areally, and to document accompanying changes in pressure, temperature, and brine chemistry during and in the months following injection. Tools used for in-zone monitoring included five repetitions of logging with the Schlumberger pulsed neutron capture reservoir saturation tool (RST), which under conditions of a maximum 35% porosity and 125,000-ppm salinity was predicted to be successful in obtaining high-resolution saturation measurements across the injection interval. The log analysis team includes researchers from BEG and Schlumberger–Doll Labs. An innovative geochemical sampling tool, developed and operated by Barry Freifeld and Rob Trautz of LBNL to support in-zone fluid chemistry sampling, is the U-tube. The U-tube is composed of a double length of 9.5 mm O.D. × 1.2 mm wall thickness stainless steel tubing, with a check valve open to the reservoir at 1,500 m. Formation fluid that was collected in the U-tube was driven at reservoir pressure into evacuated sample cylinders at the surface by high-pressure ultrapure nitrogen. Samples were collected hourly to facilitate accurate delineation of CO_2 breakthrough and recover uncontaminated and representative samples of two-phase fluids.

The near-surface monitoring program measured soil gas fluxes and concentrations, introduced tracers, and fluid chemistry in the vadose zone and shallow aquifer in an attempt to detect any leaks upward out of the injection zone, especially those rapid enough to cause releases in a short time frame, such as behind well casing. We also measured the postinjection geochemistry of the Frio "B" sandstone above the Frio "C" injection sandstone.

RESULTS

Hydrogeologic setting

The upper Frio in this area is composed of northwest-southeast-elongated fluvial sandstone separated by mudstones and shales that can be correlated over the field but not regionally. The upper Frio "C," "B," and "A" (in lower to upper stratigraphic order) sandstones are part of a trend of fluvial sandstones that were increasingly reworked beneath the regionally extensive 60-m-thick (200-ft) shales and mudstones of the overlying Anahuac Formation. The selected injection zone, the upper half of the Frio "C" sandstone, is an 22.8-m (75-ft) upward-fining, fine-grained, poorly indurated, well-sorted sandstone. Thin-section analysis shows that sandstones are composed of well-sorted but angular grains, dominantly quartz with about 20% fresh-to-leached orthoclase and plagioclase feldspar and altered rock fragments, trace quantities of micas, calcite, organic materials, pyrite, and minor clays as grain coats and local matrix.

Important to predicting matching modeled with observed CO_2 plume evolution is accurate definition of the flow-unit properties. The massive upper part of the upper "C" sandstone has porosities of 30 to 35% and permeabilities of 2,000 to 2,500 md. Finer grained and more layered sandstone and clayey sandstone having porosities of 24 to 28% and permeabilities of 70 to 120 md make up the mid-"C" gamma marker and the top "C" transition to the top "C" seal.

The top "C" seal is composed of shale, sands, and siltstones that form a minor seal beneath the regional Anahuac Shale but probably a major barrier to vertical flow out of the "C" sandstone.

Structural analysis of the injection interval using logs and a 3-D seismic volume shows that the upper Frio Formation at the test site is within a fault-bounded compartment that is part of a system of radial faults above the salt dome (Figure 1). Dips within the injection compartment are steep. Hand-picked interpretation of the FMI log by Schlumberger measured dips of 18 degrees to the south at the injection well; interwell correlation measured an average dip of 16 degrees south. Neither FMI nor seismic surveys identified fractures or faults in the interwell area, although the steep dip is compatible with deformation band structures interpreted in core C-T scans.

