Optimization of Geological Environments for Carbon Dioxide Disposal in Saline Aquifers in the United States

by

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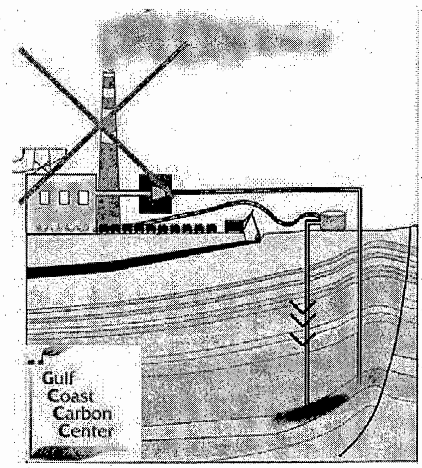

Bureau of Economic Geology
Jackson School of Geosciences, The University of Texas at Austin

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Abstract

High permeability sandstones of the Frio Formation east of Houston, Texas, were selected to test the feasibility of using carbon capture and storage (CCS) in geologic formations as a method to reduce atmospheric buildup of greenhouse gases. The Frio Brine pilot study was based on two small-volume and short-duration CO_2 injections into two previously unperturbed brine-bearing sandstone beds typical of the region. These injections were designed to answer key questions about CCS using a process of intensive multiphysics monitoring, pre-, syn-, and post-injection monitoring, and then history-matching to test the correctness of numerical models of flow and geochemical changes. The first test, conducted in September 2004, injected about 1,600 tons of CO_2 at a depth of 5,050 ft (~1,540 m) below the surface over 10 days and collected observations over 18 months. The second injection, in September 2006, injected more slowly, about 250 tons over 5 days, into thicker sandstone at 5,400 ft (~1,650 m) below surface. The injection period was brief, and the formation was on the flank of a steeply dipping structural compartment, resulting in monitoring over 5 years and lasting well into the post-injection phase of plume stabilization. This provided the experience and measurements of a complete project that will be helpful in predicting performance of large-volume injections potentially decades-long. The site was closed at experiment end in May 2009.

Key findings provided to support policy, outreach, and design of large-volume demonstrations and experiments are:

- Measurements confirm the correctness of models and conceptualization that significant CO_2 is trapped post-injection as relative permeability to gas decreases over time (two-phase trapping).
- Site hydrogeology is shown to be critical for prediction of site performance and monitoring strategy design.
- Numerical simulation of flow is required to guide site selection, well design, and tool selection, as well as to assess test results.
- Commercial tools used in time lapse mode, prior to injection and repeated one or more times after injection) were successful in measuring changes in fluid distribution and saturation: Neutron logging, cross-well acoustic tomography, and velocity seismic profiles (VSP) are recommended for further use under proper conditions.
- A novel tool, continuous active source seismic monitoring (CASSM), tracked the plume during injection between wells and provides high value in research and possible commercial applications.
- Geochemical techniques proved to be more sensitive than geophysical techniques. These include tracers used to quantify CO_2 saturation and assess leakage, pH changes, gas composition, and major and minor elements.
- An innovative sampling devise, the U-tube, provided high frequency and minimally altering samples of two-phase fluids in the wellbore during injection, an important improvement for the research test. A version was subsequently deployed at the Otway project of the Australian Cooperative Research Center for Greenhouse Gases (CO2CRC).

- Complex and rapidly changing surface environments, as well as interference among test elements, created challenging conditions for monitoring CO_2 leakage in groundwater and soil. Monitoring in the sandstone above the injection interval provided better signal.

Executive Summary

Overview

Nonproductive brine-bearing formations below and hydrologically separated from potable water have been widely recognized as possessing high potential for very long term sequestration of greenhouse gases; sequestration on the scale of geologic time. The Frio pilot test provided a field-scale test with intense subsurface monitoring. The test documented how closely numerical models match observed changes from pre-injection baseline, through injection, to post-injection stabilization. For the original Frio I test a close match existed between observations and geochemical models and several multi-phase flow models as well. A close match also existed in the repeat Frio II test, conducted in another sandstone located in the same two wells.

The three-phase project was designed to develop criteria for identifying optimal conditions of saline aquifers (brine-bearing formations) for long-term storage of CO_2. Phase I concerned selecting the types of information needed to assess suitability of the saline formations for CO_2 sequestration. During this phase, the feasibility of collecting these data was tested by characterizing two formations, the Frio and Woodbine Formations of Texas. During Phase II, injection and seal properties of 19 additional representative saline water-bearing formations in on-shore U.S. sites were characterized in a geographic information system (GIS) database. During Phase III, two field tests were conducted to test the conceptualization of optimal characteristics of saline aquifers for storage. These tests utilized an injection program with intensive monitoring during injection and an extended period following injection. Observed responses to the injection and stabilization were compared to predicted responses using numerical and conceptual models. Phase I and II results have been previously summarized and made available online (Hovorka and others, 2000). This final report integrates Phase III field test results.

Prior to this study, decades of research and experience with the performance of subsurface strata in trapping economically significant buoyant fluids such as oil, methane, and CO_2 provided reason for optimism that CO_2 injected for storage will be retained in analogous settings for long periods of time. However, the volume of these demonstrated that buoyant fluids are only a fraction of the volumes of CO_2 produced from combustion of fossil fuel, meaning brine-bearing formations that have never held hydrocarbons must be used for storage. Moreover, the natural charge rate of reservoirs by oil or gas is typically much slower than would be used to sequester large volumes of CO_2 for the purpose of reducing to its atmospheric release. Thus, additional evaluation was needed to demonstrate that the current understanding of the performance of subsurface strata is accurate. This includes: (1) identifying the processes by which CO_2 can be trapped in saline formations where there is no history of hydrocarbon accumulation, and (2) determining how trapping processes can be assessed and validated in a rigorous, effective manner. Field testing using an experimental method is needed to validate modeled and conceptualized understanding of the processes, effectiveness of storage, risk, and select monitoring strategy to document the permanence of storage and to increase public, industry, and policy-maker confidence.

Field studies-Phase III

Phase III efforts, using a carefully designed experiment, focused on field testing the ability to predict and then observe perturbation of fluids within brine-bearing sandstones. The target is to test the extent to which sufficient information can be collected to scale to large-volume injection with storage assurance over a 1,000 year time frame. The experiment included (1) state-of-the art assessment of the rock and fluid characteristics in the injected target interval; (2) development of fluid-flow and geochemical models predicting the response of these units to injection of CO_2 followed by a long period of equilibration, (3) time-lapse measurement of key parameters prior to, during, and post-injection, and (4) history matching of modeled to observed subsurface changes in geochemistry and plume evolution.

An extended (2001-2003) pre-injection design, site selection, and proposal period conducted in concert with the Lawrence Berkeley National Lab (LBNL)-lead GEO-SEQ project documented that a small area could be more rigorously monitored than a large area, and that a short period of injection would allow the stages of a project through post-injection stabilization to be observed. These steps are essential elements to collect information relevant to performance of large scale, long duration tests. In addition, high permeability, steep local dip, and limited lateral flow (known boundary conditions) were desirable to allow rapid equilibration so that it could be observed within the experiment time period.

Phase II characterization identified the Frio Formation as a unit likely to host such a test as well as to provide information about a large-capacity regional target. The need for best available characterization, as well as budgetary and public acceptance considerations, led us to seek brine-bearing sandstones within an oil field setting. A search for operators willing to host this experiment identified one, Texas American Resources Company (TARC), who made available two possible fields, from which a site in South Liberty Field, south of Dayton, Texas, was selected. High-permeability sandstones of the upper Frio Formation at depths between 4,800 ft (~1,500 m) and 5,600 ft (~1,700 m) were selected as an injection target. The Frio Formation is above oil production in the Yegua Formation at 9,000 ft (~2,700 m) to 10,000 ft (~3,000 m), and below a well-known regional shale confining zone, the Anahuac Formation. TARC made available a 3-D seismic data set and historic and new wireline logs, and donated access to a well that was converted into a monitoring well. The project design focused on one radius of a plume with azimuthal VSP to surveys to add detail on plume extent.

The first injection and monitoring experiment, Frio I (October 2004 – May 2006), was focused on conducting an early successful injection into a high-permeability, high-volume sandstone. The second injection and monitoring period, Frio II (September 2006-May 2009), further refined the quantification of key rock-fluid properties and tested additional monitoring technologies.

From October 4-14, 2004, the Frio Brine Pilot team injected about 1,600 tons of CO_2 approximately 4,900 ft (~1,500 m) below surface into the steeply-dipping, high-permeability brine-bearing “C” sandstone of the Frio Formation beneath the Gulf Coast of Texas, USA. A dedicated bottom-hole sampler, the U-tube, was developed by LBNL to allow high-frequency collection of high quality samples of multiphase fluids supporting a tracer and geochemical program. Reservoir characterization and numerical modeling were used to design the experiment, as well as to interpret the results through history matching. Closely spaced measurements in space and time were collected to observe the evolution of immiscible and dissolved CO_2 and pressure changes during and after injection.

Testing the validity of conceptual hydrologic and geochemical models was an important part of the test; this required best possible characterization. Reservoir characterization by Bureau of Economic Geology (BEG) to provided inputs to the simulations and used existing and newly collected wireline logs, existing recent three-dimensional (3-D) seismic surveys of the area, baseline geochemical sampling by U.S. Geological Survey (USGS) and Schlumberger, core analyses by Core Labs, and petrographic and geochemical study of rock samples by BEG, Lawrence Livermore National Laboratory (LLNL), and Oak Ridge National Laboratory (ORNL). A drawdown interference test and a dipole tracer test conducted by Lawrence Berkeley National Lab (LBNL) researchers provided interwell permeability estimates and confirmed the critical importance of good reservoir characterization for model validation. Detailed modeling by LBNL using TOUGH2 supported all phases of the project. Good matches between modeled and observed CO_2 saturation obtained by test conclusions for both tests improved and validated the modeled approaches to prediction of CO_2 movement and permanent storage. The modeling effort was independently duplicated by a team from The University of Texas at Austin Department Petroleum Geosystems Engineering using the simulation code GEM.

Measurement and monitoring of the subsurface CO_2 plumes were accomplished using a diverse suite of technologies in the injection zone. Each monitoring strategy used pre-injection and post-injection measurements. Wireline logging, pressure and temperature measurement, and geochemical sampling were conducted during injection as well. In-zone objectives were to measure changes in CO_2 saturation through time, in cross-section, and aerially, and to document accompanying changes in pressure, temperature, and brine chemistry during the months following injection. The in-zone measurement strategy was designed to test the effectiveness of selected suites of monitoring tools in measuring these parameters. The high-permeability, steeply-dipping sandstone allowed updip flow of supercritical CO_2 as a result of the density contrast with formation brine and absence of a local structural trap. During the first test, the front of the CO_2 plume moved more rapidly than had been modeled. By the end of the first test's 10-day injection, however, the plume geometry in the plane of the observation and injection wells had thickened to a distribution similar to the modeled distribution. As expected, CO_2 dissolved rapidly into brine, causing pH to fall and calcite to be dissolved. Unexpectedly large amounts of iron and manganese were also dissolved in the initial fluids as CO_2 first moved through the rock-water system. Concentration then decreased post-injection, but did not fall to initial values. Geochemical modeling conducted by USGS and LLNL predicted that iron would be present only in minor amounts, and no manganese phase was predicted from the mineralogic study. The field iron spike results were duplicated in the laboratory when reaction of Frio "C" sandstone with CO_2 and brine liberated an early spike of iron and manganese. We deduce that these metals were released by small amounts of high-surface-area reactive trace minerals, such as those complexed with clay or as fine pyrite, which were then depleted. In addition, brine formation contamination by fluids that had reacted during storage with the steel tubing contributed to the amount of iron liberated. These effects are difficult to eliminate with this well construction.

Post-injection measurements, including time-lapse VSP transects along selected azimuths, cross-well seismic topography, and saturation logs, show that CO_2 migration under gravity slowed greatly 2 months after injection, matching model predictions that significant CO_2 is trapped as relative permeability decreases. Analysis completed during the 15 months following the end of injection, using wireline reservoir saturation tool (RST) pulsed neutron techniques, showed that a high percentage of CO_2 is retained and immobilized by two-phase capillary effects. A production test at 18 months after the end of injection was unable to produce significant CO_2 because it was effectively trapped because saturation had decreased to near residual saturation, and relative permeability to CO_2 was near zero.

A feasibility test of near-surface monitoring in this setting monitored soil gas fluxes and concentrations, introduced tracers, and monitored shallow aquifer response. High complexity was noted in this high water table, warm, perturbed environment. High water table and high biologic activity provided complicating signals. Aquifer monitoring showed strong perturbation in salinity, a variable which is unlikely to be related to CO_2 injection but is tentatively attributed to flushing high-TDS surface waters with pad trenching or mud pit water. Introduced tracers documented no leakage to surface using Praxair Seeper Trace technology, and the National Energy Technology Lab (NETL) research team collected fluid samples with a cased-hole formation tester and were unable to identify tracers above the injection zone behind casing.

A second injection test was initiated on September 25, 2006. The Frio II Brine Pilot was conducted using the same injector/monitoring well pair developed and characterized for the 2004 Frio Brine Pilot CO_2 sequestration experiment, but the injection occurred in the "Blue Sand," a hydrologically separate sandstone 390 ft (~120 m) below the previously investigated "C" sandstone. The Frio II injection consisted of a small volume (about 250 tons) of CO_2 over 5 days into the lower part of a 10-m-thick flow unit in a heterogeneous fluvial sandstone 5,510 ft (~1,650 m) underground, and closely monitored the stabilization over the next 30 months. The low injection rate was to simulate processes at the edge of the plume, where attenuated injection pressure results in significant influence of buoyancy on flow processes, which was observed in the results. The project used an array of techniques to provide information about CO_2 flow, trapping, and dissolution: wireline saturation logs, cross-well seismic, downhole pressure and temperature monitoring, geochemical sampling with LBNL U-tube and USGS Kuster sampler, and a tracer program. One of the new tools tested, a tubing-conveyed source and receiver string (continuous active source seismic monitoring, CASM), developed by LBNL was designed to fully integrate seismic measurements with other downhole data. In this application of seismic tomography, the seismic source is fixed downhole, above the packer. Since the seismic source is fixed, error from the placement and replacement of equipment using traditional means is minimized. Continuous data collection allows statistical refinement of measurements by stacking. In addition, real-time data are collected every 10 seconds, allowing researchers to know exactly when CO_2 breaks a given ray-path between the source and receiver as it rises in the reservoir.

During injection the CO_2 traveled vertically near the injection wall and laterally through a thin high-permeability zone and was detected near the top of the Blue

Sandstone at the observation well 100 ft (~30 m) away. Comparison between the first and second injections illustrates interactions among injection rate, injection strategy, and heterogeneity of the injection interval and their impact on plume evolution. Both experiments illustrate the utility of combining several monitoring tools with modeling assessments to describe plume evolution. Monitoring continued throughout summer 2009 to measure the stabilization process of this small plume.

Partners

University of Texas at Austin

BP America

Schlumberger

Austin Texas

Lawrence Berkeley National Laboratory (LBNL)

Lawrence Livermore National Laboratory (LLNL)

Oak Ridge National Laboratory (ORNL)

Paulsson Geophysical

Praxair

Sandia Technologies

An important objective was accomplished through outreach for both tests, which included site visits by researchers, local citizens, and environmental groups, media interviews, an online log (www.gulfcoastcarbon.org), a technical e-newsletter, and an informal non-technical "neighbor newsletter." Public and environmental concerns were moderate, practical, and proportional to minimal risks taken by the project, and included issues such as traffic and potential risks to water resources. Press coverage was balanced and positive toward research goals. Safe site operation was provided by professional vendors.

The Frio experiments strongly supported a final objective, which is the development of the next generation of larger-scale CO_2 injection experiments and input to evolving policy. Extensive presentations and publication have been the main contribution to this effort, as have talks, sitting on panel discussions, and numerous one-on-one discussions.

Frio I objectives accomplished

- Demonstrate to the public and other stakeholders that CO_2 can be injected into a brine formation without adverse health, safety, or environmental effects.
- Measure subsurface distribution of injected CO_2 using diverse monitoring technologies.
- Verify the accuracy of conceptual, hydrologic, and geochemical models.
- Develop experience necessary for development of the next generation of larger-scale CO_2 injection experiments.
- Favorable interaction with press and public.

Frio II objectives accomplished

- Duplicate key Frio I results using improved methodologies, in particular:
  - Residual trapping mechanism
  - Solubility of CO_2 into brine as plume advances

    - CO_2 -rock-water interaction
    - Changes in acoustic velocity during CO_2 migration
- Inject deep and slow rates where the interaction of injection pressure and buoyancy can be observed.
- Test novel and improved monitoring technology.
- Well-integrity follow-up shows no leakage out of permitted injection zone; promising use of tracers and geochemistry for detection of well-bore leakage.

Programmatic significance of this contribution

Data compiled from the Phase I and Phase II stages of this project have provided concepts and data to Phase I of the Regional Carbon Sequestration Partnerships, which has then refined and extended the national inventory of geologic sinks compiled into NATCARB. Phase I and Phase II data were provided also to those preparing capacity inventories for other nations.

Results of the Phase III Frio Pilot have provided confidence in the correctness of conceptual and numerical models and also in the effectiveness of monitoring tools. These monitoring tools allow the test to be widely duplicated and encourage larger scale, longer duration demonstration projects. The Frio Pilot results provide a model for the U.S. Regional Partnerships Program participants as well as international collaborators to design test programs in various settings. The Frio I project was recognized by the Carbon Sequestration Leadership Forum (CSLF) because of international collaboration with Australian CO2CRC and with the Alberta Research Council (ARC).

Remaining work

The Frio project was designed to achieve early success for the DOE CCS program. It therefore avoided investigation of complex factors, many of which will need to be included by follow-on tests. The role of stratigraphic and structural heterogeneity is one such aspect that the Frio tests only started to explore. Upscaling to very large projects needs additional work, especially with regard to the pressure response of the reservoir. The Frio project did not test fault seal or well construction issues to a critical limit; starting only a few initial investigations into these important aspects. Many promising technologies, such as tilt, microseismic techniques, electrical techniques, soil and aquifer monitoring, and surface-deployed 3-D seismic, were not used or were conducted only in preliminary tests at the Frio project.

Project Overview and Phase I and Phase II Pre Field Test Studies

This study, titled Optimal Geological Environments for Carbon Dioxide Disposal in Saline Aquifers in the United States, was conducted in three phases over a 10-year period. Phase I, launched in 1999, was primarily a scoping study to develop a methodology for assessing the suitability of subsurface brine-bearing formations for storage of large volumes of CO_2 in order to reduce its atmospheric release. Phase I of the project plotted the output and distribution of CO_2 emissions in 1996 from power plants in the United States against a USGS map of thickness of sedimentary cover to identify major basins that could potentially be used for the geologic sequestration of CO_2. Geologic screening criteria for identifying suitable saline water-bearing formations for CO_2 sequestration were developed through literature review and extensive consultation. These criteria were needed in order to advance beyond the assessment of bulk properties of sedimentary rocks used in the initial capacity study and feasibility assessment of Bergman and Winter (1995). Sufficient data on the properties of saline water-bearing formations in the test formations, Frio and Woodbine of Texas, were obtained to develop a prototype GIS in order to demonstrate the effectiveness of this approach for regional capacity assessment. The pilot study confirmed that information is available from a number of diverse sources.

The favorable outcome of Phase I prompted competitive proposal to proceed with the Phase II study. This resulted in compilation of a reconnaissance national survey of 21 prospective brine-bearing sites that underlie a large number of significant anthropogenic CO_2 sources (Hovorka and others, 2000). Phase II involved a regional inventory of geological properties of saline water-bearing formations and confining (sealing) units with potential to be targeted for CO_2 injection. This effort compiled data at basin scale to describe the injectivity and isolation of 21 diverse and representative saline formations in 19 onshore U.S. basins. This project included data collected by Neeraj Gupta as part of the sister project assessing the Mt. Simon Formation of Ohio. The Phase II results served as a prototype that has since been used by the Australian GEODISC national capacity assessment, early European Union capacity assessments, and MIDCARB -- a DOE Regional Carbon Sequestration Partnerships (RCSP) Phase I effort that served as a prototype for the US national GIS database, NATCARB, and the US National Sequestration Atlas.

From the Phase III database, one can readily observe that the thick wedge of Mesozoic-Cenozoic sediments that rim the Gulf of Mexico is one of the key source-sink pairs to serve the continental US (Figure 1).

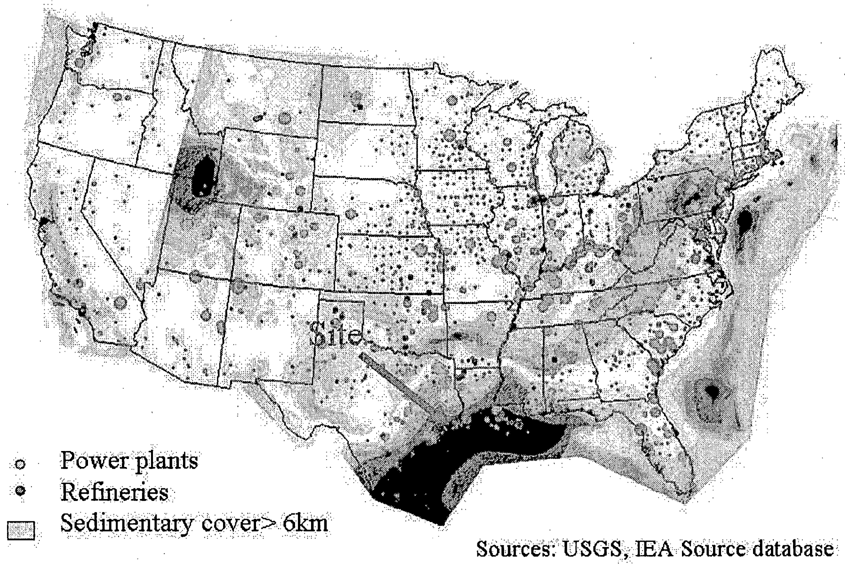


Figure 1. USGS thickness map of sedimentary cover shows that the thick wedge of Mesozoic-Cenozoic sediments that rim the Gulf of Mexico is one of the key source-sink pairs to serve the continental US. Power plant and refinery locations and relative emissions are from an IEA report, and the thickness of sedimentary cover is modified from USGS.

Therefore, a search was undertaken for a representative test site of this large-capacity area, and a study plan was developed over the course of several years. Upon successful completion of a competitive proposal, this study plan was implemented as a Phase III study at a site in Liberty County, Texas, known as the Frio Brine Pilot.

Data reported below drew heavily from primary sources, including 50 papers and presentations (Appendix 1), permits, daily field reports from Sandia Technologies and other field workers, 64 logs, and core photographs (Appendix 2). Selected media coverage is included in Appendix 3.

Phase III Field Tests

2003-2006 Frio I – "C" Sand

The first field test was conducted in five steps: (1) site selection and preliminary studies, (2) site preparation, vendor selection, and permitting, (3) pre-injection well work and baseline data collection, (4) injection and during-injection monitoring, and (5) post-injection monitoring. The test also had significant outreach, publication and technology transfer efforts. Figure 2 shows the Frio I timeline.