A set of single-phase hydrologic tests helped to better define the flow system near the injection well. A drawdown test defined the average permeability in the area of the perforated zone in the injection and observation well as 2.3 Darcys, a good match to that defined by core-plug analysis. A two-well tracer test resulted in a breakthrough time of the tracer that was somewhat slower than predicted. Because porosity is relatively well constrained by measurements on core plugs, we refined the effective aquifer thickness to 7.2 m from the original 6.5 m used in the initial predictive model. The 10% greater thickness required to match the single-phase tracer test might be conceptualized as a result of stratigraphic or structural heterogeneity that thickened the upper "C" unit/sandstone or of discontinuities in the muddy and laminated sands at the top and bottom of the "C" unit/sandstone so the flow field occupied a larger volume of sandstone.
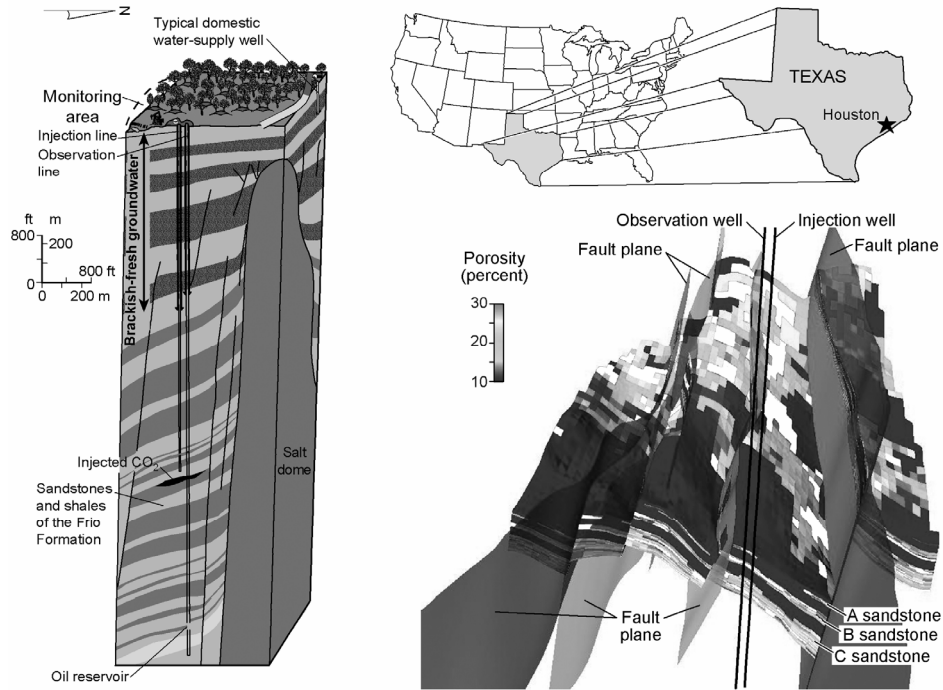

Figure 1. Frio experimental site setting showing geologic context near South Liberty Salt Dome and detail of injection well location within a gridded reservoir model made using seismic data of the fault block.

Numerical simulation

Simulation supported all phases of the experiment. Initial realizations using probabilistic data constrained by predicted ranges and heterogeneity of rock and fluid properties were used to design the experiment (Hovorka and others, 2004). As site-specific data were developed they

were incorporated into the model. Model runs identified poorly known parameters, in particular the correct value for residual saturation, allowing improvement of these parameters to be a focus during additional data collection. Model results were used to select the field site, select the placement of the new injection well relative to the existing well (used as an observation well), define the perforation and injection zone, and optimize the volume and duration of injection. Modeled saturations of CO_2 were used to select monitoring tools and resulted in rejection of some tools as unlikely to be successful and identification of replacements.

It is helpful to describe the modeled flow system as four sequential but partly overlapping phases. Before injection, the flow field contains only brine. Hydrologic and geochemical tests showed that methane detected in the brine is present as a dissolved gas, not free gas. During injection, flow was mostly radial, dominated by the injection pressure. Shortly after injection, as pressure equalized near the wells, modeling predicted that density contrast between CO_2 and brine (0.6 to 1) will cause gravitational forces become the more important force in controlling flow. During this phase, the plume of CO_2 is predicted to migrate laterally, updip through the high-permeability, steeply dipping "C" sandstone, and become larger and more asymmetrical around the injection well. It also increases saturation in the upper beds of the "C" sandstone. During the last phase of plume evolution, modeling predicts that relative permeability to CO_2 will decrease, resulting in decreasing mobility, so that CO_2 migration slows to almost nothing and saturations approach residual saturation. With high permeability and steep dips favoring rapid lateral migration during the third phase, and a short injection period, the period of almost no migration is predicted to be reached within a few months.