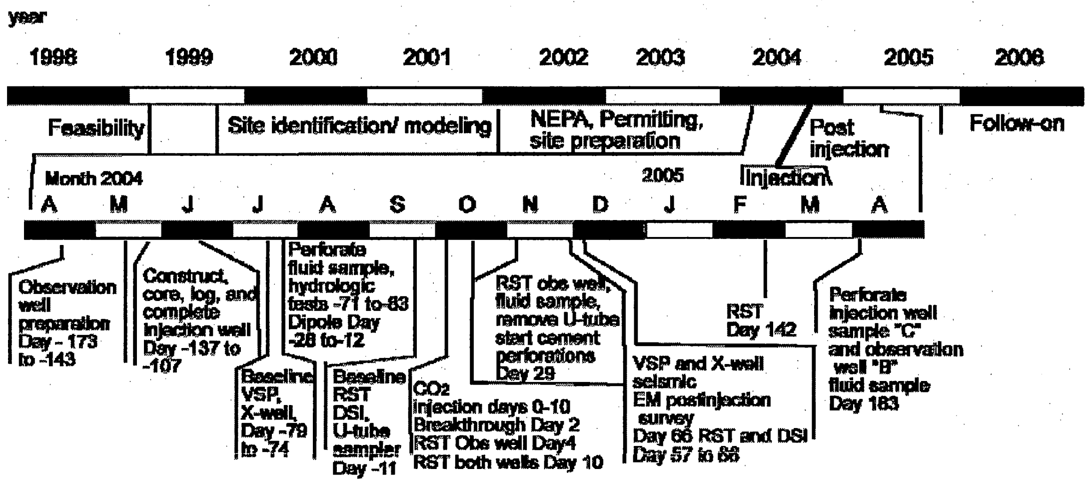


Figure 2. Frio I timeline showing the relationships among characterization, modeling, pre-injection baseline collection, injection, and post-injection monitoring.

Site selection and preliminary studies

The site for the experiment was selected after a national evaluation of saline formations (Hovorka and others, 2000) that inventoried areas of high storage capacity that also underlie numerous large point sources of anthropogenic CO_2. Sandstone of the Tertiary (Oligocene) Age Frio Formation was selected as a target for large-volume storage because it is part of thick, regionally extensive sandstone trend with numerous, well-known shale seals, and it underlies a concentration of industrial sources and power plants along the Gulf Coast of the United States (Figure 1). An additional advantage of this area is the possibility of the future development of "stacked storage," in which CO_2 is first used in declining oil reservoirs to enhance production and is then stored in the underlying saline sandstones (Figure 3).

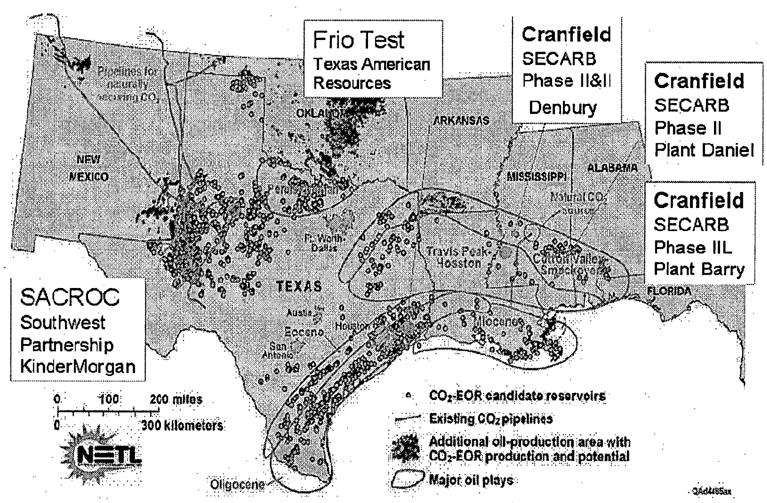


Figure 3. Coincidence of the Frio test site with major oil and gas plays, and other field tests in the region that have followed on the Frio tests, showing partnership, phase, and host. Modified from a figure by Bill Ambrose and others.

Site selection was the result of a model-driven activity that matched project goals and site characteristics to maximize the research product while minimizing risks. Risks to be reduced include: (1) failure to complete the experiment because of regulatory, property owner, or public opinion concerns, (2) accidents or unexpected incidents that might cause risk or damage to humans, animals, property, or ecosystems, and (3) failure to collect meaningful or interpretable research results. Research products to be maximized include: (1) creating predictive models of changes resulting from injection of CO_2 into the subsurface, (2) testing as many different monitoring tools as possible to determine how best to measure these changes, and (3) matching the predicted to the observed changes.

Iterative consideration of site characteristics, injection strategies, and modeling the response of various monitoring tools resulted in selection of experimental conditions. We determined that the best site would be within an existing oil field where available wireline log, seismic, production, fluid property, and geological data would support development of a quantitative model. Working in an existing oil field would also minimize project costs and environmental damage because existing roads, well pads, and wells could be used to support the experiment. It also would minimize risks because the local community was familiar and comfortable with subsurface activities. Injection into a porous sandstone that contains only brine as the pore fluid (described as a "brine-bearing formation") rather than a zone that produced oil was best for this experiment for two reasons: (1) the interaction of oil and CO_2 would be difficult to model correctly and could mask conceptual errors and (2) many tools were predicted to fail to adequately distinguish between existing oil and introduced CO_2. Thus, monitoring might be unacceptably imprecise in an oil-bearing environment.

The research was intended to document the performance of regionally extensive, thick, high-volume sandstones of the Frio Formation. However, for the experiment we selected a small volume within this trend - a thin sandstone in a structurally isolated compartment. Selection of a structurally isolated compartment was useful in assuring adjacent operators and land owners that no impact was expected outside of the experiment lease. Although the CO_2 was injected into a small compartment, the plume was not predicted to reach the boundary faults, providing an additional element of control of the plume. Modeling suggested that a steep dip would provide an interesting opportunity to observe the post-injection movement of CO_2 under buoyancy forces.

Measurements of changes in CO_2 saturation, fluid chemistry, and reservoir temperature and pressure at closely spaced intervals in time and space were required to obtain a good comparison with predictive models. Measurements during the post-injection period were determined to be especially significant for predicting permanence of storage. These considerations resulted in minimization of the proposed injection volume and placement of the injection and observation wells close together, so that CO_2 breakthrough to the observation well would be rapid. During this brief period, monitoring data could be collected with a frequency designed to "catch" critical phases of plume development. Minimizing the volume and duration of the experiment also reduced operational risks such as an accident during transportation or surface handling of CO_2, or unexpected leakage out of the injection zone. Closely spaced wells also reduced uncertainties in interpolation of interwell properties. We therefore redesigned the experiment to reduce the amount of CO_2 and used the funding planned for the forgone CO_2 to drill a new injection well rather work-over and retrofit two existing wells as originally planned. This change reduced risks inherent in reuse of an existing well and also provided core and open-hole logs that provided high value to the project. Cost overruns during retrofit activities that preceded the second injection confirm the value of this judgment.

Site preparation, vendor selection, and permitting

From 2002 to 2004 the BEG completed contract negotiations, built a research and engineering team, revised experimental designs, completed required National Environmental Protection Act (NEPA) documents, and obtained leasing and permitting for well drilling, injection, and seismic monitoring. These activities took place concurrently and were somewhat iterative. The research team undertook several months of intensive effort to identify a suitable site where surface and subsurface rights could be obtained, calling many operators who worked with the Bureau in the past and also "cold calling" many operators in the target setting. An independent operator based in Austin and Houston, Texas, and with connection via alumni to the University of Texas, responded favorably; this was the only negotiation that did not break down. This operator, Texas American Resources Company (TARC) provided access to two Frio salt dome fields, Goose Creek and South Liberty. South Liberty field had a 3-D seismic survey that provided important information; therefore, an experimental site was selected in the approximate center of a steeply dipping, fault-bounded block on the flanks of the South Liberty Salt Dome in the Sun-Gulf-Humble Fee 1 lease (Figures 4, 5, 6, 7).

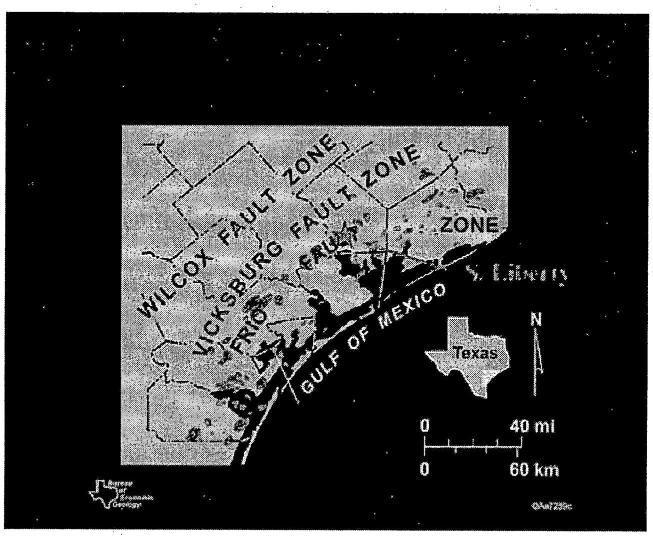


Figure 4. General site location showing relationships to regional trends. Slide prepared by Paul Knox.

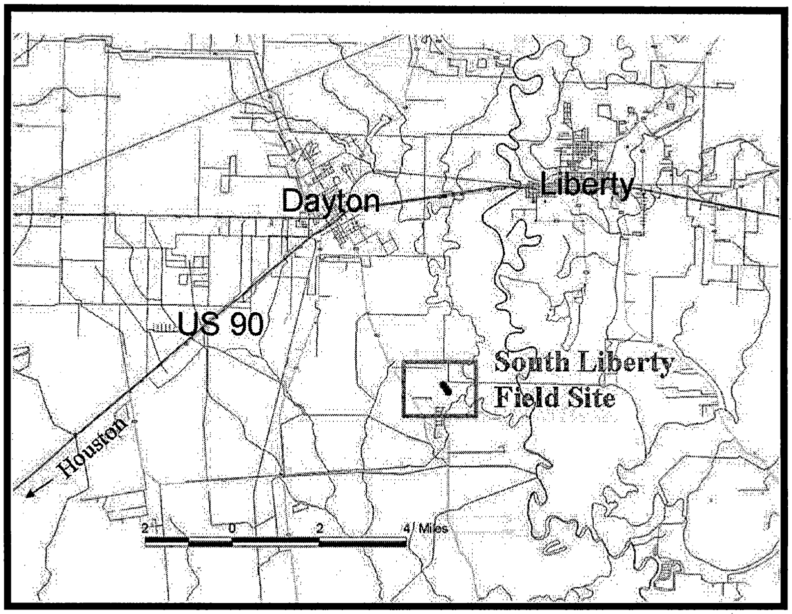


Figure 5. Detailed site location showing cultural features.

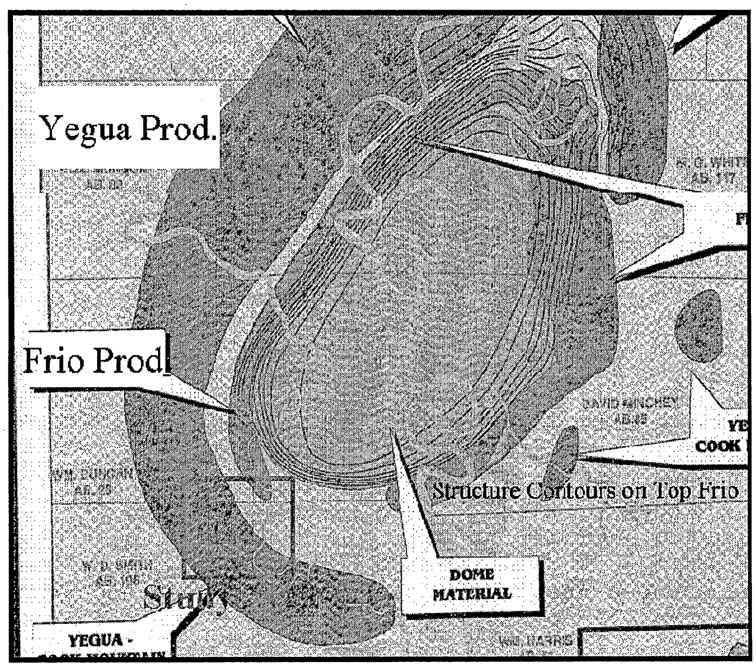


Figure 6. Location of the study area relative to South Liberty Salt Dome and oil production.