Geochemical monitoring of the plume

Geochemical tools were successful in monitoring the evolution of the CO_2 plume. During rapid evolution of the plume, the U-tube sampler was critical in obtaining samples of two-phase fluids at high frequency. The sampler produced native formation fluid for two days after injection started. Conductivity remained stable as injection began, then pH dropped from 6.7 to 5.9, then rose again. A dramatic change in fluid composition was observed in the sample collected 51 hours after the beginning of injection. Carbon dioxide replaced methane as the dominant gas analyzed in the quadrupole mass spectrometer. The pH decreased rapidly during the next hour to less that 5.8. These changes mark the first appearance, or "breakthrough," of supercritical CO_2 in fluids produced at the observation well. Over the next 24 hours, sharp increases in concentration of reaction products were measured: alkalinity increased from 100 to 3,000 mg/L as bicarbonate, and dissolved Fe increased from 30 to 1,100 mg/L; Mg and Ca also increased (figure 2). Brine produced at atmospheric pressure outgased vigorously, and precipitated calcite, iron, and manganese oxides, so that brine samples appeared dark brown. Sampling 20 days and 184 days after injection showed increased pH and decreased metals in the subsurface volumes still occupied by CO_2. The concentration of dissolved organic carbon (DOC) was low in native brines (1–5 mg/L), and increased slightly to 5 to 6 mg/L during injection. However, 20 days after injection, DOC increased by a factor of 100, and then declined to 4.5 to 7.5 mg/L six months after injection. Organic molecules identified in high-DOC samples include formate, acetate, and toluene. It is possible that this represents a similar phenomenon to iron, in that CO_2 dissolved and mobilized minor amounts of organics.
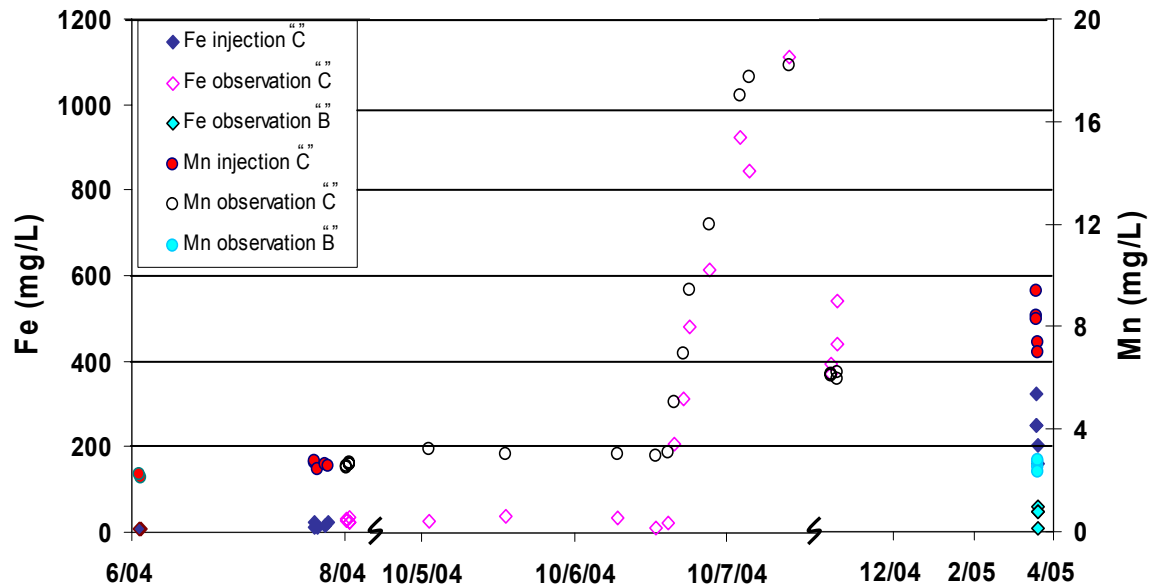
Figure 2. Evolution of metals in brine. The increase mid-day 10/6/04 represents arrival CO_2 and low-pH brine at the observation well.

The ratio of CO_2 to brine produced by the U-tube at the surface increased during the 24 hours after breakthrough, until almost no brine was produced. CO_2 breakthrough was faster than model predictions, and sweep efficiencies were relatively small, suggesting that gas movement occurred along preferential pathways. Gas-phase tracer arrivals (corrected for transport up the U-tube) range from 48 to 53 hours, with a typical measurement error of 0.5 hour (Freifeld and others, 2005), which generally agrees with the CO_2 breakthrough time of ~51 hours.

Wireline log and geophysical monitoring of the plume

Saturation logs collected with the RST tool, cross-well seismic tomograms, and VSP document that the CO_2 plume developed similarly to that predicted by modeling. The CO_2 moved radially out from the injection well over the 3-m perforated interval, with fastest flow in the upper and higher permeability zones. Comparing changes in saturation in the observation well over time calculated from the RST to the modeled saturation in this same well (Figure 3) shows that by the time the log was collected 4 days after injection, the plume was slightly better developed than had been modeled. The assumptions, simplifications, and corrections used in the calculation of saturation from RST log response are significant and are described by Sakurai and others (2005) and Müller and others (2005). The modeling conditions are reviewed in Doughty (2004).