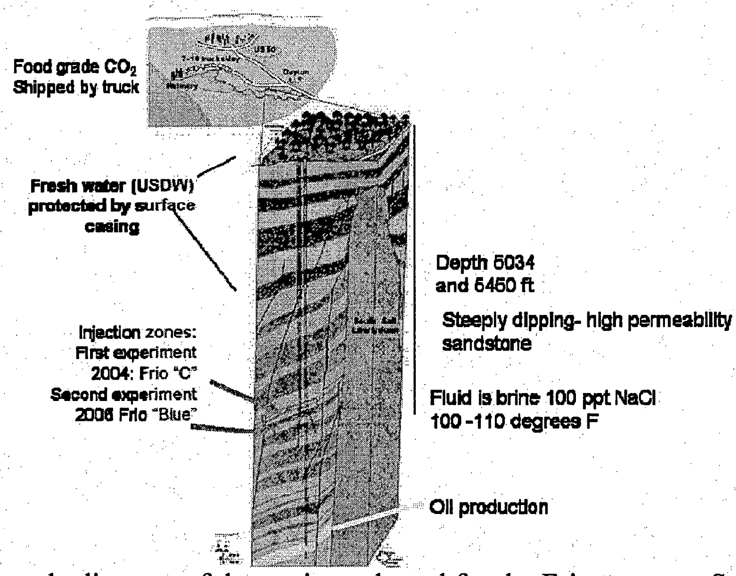


Figure 7. True scale diagram of the setting selected for the Frio test near South Liberty Salt Dome, Liberty County, Texas.

Besides data, TARC agreed to provide access to two wells that could be worked over by the project (Figure 8). Negotiations were then undertaken to identify surface ownership that had evolved from the original oil company's ownership, and to sign access agreements suitable for conducting a small experimental injection. This resulted in satisfactory, albeit ad-hoc, agreements for injection at an experiment scale to proceed. A local landowner in Dayton, Texas, Mr. Alders, provided well pad development and road improvement, which are the customary return in value to the local community.

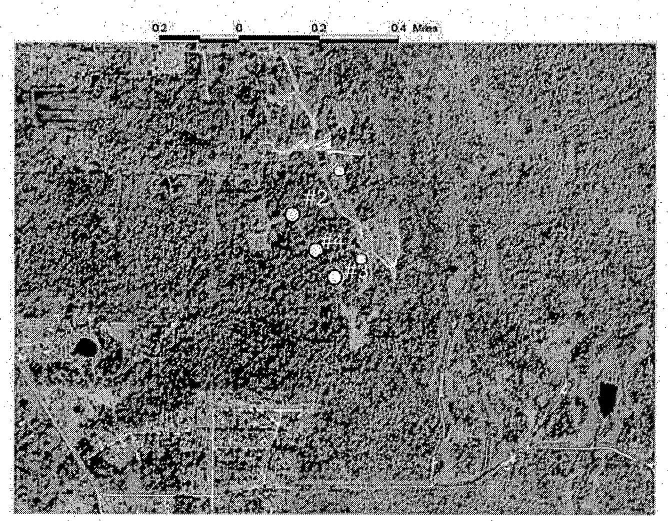


Figure 8. Well locations at the start of experiment on a Digital Ortho Quad (TNRIS) base, showing two wells (#4 and #3) made available to the project by Texas American Resources Co.

Texas has primacy for all classes of Underground Injection Control (UIC) wells. The permitting strategy for the test was negotiated prior to site selection through discussion with Mr. Richard Ginn, then UIC supervisor for the Texas Railroad Commission (RRC), and Mr. Ben Knape, UIC Department Director for the Texas Commission on Environmental Quality (TCEQ). It was determined that permitting for the injection well and injection itself for the experiment were somewhat unusual, in that the desired site was within an oil field, which is traditionally regulated under the RRC. However, the injection did not fall under Class II hydrocarbon related activities, as it planned to inject into a brine-only reservoir, failing to meet the specifications in CFR 144.6 for Class II (Table 1). We then discussed permitting the injection as through TCEQ as a Class I non-hazardous project. However, Texas has an extended process for all Class I wells that seemed inappropriate for short-duration, small-volume tests, and that further indicated that injection into an oil field might not pass the stringent area of review (AOR) requirements associated with Class I wells. TCEQ proposed that the research team should apply under the Texas version of Class V "other" wells, which specifies that experimental wells may be constructed under this class, which was appropriate for the purpose of use. TCEQ reviewed with the research team and contractors the information that they would require to confirm this application, which constituted most of the requirements of a Class I well in terms of information and well construction. This information was provided to TCEQ as a report to accompany a Class V application (Hovorka and others, 2003) along with the short Class V application. The report was posted online to serve as a prototype for others. The BEG requested that we, as part of university activities, provide the stakeholder information, which would then serve the dual-purpose of DOE public outreach as well as meeting TCEQ requirements.

144.6: Class II wells are defined as wells which inject fluids: (1) Which are brought to the surface in connection with natural gas storage operations, or conventional oil or natural gas production and may be commingled with waste waters from gas plants which are an integral part of production operations, unless those waters are classified as a hazardous waste at the time of injection. (2) For enhanced recovery of oil or natural gas; and (3) For storage of hydrocarbons which are liquid at standard temperature and pressure.

Table 1. Definition of Class II wells in the Safe Drinking Water Act (Code of Federal Regulations, 2002).

The upper Frio Formation was defined as the injection interval, in which a number of high-quality sandstones were identified. The sandstones were labeled top-to-bottom "A", "B," and "C" (Figure 9). Thicker and somewhat deeper Frio sandstone was used for correlation. This sandstone was marked in blue and became known as the Frio "Blue" sandstone. The regulatory confining system was identified in the Anahuac Formation, which has a regulatory definition as confining for many Class I injection wells and serves as a seal for many oil and gas reservoirs. Numerous overlying sandstone-shale pairs provide redundant confining zones (Figure 10).

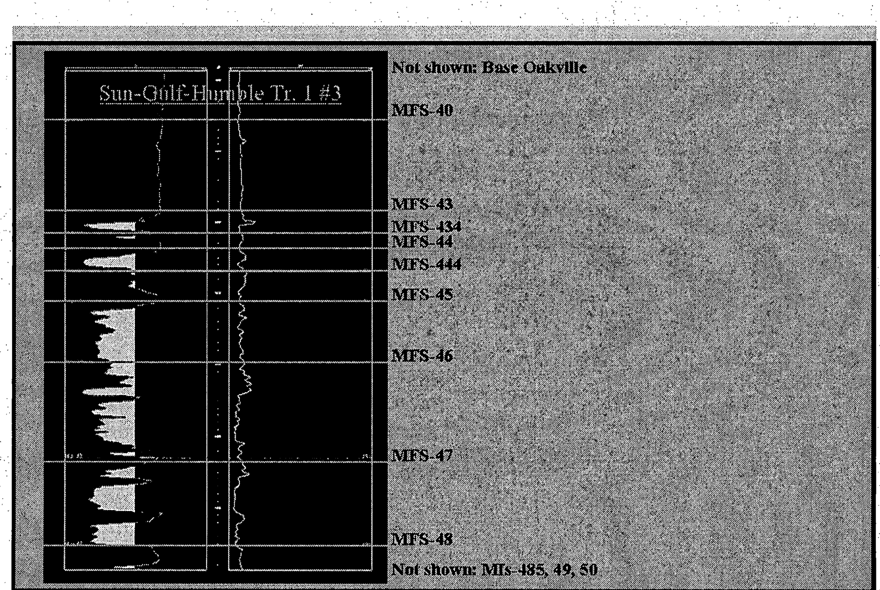


Figure 9. Detailed stratigraphic section showing the prospective upper Frio injection interval. The upper Frio "C" sandstone was selected for Frio I injection and the Frio "Blue" sandstone for the Frio II injection.

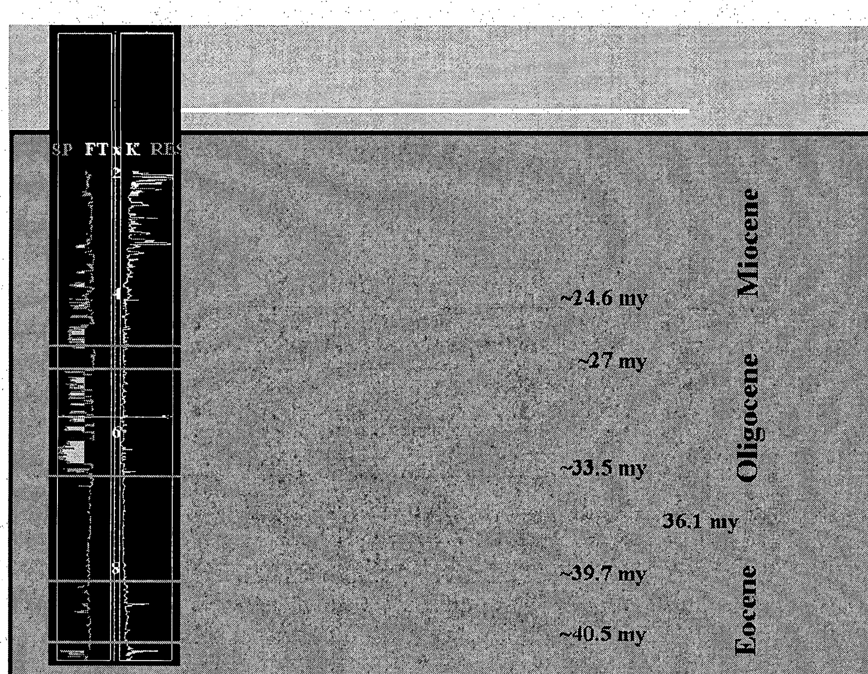


Figure 10. Log-stratigraphic section showing the relationship of the Frio Formation shown in detail in Figure 9 to the Anahuac Formation confining zone and the Yegua Formation depleting oil reservoir.

The TCEQ authorized construction with a letter that approved the characterization and construction plans. Permission to inject was granted following successful construction and testing of the injection well. On September 1, 2004, an annulus pressure test and radioactive tracer test was performed on the injection well. Testing was witnessed by Mr. Bryan Smith of the TCEQ (see permits in Appendix 2).

In addition, federal spending on the project required preparation of documents under NEPA. Because the project was the first of its kind, a draft Environmental Assessment (EA) was prepared. DOE then granted a categorical exclusion (CX), without finalizing the EA. The draft EA was also provided online as a prototype for future work (Knox and others, 2003).

One activity that had to be completed early in the pre-injection process was contracting with a field services provider (FSP) who could provide engineering experience and could subcontract other needs such as drilling rigs, workover rigs, diverse equipment, and Health, Safety, and Environmental (HSE) protection, and who could obtain insurance for active operations. The TCEQ also suggested that a using a company with UIC experience might be desirable in the state permitting process. The BEG put the FSP job up for competitive bidding and received four viable responses. One company, Sandia Technologies LCC, based in Houston, Texas, stood out in understanding the research and early demonstration character of the study, providing in their proposal suggestions of how to maximize measurements. Sandia was selected to serve as FSP, and Sandia developed a number of engineering solutions to support the research team.

Experimental design, pre-injection well work, characterization, and baseline data collection

It has become customary to assume that characterization, design of the experiment, well preparation, and baseline data collection are separate and sequential activities. In the Frio test, these activities were conducted concurrently and iteratively. Initial characterization data were provided to design the experiment. As more characterization information was obtained, some redesign was undertaken. Modeling was the element that was used to integrate the components. In one such instance, it was initially assumed that the observation well should be updip of the injection well. However, in spite of steep dip, modeling showed that injection pressure was more important than gravitational forces at feasible injection rates, so relative placement of wells became less important. This enabled avoidance of costly injection well directional drilling. Ultimately, the injection well ended up approximately down-dip from the observation well; however, it was not critical to project success.

Experimental design

Substantive input into experimental design took place through a productive collaboration with the DOE-funded GEO-SEQ consortium (GEO-SEQ, 2009). Through GEO-SEQ a number of preliminary models were developed (Hovorka and others, 2004), monitoring tools were explored and later funded, and expert review panel advice obtained. The initial TOUGH2 models of the site were prepared by Christine Doughty using data from several typical fields. This non-site-specific model was used to select the size and attributes of the test site. GEO-SEQ national lab participants LBNL, LLNL, and ORNL contributed significant expertise and DOE funding to this test. ARC was a GEOSEQ participant who initially provided geochemical sampling expertise, and later invited USGS participation in this role. NETL staff joined the project at the request of the DOE project manager. Australian consortium CO2CRC joined the effort initially through contacts with LBNL.