The highest saturation measured was on day 10, at the end of the injection period. Saturation then declined quickly as CO_2 moved away from the injection site. By the time the day 29 log was collected, this process was decreasing as gas permeability decreased as a function of decreasing saturation. Only minor changes in saturation were observed in the next four months. The largest noncorrespondence between the predicted and observed CO_2 saturation is that the observed CO_2 plume moved more effectively upward through the layered muddy sandstones at the top of the "C," showing that layering was more discontinuous than assumed in the model. A repeat logging is planned at 17 months.

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Another view of the observed distribution of CO_2 compared with the modeled distribution is shown in Figure 4, which compares the cross-well tomogram showing impedance contrast that developed as a result of CO_2 and is inferred to represent supercritical CO_2 saturation. The cross-well survey was completed on day 57 after injection. An azimuth VSP survey tested the symmetry of the CO_2 plume outside of the plane of the two wells and shows that the plume is more asymmetrical than modeled.
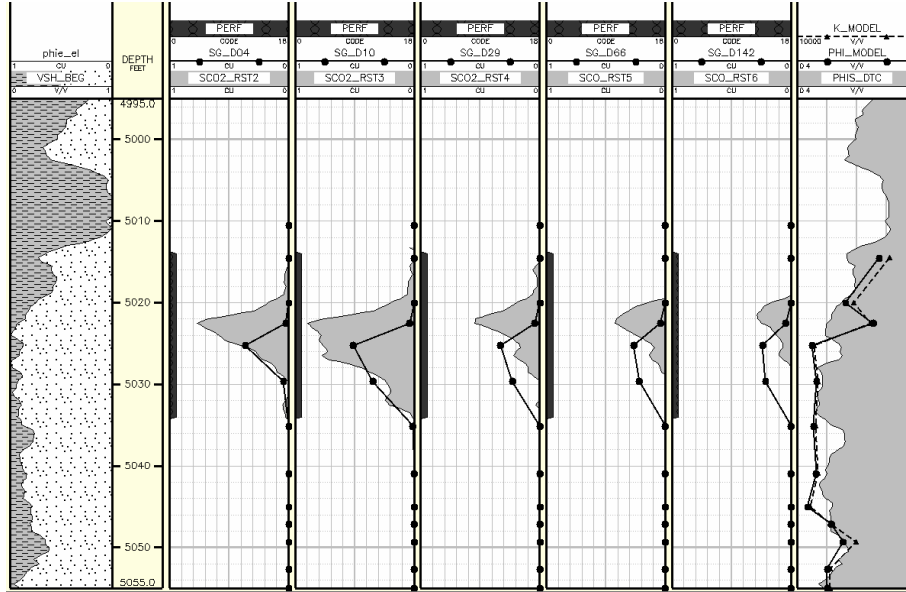

Figure 3. CO_2 saturation at the observation well calculated from RST logs, compared with modeled changes in saturation per layer plotted at layer midpoint. Day 66 and 142 logs are corrected for borehole effects by simple subtraction of the above-background saturation, and they should be considered less quantitative. Porosity from log is compared with simplified model input porosity, elevations KB datum.

Surface monitoring

Monitoring at the surface for leakage signal was not effective because the natural and induced noise was large and the preperturbation baseline period was short. Examples of natural variability include a variably high water table, which resulted in little or no soil gas, and high natural CO_2 flux because of the swampy forest setting (Ron Klusman, Rome, October 2004). This warm and wet region does not have a period of quiescent biological activity during which to identify a leakage signal. Examples of perturbation include atmospheric release of tracer during sampling and perturbation of groundwater recharge by well-site activities. Venting CO_2 during the purge cycle of the U-tube sampler released tracer to the atmosphere, which resulted in a rapidly developed plume of tracer detection in the soils around the injection wells (Art Wells, Rome, October 2004). This aerosol contamination obscures any leakage signal that might have formed later at other possible leak points. Groundwater chemistry changed rapidly during the monitoring period, with a preinjection region of high salinity migrating down-gradient across the monitoring array. We tentatively attribute these groundwater changes to improvement of the well pad and construction of a large fresh-water-filled mud disposal pit. Bicarbonate, which might serve as a leakage signal, was variable, but against this background of groundwater evolution, it is difficult to interpret.
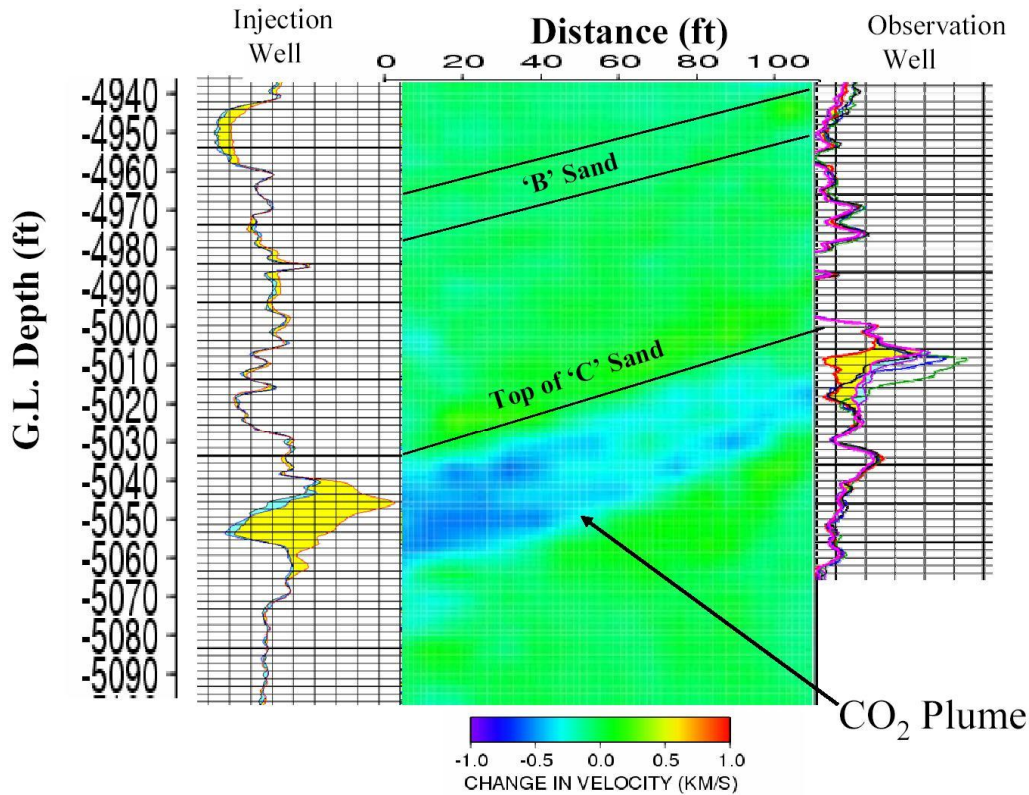
Figure 4. Cross-well seismic difference tomogram on day 57. Saturation values calculated from RST logs for each well are aligned with the tomogram.

Monitoring above the injection zone proved somewhat more interpretable. Brine from the "B" sand, first sampled eight months after injection, showed detectable amounts of PFT tracer and slightly elevated bicarbonate, Fe, and Mn relative to preinjection "C" composition (figure 2). This is interpreted as evidence of leakage from the injection interval in the "C" sandstone to the overlying "B." This signature increases confidence that geochemical indicators and tracers may be useful in identifying leakage. Additional testing is under way to determine if this leakage is because of flaws in remedial well engineering (imperfect remedial squeeze or failed squeeze on perforations in the "C") or indicates that the top "C" shale did not retain CO_2. Interpretation of seismic data in the injection well also suggests an anomalous area that might be interpreted as supercritical CO_2 behind casing within the Frio but above the "C." Follow-up research is in design.

CONCLUSIONS

Description and quantification of injection zone hydrogeology is a low-cost but important element. This information is required to support modeling and to interpret the test results. Numerical simulation of flow is a second highly effective, low-cost tool that should guide site selection, well design, and tool selection.

Geochemical techniques were successful in documenting the evolution of the CO_2 plume. Gas analysis detected CO_2 breakthrough at the observation well, and aqueous geochemistry documented evolution of formation waters as CO_2 interacted with rock and brine. Introduced tracers provide a unique fingerprint for CO_2 and are used to quantify CO_2 saturations and CO_2

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dissolution. The U-tubes sampler was a novel mechanism to obtain high-frequency, minimally altered, samples of two-phase fluids in the wellbore during injection .

Geophysical measurements of CO_2 saturation using neutron logging (RST), cross-well seismic, and VSP were successful in measuring plume evolution and CO_2 retained in the formation over time. This analysis supports the conceptualization that significant CO_2 is retained as relative permeability to gas decreases over time (two-phase trapping). Complex and rapidly changing surface environments and interference among test elements create challenging conditions to monitor for CO_2 leakage in groundwater and soil; however, above-injection-unit monitoring shows promise for leak detection.

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