One experimental goal was to test as many different monitoring tools as possible. Numerous compromises in scheduling access for tools, and optimizing the wellbore conditions for data collection, were required to accomplish this goal. The main monitoring approach used was the collection of baseline measurements prior to injection, intensive geochemical sampling, pressure and temperature measurement and geophysical logging during the CO_2 injection, followed by periodic post-injection measurements to observe and measure the change of various parameters through time.

The new down-dip well was designed to serve as the injection well, and the updip well was perforated in the same zone to serve as the observation well. Modeling (Hovorka and others, 2004) suggested that flow was essentially radial during the injection phase. Models show that as pressure declines at the end of injection, gravitational forces become dominant. The observation well was positioned to monitor this post-injection updip migration of the buoyant plume of CO_2.

After examination of open hole logs and cores, several completion options were considered. Modeling showed that Frio "B" sandstone would be the right thickness to ensure that CO_2 injected at one well would spread far enough laterally that it would intersect the other well (breakthrough to the observation well). However, the thinness of the sandstone increased concern that it might be offset by faults with offsets below the limits of seismic resolution. We then selected the underlying "C" sandstone as a target, but in turn the greater thickness raised concern that the CO_2 might become lost and never break through the observation well. Log interpretation suggested that a thin high-gamma zone in the middle of the Frio "C" sandstone might be a local seal. However, examination of core showed that it was a laminated sandstone with 100 md permeability, and it would not act as a seal. We selected the upper part of the "C" between the laminated zone and top "C' dark mudstones as the injection zone. This interval was the right thickness to increase chances of breakthrough. The top "C" mudstone was predicted to be thick and continuous enough to serve a guide while concentrating CO_2 beneath it. Acting conservatively for the first test, we perforated the whole upper "C" interval in both wells.

The use of the wells was carefully sequenced to allow collection of geochemical and geochemically sensitive data as well as data for which the tools need to run in prepared (non-natural fluid) filled boreholes. Fluid sampling and RST required that natural fluids be near the wellbore. EM and cross-well seismic required that the wells be filled with a non-corrosive fluid and that any CO_2 be pushed back from the perforations to avoid all risk of the wells self-lifting by producing gas at the perforations. These conditions are accomplished by introducing a dense brine known as "kill fluid." In order to resume geochemical sampling, kill fluids must be produced and sent to disposal, which requires prolonged and expensive pumping.

The large contrast between thermal capture cross-section (notated $\sum$ = sigma) of CO_2 ($\sum_{CO2}$) and formation water ($\sum_w$) was the basis for selection of the Schlumberger

Reservoir Saturation Tool (RST) as a wellbore monitoring tool. This tool works by pulsed neutron capture. Because $\sum_w$ depends on salinity, a series of water analyses was performed on samples from the hydrologic tests. These analyses resulted in a formation water salinity of 93,000 ppm, and we therefore took a $\sum_w$ of 55 capture units (cu). After running the Schlumberger SNUPAR model, for CO_2 we assumed a value of 0.03 cu.

Pre-injection well work

The site selected was on an existing well pad that had to be substantially enlarged, and additional gravel was need to provide space to drilling the injection well as well as room to later host a bank of CO_2 storage tanks (Figure 11). A number of features were added for safety, including a loop road that allowed CO_2 trucks to make a one-way trip across the site, and two telephone poles that provided lighting and tree-height wind socks for HSE. These also provided mounts for alarmed, person-height CO_2 gauges.

Figure 11. Layout of the Frio well pad during injection well drilling operations. Photograph contributed by P. Papadeas, Sandia Technologies.

An existing production well, Sun-Gulf-Humble Fee #4 (Figure 8), was selected to become the observation well. The term “observation well” was used in preference to “monitoring well” because this well is only for research and has no regulatory significance. Prior to the experiment, the observation well was idle by virtue of possessing static fluids. Oil that accumulated in the well was swabbed and put in TARC production tanks. During the summer of 2003, a baseline temperature survey and a Schlumberger ultrasonic imaging tool (USIT) were run to determine whether the well was fit for remediation. Review of casing thickness obtained from internal and external radius measurements indicated the casing to be in good condition. No holes were found, and at least 90% of the original casing thickness was preserved. However, the log showed that, as is normal for a 1952 oil field production well, it had no cement placed behind the 7- inch (~17.8 cm) casing above the production interval or below the 10.75-inch (~27.3 cm) surface casing [surface to 2,040 ft (~622 m)]. Absence of cement behind the casing was confirmed by low impedance, visualized as blue shading on a color USIT log, over planned perforation intervals within the Frio "C" sandstone.

Some bridges of sediment had formed by creep or sloughing, especially at major shale zones. However, remedial work to place cement between the rock wall of the borehole and the steel of the casing was required for two reasons: (1) to control the movement of fluids so that as pressure increased and supercritical CO_2 spread to the observation well the fluids would not migrate in an uncontrolled manner up and down the open space between the casing and the rock, and (2) to provide acoustic coupling to transmit acoustic energy to support a successful cross-wells survey. Without cement, the loose casing rings and reduces resolution of seismic surveys.

Pool Oilfield Services, working under the supervision of Sandia Technologies, provided a workover rig to plug-back the observation well from the original total depth drilled of 9,516 ft (~2,900 m) to a new total depth 6,140 ft (~1,871 m) (Figure 12). Well depths are given in feet below historic datum known as Kelly Bushing (KB). This included abandoning the production perforations from 8,489 ft (~2,587 m) to 8,500 ft (~2,560 m), setting a cement plug 7,931 ft (~2,417 m) to 8,414 ft (~2,565 m), filling the casing with drilling mud at density of 10.6 pounds per gallon (ppg) (~1.27 kg/L), and setting an upper cement plug made from 23 sacks of Class H cement from 6,129 ft (~1,868 m) to 6,327 ft (~1,928 m).

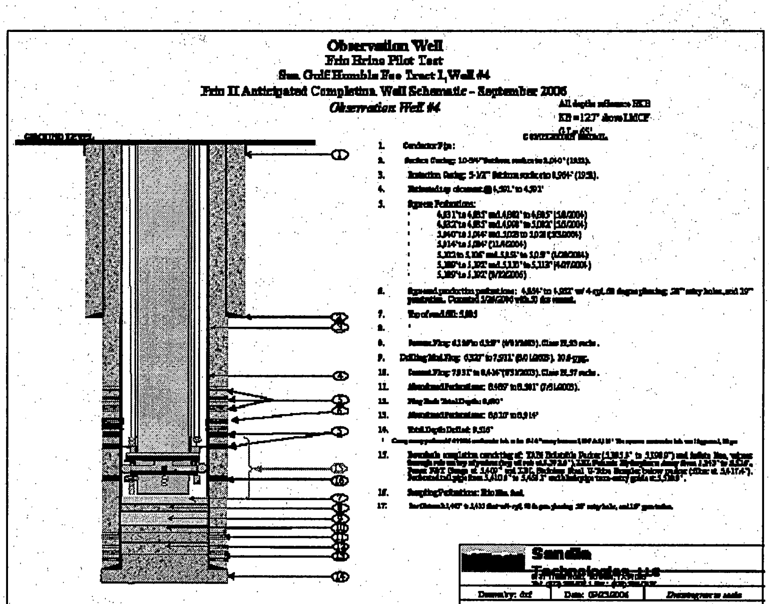


Figure 12. "As built" construction of the Sun-Gulf-Humble #4 well used as an observation well at the end of the project.

The wellbore was circulated clean with brine fluid for pressure control following perforating. A series of seven sets of perforations were placed sequentially from bottom to top from 5,192 ft (~1,583 m) to 4,835 ft (~1,474 m) below. In each pair of perforations the workover rig set a cement retainer between the perforations and attempted to circulate Class H cement behind pipe since circulating cement creates a better bond. In intervals where the material behind casing prevented circulation, a block squeeze was used to force as much cement behind the casing as possible. After each step the cement was cured and then the well reentered and tested to see if pressure held, which indicates that the squeeze was successful, and then the next set of perforations was shot. Cement was emplaced behind casing to a depth of shallower than 4,791 ft (~1,460 m) to seal the wellbore against the major regional confining zone, the Anahuac Formation.

During July 2004, a second run of USIT was made for the observation well, and an improvement in zonal isolation resulted. The well was then recompleted in the planned injection zone of the Frio "C" sand, 5,014 ft (~1,523 m) to 5,034 ft (~1,529 m) Kelly Bushing (KB). The success of the remedial squeezes in limiting vertical flow was tested by conducting a radioactive tracer test (RAT), in which a short half -life iodine isotope was dissolved in water and injected into the well at the perforations. At the end of the test, a gamma-ray log was run, and no tracer migrated behind casing above or below the perforations, indicating an adequate cement job. However, because the formation has greater than 1 darcy permeability, the possibility of some remaining flaws in the remedial cement cannot be eliminated.

Starting on May 19, 2004, a 5½ inch (~14 cm) casing in a new injection well (TCEQ No. 5X2500071) was drilled to 5,741 ft (~1750 m) below surface (5,755 ft (~1,754 m)] KB under the supervision of Sandia Technologies using a design to Texas Class I UIC standards. Well datum is 12 ft (~1 m) KB above ground level. It was cored in three intervals, one in the Anahuac shale seal, which is the major confining zone, one in the Frio "C" sandstone, which was the injection target, and one in the Frio "Blue" sandstone, which was an alternate injection target. The well construction program (Figure 13) included:

- 0-102 ft 14 inch surface conductor;
- surface to 2,667 ft 9-5/8 surface casing placed in a 12-1/4 inch borehole and cemented to surface with 880 sacks of Class A cement;
- 5½ protective casing set in a 7- 7/8 inch borehole, and cement to surface with 819 sacks of Class H cement, using a staging tool at 3653-3655 ft.

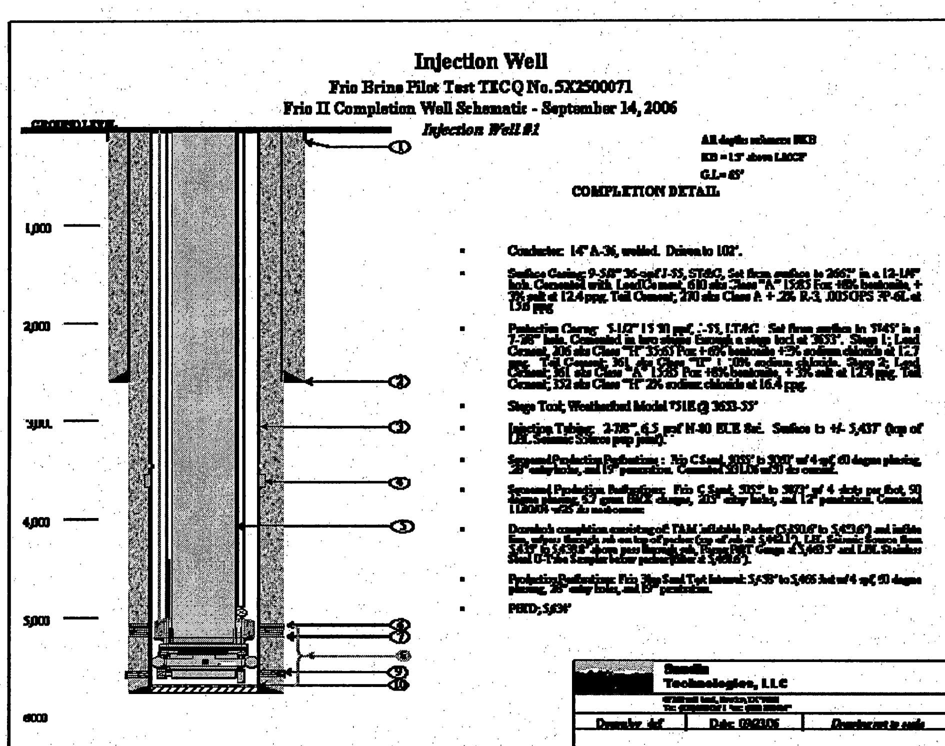


Figure 13. "As built" construction of the Sun-Gulf-Humble Fee injection well at the end of the project.

For the Frio I test, the casing was perforated using 60-degree phasing, .28" entry holes, and 19" penetration in the upper part of the upper Frio "C" sand between 5,053 ft (~1,500 m) and 5,073 ft (~1,546 m). Since the experiment was designed to be short in duration and not be part of a permanent installation, standard steel and Class H cement were used for well completion. Water-based drilling mud and workover fluids were tagged with Rhodamine W-T to flag fluids. A radioactive tracer test was used to test the isolation of the perforated zone and was found to be satisfactory. Downhole deviation surveys were run on both wells to determine the orientation of the wellbores and to calculate the interwell geometries at depth that were used for modeling, distance for tracer calculation, and input into seismic surveys.

Following construction of both wells, several tests were conducted. A baseline cross-well seismic survey was conducted by Paulsson Geophysical under contract to LBNL. The wells were then perforated and backflowed using nitrogen lift to prepare for sampling. USGS personnel observed the Rhodamine W-T concentrations and conductivity until the contamination by workover fluids was reduced below detection. USGS staff also ran downhole samplers to Frio "C" sand perforations and obtained fluids and gases. Following sampling, both well were "killed in" with 8.7 lb/gal NaCl brine to prevent sanding during the Cross-Well EM Survey and to allow completions with tubing, packers and instrumentation to run in the wells. A 2-7/8-inch (~7.3 cm) injection tubing with a Baker Hughes Hornet Mechanical Tension Set Packer, pressure gauge carrier was made up just above the packer and a Panex pressure/temperature gauge was set in the carrier with wireline strapped to the outside of the tubing. The tubing, packer, and pressure/temperature gauge were run in the well, and the packer was set at 4,890 ft (~1,490 m) to 4,898 ft (~1,493 m). This placed the pressure/temperature gauge port at 4,886 ft (~1,489 m). Prior to setting the packer, inhibited 10-lb/gal brine was circulated as annulus fluid.

Characterization

Initial characterization data included interpretation of a 3-D seismic survey and correlation of about 70 wireline well logs, mostly SP-resistivity open-hole logs collected during 1950's field development (Figure 14). Extensive background information about the depositional setting of the Frio Formation and typical structure of reservoirs associated with salt piercement structures was acquired from literature and other sources. Core from geologically similar fields was used for early scoping studies to estimate reservoir properties. These were acquired prior to proposal preparation and used in scoping for model preparation. Log analysis in the region and within the South Liberty Field shows that the upper Frio Formation is a series of upward-fining, fine-grained, well- sorted sandstones with dip-elongated thickness trends (Figures 15 and 16). Sandstones are separated by shales that can be correlated within a field but not over large regions. Toward the top of the Frio Formation, the sandstones become thinner and have a blocky log character. These are interpreted as fluvial sandstones that were partly reworked as marine transgressions became more pronounced toward the flooding event that deposited the regionally extensive 200-ft (~60 m) thick shales and mudstones of the overlying Anahuac Formation. Estimates of the reservoir properties, based mainly on published data from nearby Frio fields, were up to 30% porosity and up to 250 md permeability in the main sand body.

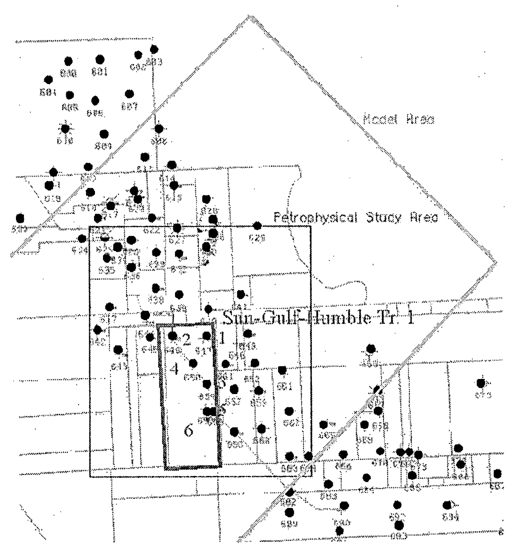


Figure 14. Distribution of wells in the model area. Of the 54 wells in the model area, 19 had logs. The study area and well numbers of the nearby wells are shown in red. Figure prepared by Paul Knox.

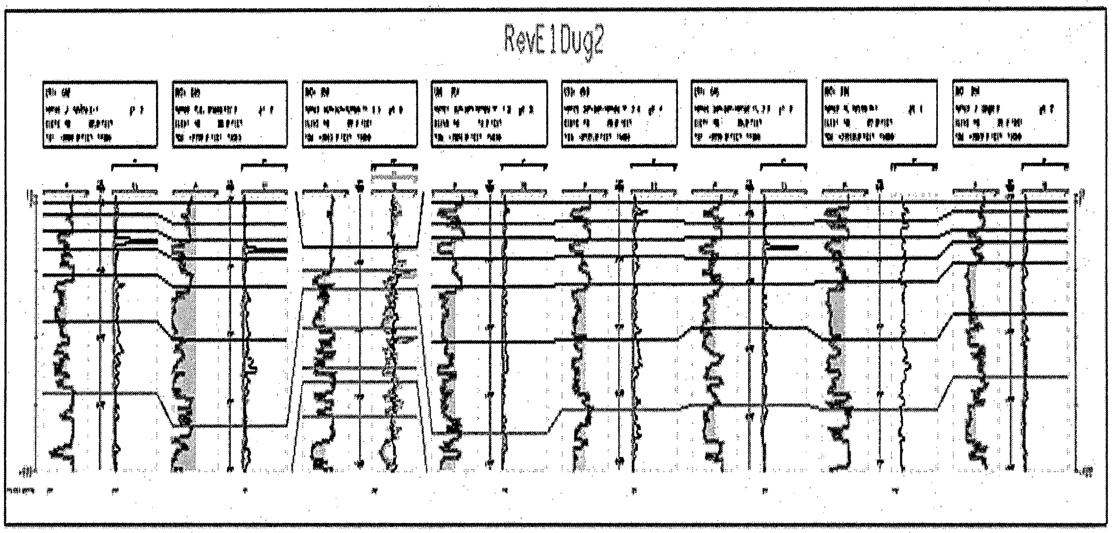


Figure 15. Stratigraphic cross-section through the Frio Formation. Figure prepared by Paul Knox.

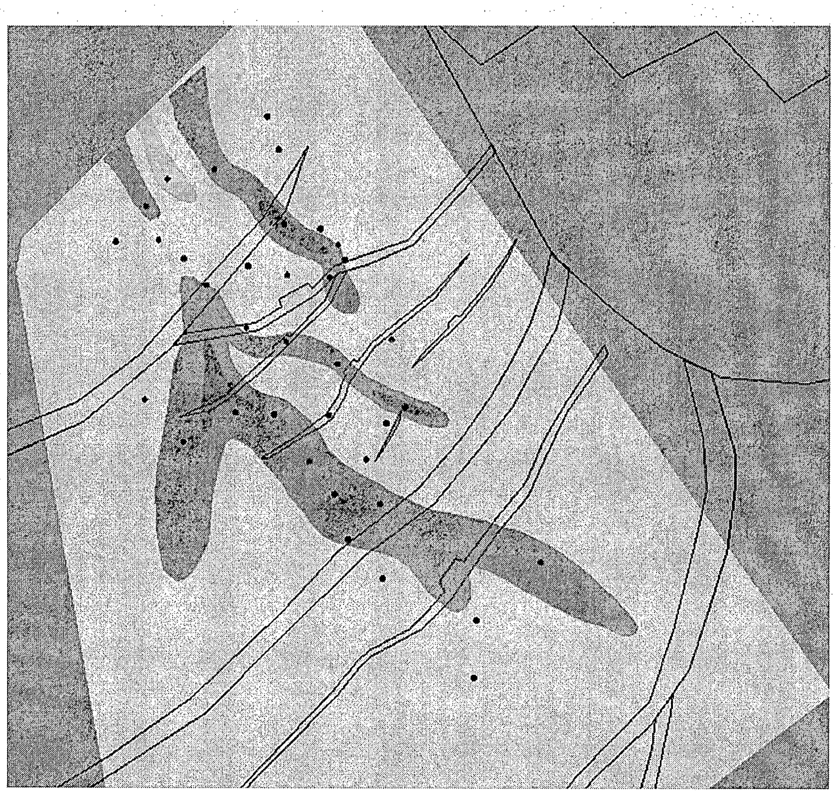


Figure 16. Facies interpretation of the Frio "C" sandstone, showing dip-elongation of sand bodies interpreted as fluvial channels. Figure prepared by Paul Knox.

After the injection well was drilled, site-specific characterization was undertaken. Open-hole logs, fullbore Formation Microimager (FMI), and three conventional cores were collected during drilling of the injection well. Plugs from representative core intervals were cut for core analysis (porosity and permeability), X-ray diffraction (XRD) analysis, and thin section petrography. Because of the shallow depth and expectation of friable and soft sediments, we paid special attention to cutting cores and preservation at the well site.

As soon the core arrived at the surface, we cut an aluminum barrel into 3-ft (~.91-m) segments and froze the samples in dry ice containers. Several conservation options were considered; however, with very friable and reactive core we decided that freezing would at least eliminate geochemical and gross fabric disruptions that otherwise would have occurred during handling.

After the core samples were transferred to the contractor's laboratory, CAT scans were run to check core condition inside of the aluminum barrel. After we selected preserved intervals for future use, cores were slabbed for core description and core photography. Because of their friable nature, special care was taken in cutting core plugs by drilling them using liquid nitrogen, sleeving them in aluminum, and setting a screen at both ends. Samples of the Frio cores have been provided to sequestration workers world-wide for laboratory projects to follow-on the field work presented here.

The upper half of the 75-ft- (~23-m) thick Frio "C" interval was cored in the injection well, and this was the interval selected for the injection. The core contains 32 ft (~10 m) of fine grained, poorly indurated sandstone with a strongly reduced blue-gray color (Figure 17). The base of the cored interval is the mid-"C" marker, a finely bedded, sparsely burrowed, fine sandstone and siltstone with minor organic material that was likely to have been deposited in fluvial overbank environments. Core plug analysis in the base of the core indicates porosities of 25 to 28% and horizontal permeabilities of 100 to 120 md. Overlying this basal unit are high-angle cross beds that represent fluvial channel facies; these have the highest measured porosity of 35% (Figure 18). The massive upper part of the upper "C" sandstone has porosities of 30 to 35% and permeabilities of 2,000 to 2,500 md and is interpreted as the product of marine reworking and winnowing. The top of the "C" sandstone is characterized by about 2 ft (~.6 m) to 3 ft (~1 m) of muddy sandstone, which has a porosity of 24 to 26% and a permeability of 70 to 90 md. Overlying this is about 2 ft (~.6 m) to 3 ft (~1 m) of the top "C" seal, a minor seal beneath the regional Anahuac Shale.

Thin section analysis of sandstones shows that they 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. Conventional core analysis performed under an overburdened pressure of 1,800 psi (~1,800 bar) measured porosity and permeability. Along with conventional core analysis, thin sections were made to examine pore geometries, mineralogy, and cementing materials. Measured porosity was 33.1% and permeability was 1,150 md. Several capillary pressure tests were made on these cores, and the shape of the saturation curve indicates very high reservoir quality: low threshold pressure, and good sorting of pore size. The "C" sandstone is overlain by the Anahuac Formation, which is a 250 ft (~76 m) thick, regionally extensive unit of mudstone and shale considered to be a competent confining zone A capillary-pressure test made for an Anahuac Formation sample shows the high entry threshold pressure of 3,500 psi (~241 bar), confirming expectations that the Anahuac will be an ultimate top seal for CO_2.

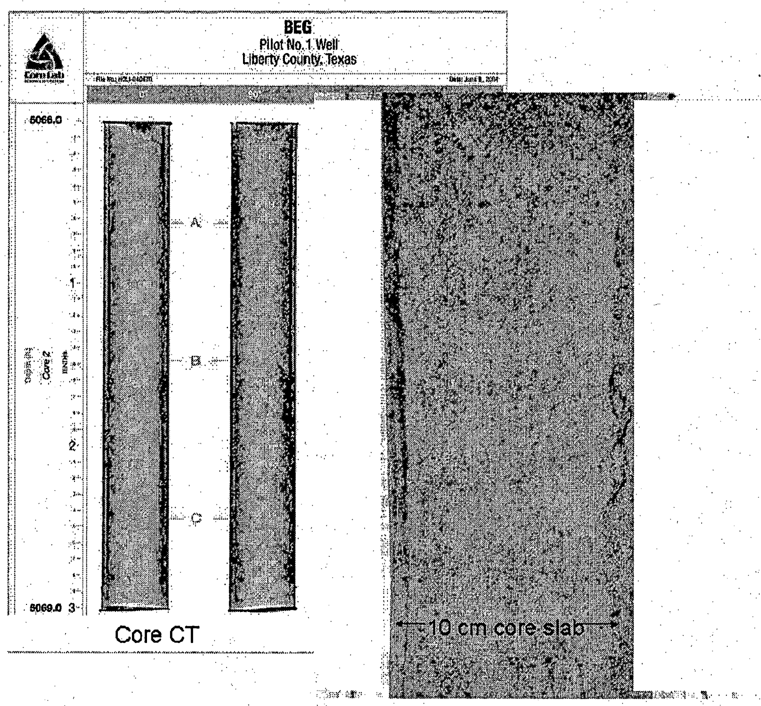


Figure 17. CT scan and slabbed core of the Frio "C" sandstone.

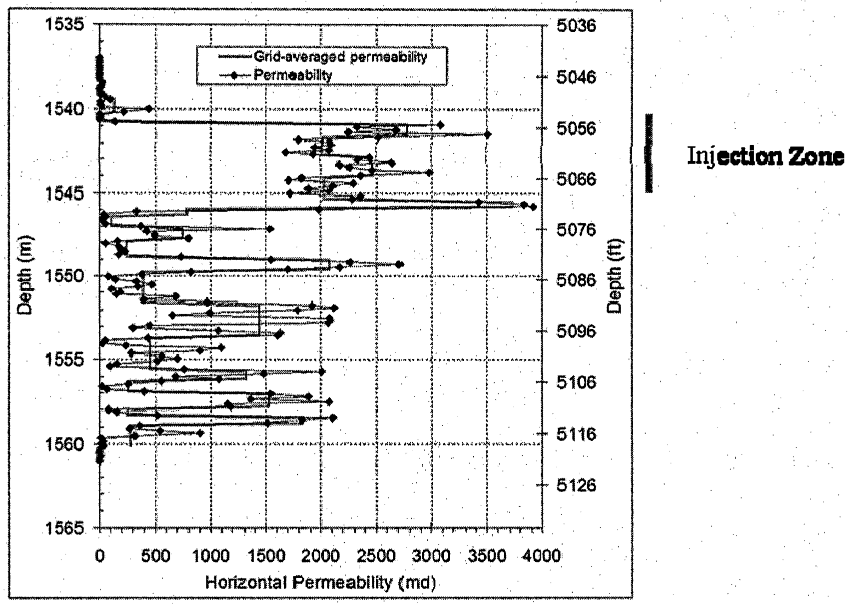


Figure 18. Permeability from log calculations and averages used in TOUGH2 simulation. Figure prepared by Christine Doughty from data provided by Shinichi Sakurai.

The open-hole logging program in the injection well used a Schlumberger triple combo, along with Schlumberger dipole shear imager (DSI). Results from the DSI log were used for comparison between baseline compressional and shear velocity and post-injection data, as well as for calibrating VSP and seismic data. The Schlumberger fullbore Formation Microimager (FMI) was run over the Anahuac and the Frio intervals. FMI is used to meet TCEQ requirements to look for faults or fractures within injection and confining intervals that might lead to leakage risk. As expected, the FMI showed no evidence of faults or natural fractures within the intervals of interest. The FMI was also used to find the structural dip information at the injection well. Manual dip picking provided a detailed correlation of the shale at the Frio sandstone interval, and it was estimated the structure had an average dip of 18° down to the south. This result agreed well with the structure map that was based on 3D seismic data.

To complement historic SP-resistivity logs in the observation well, a dipole sonic log through the casing was run during August 2004. Using gamma ray and compressional sonic transit time, we computed shale volume and porosity. Throughout the program, the mis-match between petrophysical properties from the historic log set compared to the new open hole logs in the injection well provided uncertainty. It was difficult to determine which lateral variations were real, and which were an artifact of different data collection. After a number of iterations, the properties of the injection well were used in constructing a TOUGH2 model (ignoring interwell heterogeneity). In the "C" sandstone this assumption only led to small depth errors. A muddy sandstone near the top of the "C" sandstone in the injection well was made more continuous by this assumption than was shown by CO_2 movement in reality.

At the end of open hole logging, the Schlumberger modular formation dynamics tool (MDT) was run to obtained early confirmation that the inputs to the model were reasonable, and that the monitoring design did not need to be substantively revised. Formation pressure and temperature of the "C" sandstone were found to be 2,211 psi (~152 bar) and 134.5°F (~56.9 °C), respectively, at 5,084 ft (~1,550 m). These values were used for simulation models and also for borehole correction of cased-hole log data. After running the MDT, we learned that formation fluids were brine, that no oil existed, and that gas was dissolved, not in free phase in the reservoir, and the permeability estimates support perforation design. Permeability ranged from more than 1 darcy to 50 md. Geochemical samples obtained with the MDT were carefully sampled by pumping fluids until conductivity stabilized. However, analysis of the fluids showed that they were strongly contaminated by drilling fluids, as evidenced by Rhodamine W-T and salinities well below produced fluids from the same interval. In this high-permeability system, the equilibrium reached seemed to be between contaminated-near wellbore fluids and formation fluids. We tried to fluid sample the Frio "B" and "A" sandstones to obtain baseline of above injection zone monitoring zones, but the MDT was unable to make a seal with the very friable formation. As a result, we were unable to collect a sample. It was therefore determined that we would have to rely on detection of tracers rather than comparison of baseline chemistry for the planned above-zone leakage study.

Analysis of the 3-D seismic volume and wireline logs (Figure 19) defined the northwest and southeast structural margins of the injection compartment as northwest-dipping normal faults with 50 ft (~15 m) to 150 ft (~45 m) of throw, that are part of the radial system of faults above the salt dome (Vendeville and others, 2003). A normal fault with the same trend but a smaller throw partly bisects the compartment (Figure 20); this is the only fault that was intersected by the small volume of CO_2 injected. The northeast end of the compartment is the structurally complex margin of the salt dome. The quality of the seal in this area is uncertain and was not tested by this experiment because the CO_2 plume did not spread to this area.

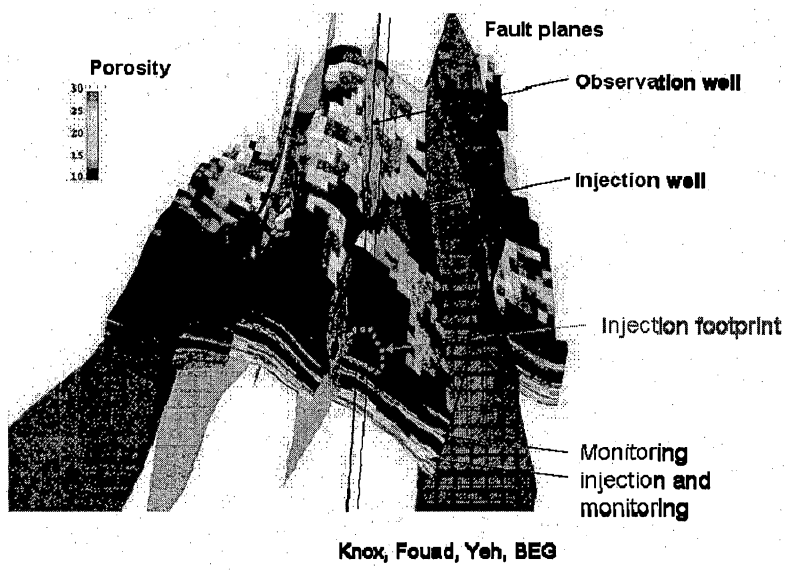


Figure 19. Gridded reservoir model made using seismic data to define fault block and wireline data to distribute porosity. Figure prepared by Joseph Yeh.

Figure 20. Location of structural cross-section shown in Figure 21 on structural base derived from the 3-D seismic. Red dots show the locations of the #4 and #3 wells. Figure prepared by Paul Knox.

Dips within the injection compartment are complex: beds dip away from the dome center but are also warped down toward the southwest compartment margin (Figure 21). Hand-picked interpretation of the FMI log 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 CT scans.

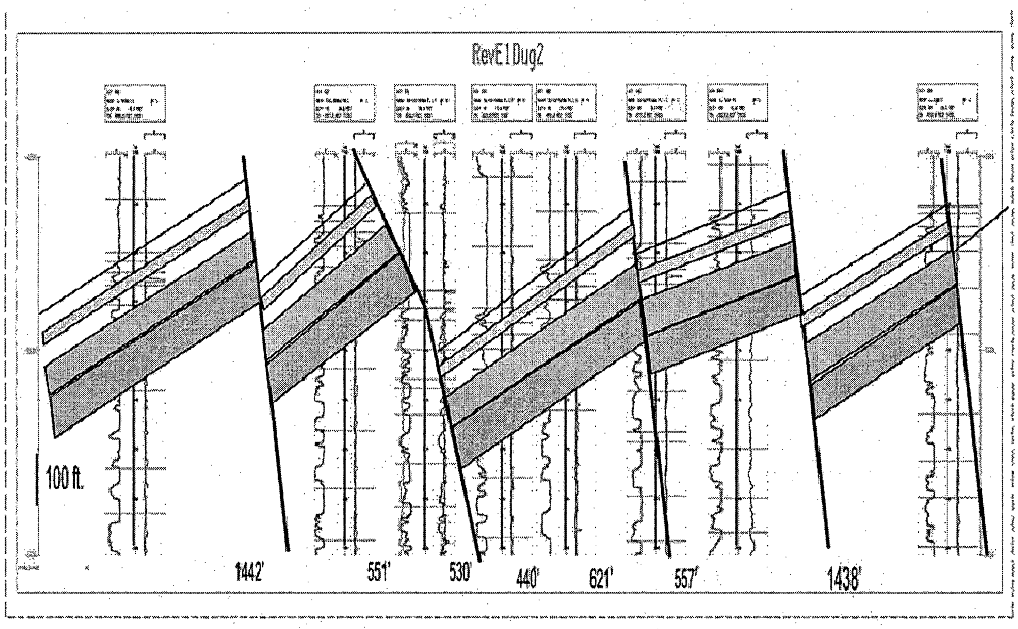


Figure 21. Structural cross-section showing steep dips and faults that cause compartmentalization. Figure prepared by Paul Knox.

A novel aspect of characterization for the Frio I test was an extended dipole hydrologic test. Single phase hydrologic testing is a high-value activity because it is closely related to the performance when CO_2 is injected and scaled to be relevant to the interwell, where data are otherwise sparse. A 24-hour pumping drawdown test followed by a single-phase (aqueous) tracer test provided detailed characterization of the hydrological properties of the formation prior to injection of CO_2. In an experiment conducted by Rob Trautz for LBNL, the observation well was pumped and the produced fluids reinjected at the injection well at 51.4 gpm (~0.194 m^3/min) for 15.7 days. Water-soluble fluorescent dye was injected into the injection well after the pumping injection doublet reached a pseudo-steady pressure (approximately 24 hours after reinjection started). Produced brine from the observation well was monitored using an automatic sampler at half-hour intervals and tracer concentration was measured with a spectrofluorometer. Monitoring to estimate the effective porosity and thickness of the continued as the tracer arrived, peaked, and then declined (elution curve).

Reservoir models were then revised from these data to increase the permeability from the initially forecast 250 md. Average permeability of 2.1 darcys was estimated based on pre-injection hydrological testing, which compares well with the core plug permeabilities, which ranged from 1.8 to 3.6 darcys through the upper Frio "C" sandstone. The single-phase two-well tracer test resulted in a breakthrough time of the tracer that was somewhat slower than predicted. Since porosity is relatively well constrained by measurements on core plugs, the LBNL modeling team refined the effective aquifer thickness to 23.6 ft (~7.2 m) from the original 21.3 ft (~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 which thickened the upper "C" unit/sandstone, or that of discontinuities in the muddy and laminated sands at the top or bottom of the "C" unit/sandstone so the flow field occupied a larger volume of sandstone. In addition detailed description of the high gamma ray interval located in the middle of the C sandstone revealed sandy silt with about 100 md permeability, which does not have the seal potential and cannot be considered as a CO_2 barrier. This raised concern that injection below this barrier would involve a large part of the "C" sand thickness, and that budgeted CO_2 volume might be insufficient to allow breakthrough. The experiment was then revised to inject into the upper "C" only, right under the local top "C" mudstone barriers.

Injection and during-injection monitoring

Safety and operational risk management

Two Process Safety Reviews (PSR) for the surface equipment and CO_2 injection activities were held at Sandia's offices in April 2004 with Trimeric and in August 2008 at the field site with vendors Trimeric, Air Liquide, and Praxair that reviewed the equipment and operating aspects of CO_2 storage, pumping, and heating prior to injection. The PSR Report recommendations became part of the Health and Safety Plan. Electrical and phone service was run to the location, and location lighting for nighttime work was placed, in addition to the planned CO_2 work safety equipment (wind socks and CO_2 meters with alarms). Sandia was charged with holding regular shift-based HSE meetings and signing in all workers, including vendors, researchers, and visitors. Work area trailers provided safe onsite work areas and relief from the heat with potable water and air conditioning for the computers. Water from the makeup water well was used for non-potable water at the trailer.

For the CO_2 injection, packers were set above the perforations in both wells to allow an adequate working distance for tools. Downhole pressure and temperature sensors were installed in both wells at the packers and open to the perforated intervals and were logged continuously throughout the injection test. This working distance was a source of uncertainty during CO_2 breakthrough when the wellbore was filled with a mixture of unknown density containing both CO_2 and brine, and was subsequently decreased during Frio II.

The CO_2 handling was modified from the operations used for conducting CO_2 reservoir stimulation by fracturing. Commercial refrigerated liquid CO_2 was trucked to the site and stored in insulated reservoirs. For Frio I, carbon dioxide availability required the use of two sources of CO_2: a Bay City, TX, refinery and a Donaldsonville, LA, fertilizer plant. The CO_2 was heated to about 60 °F (~16 °C), compressed, and injected as a gas using Praxair's commercial injection truck. Heating was used to avoid thermal stress at the wellhead and shallow tubing, which were not designed to deal with freezing.

The gas reached supercritical state as it flowed down the well tubing. The goal during injection was to keep the rate of injection stable except for pauses designed as pressure fall-off periods. The volume of CO_2 planned during test design to ensure that the CO_2 would breakthrough to the observation well and that a well-developed plume would pass the observation well was 3,500 tons of CO_2 over a 3-week period. During the experiment, injection was paused at stages of plume evolution to measure pressure fall off to estimate hydrological properties. Early attainment of the experiment objectives allowed for termination of the injection after 10 days elapsed time and injection of only 1,600 tons.

Sandia Technologies deployed an Aspen Data Acquisition System for real-time monitoring and recording, and served the data to a password-protected website so that injection could be monitoring remotely. Monitoring downhole pressure and temperature and wellhead pressure in both wells continued until the downhole gauges were removed for a cross-well repeat survey. In Frio I, flow was measured at the liquid pump in gallons per minute (gpm) by Praxair, however, probable imprecision in converting volumes to mass occurred because temperature and pressure were not constant. In both tests, comparison of the purchased CO_2 measured by net weight on the tanker trucks at source to the amount injected show that large amounts of CO_2, on the order of $1/4^{th}$, was vented during transportation, storage, and compression. This is probably a function of high summer temperature during the test. This loss was not factored into the CO_2 cost, however, because in both cases breakthrough and experiment completion were early and loss of CO_2 was not a problem.

Because a surface tracer experiment was planned at Frio I, we attempted to minimize any chance of leakage of concentrated tracer before it went into the well. Perfluorocarbon tracers (PFTs) were injected by ORNL with a syringe pump. Gas tracers were injected by several methods. In Frio I, LBNL attempted to pump the tracers into the flow line, which had varied success. In Frio II, tracer was emplaced into an empty line, which was then filled with either nitrogen or CO_2 and swept into the tracer injection manifold. In all cases a sufficient amount was injected to get detection; however, a higher precision control on input signal for gases would be desirable. The tracer tests were designed to have a sharp (1 hour) input, to observe travel time and changes in tracer concentrations at the observation well because of dispersivity.

In preparation for CO_2 injection, equipment function was tested and prepped to receive high pressure. A high-pressure/low-volume injection pump was rigged up to the packer to ensure inflation during the testing. A high-pressure/low-volume injection pump was rigged up to the casing-tubing annulus to ensure that the 100 psi (~6.9 bar) minimum positive pressure on the annulus was maintained during injection and post-injection observation, to meet TCEQ expectations and to provide warning if any component (casing, tubing, packer, wellhead) should fail. Pressure and temperature transducers were attached to the wellhead to measure tubing and annular pressure and temperature and run to the Aspen Data Acquisition System for real-time monitoring and recording. Figure 22 shows the surface geometries of the wells during Frio I. Figure 23 shows the observation wellhead, the surface parts of the U-tube, and the LBNL control room and field lab.

Figure 22. Photograph of the surface geometries of the wells during Frio I.

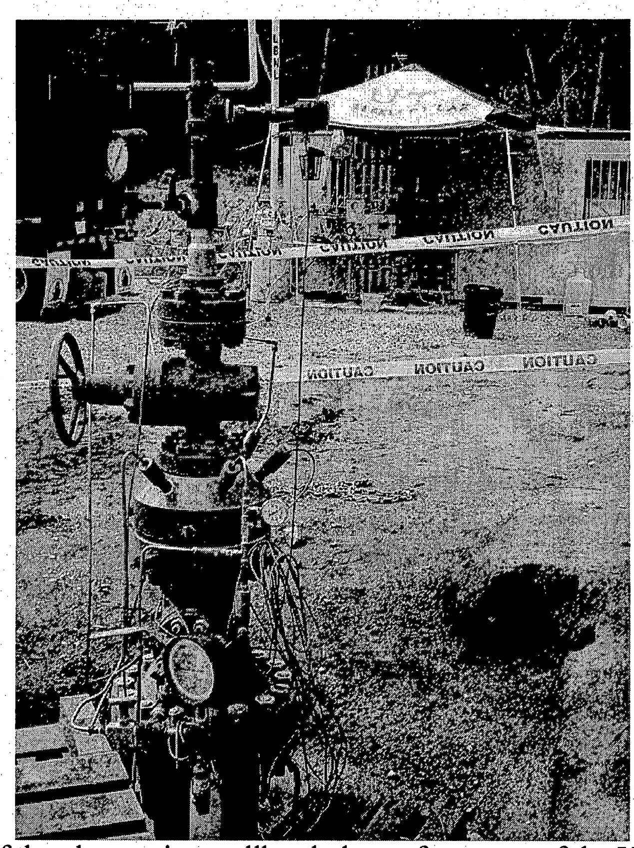


Figure 23. View of the observation wellhead, the surface parts of the U-tube, and the LBNL control room and field lab.

The injection timeline for the Frio I project, based on daily reports (Appendix 2) and supplemented by other reports and publications, is summarized below.

- TCEQ notified us that the construction and completion review was complete (see permits in Appendix 2).
- Frio I injection began at 11:34 a.m. on October 4, 2002. Surface temperature and pressure conditions were quite complex for an hour and a half as the pumper truck balanced pressure and temperature to deliver CO_2 at a constant rate. After that, the pumper truck was reasonably successful at holding the planned injection rate at about 37 gpm (~0.14 m^3/min). Fluctuations in pumping rate occurred for short periods when CO_2 trucks were off loading.
- For both tests the only evidence of injection was real-time changes in bottom-hole pressure and temperature displayed on the Aspen system. The events downhole could be traced by temperature and pressure responses. As CO_2 reached the downhole gauge in the injector, pressure rose sharply at first and then decreased as CO_2 wet the near-wellbore, increasing relative permeability. Temperature cooled from an initial 133.5°F (~56.4°C) as cool CO_2 reached bottom hole. Downhole

pressure at observation well responded immediately, the differential and lag were analyzed to determine changing relative permeability as CO_2 wets the rock volume. Initially it was about 20 psi (~1.38 bar) lower than the injection well.

- In each test, a CO_2 pump failure and down-time for repair prior to breakthrough added complexity to the experiment. The timeline therefore includes a period when pumping under pressure stopped and migration continued under differential pressure and buoyancy. This pause was used as a fall-off test through mixed-phase fluids in the interwell area.
- U-tube equipment (Figure 24) and crew were successful in obtaining 27-gallon (~102 L) samples every hour at reservoir pressure and temperature from the observation well. Gas analysis with GC MS was successful and produced results similar to those obtained by Yousif Kharaka, so that real-time data on changing composition were obtained. The test showed that the GC MS could detect PFTs also, adding greatly to sample density and allowing real-time detection. Gas samples were conserved for higher precision lab analysis by LBNL and ORNL. Brine samples were collected from most sampling events and field parameters, and pH, alkalinity, and conductivity were analyzed in real time for evidence of breakthrough in dissolved CO_2. Liquid samples were also conserved for additional lab analysis by USGS. U-tube brine waste was stored in a frac tank for offsite disposal; however, no mechanism for off-site disposal of gases (methane, CO_2, and entrained tracers) could be developed, so they were vented. This created an on-site aerosol "leakage" signal of known frequency and volume that was tested during Frio I for detection by NETL.

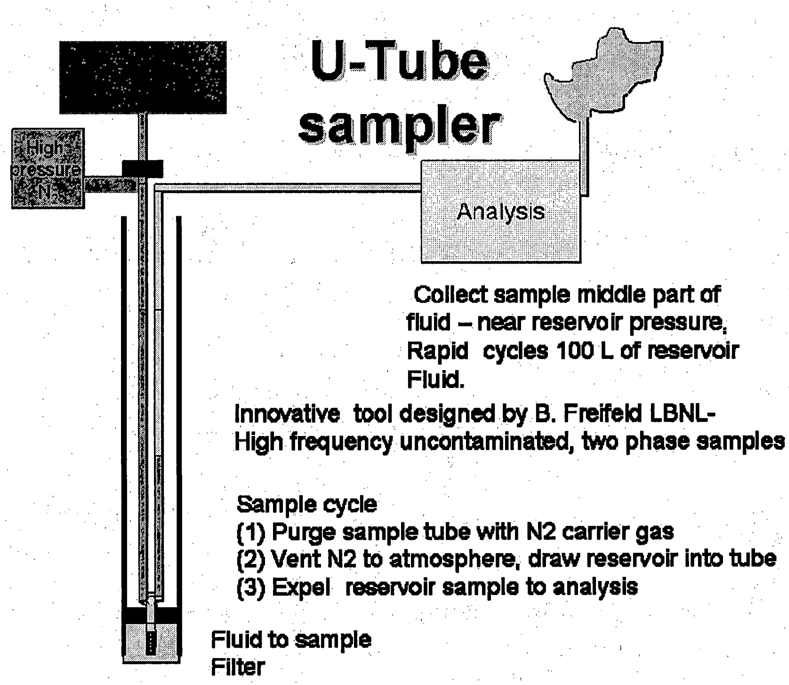


Figure 24. Schematic diagram of the U-tube sampler.

- The tracer program was conducted. The first tracer injected was water-soluble eosin in Frio I and fluorescein in Frio II in brine in the injection well right ahead of the CO_2 to investigate two-phase behavior near the well. In neither case was the aqueous tracer recovered, suggesting that a slug of brine was not pushed ahead of the CO_2 plume, but was bypassed by multi-phase flow. However, the stability of these organic tracers in the environment of high iron is unsure, and the tests should be repeated. In both tests, "cocktails" of tracers were injected attempting to produce hour-long "square" input signal. Combinations of tracers made each pulse unique, so that tracers could be repeated. Figure 25 shows details of the tracer program.

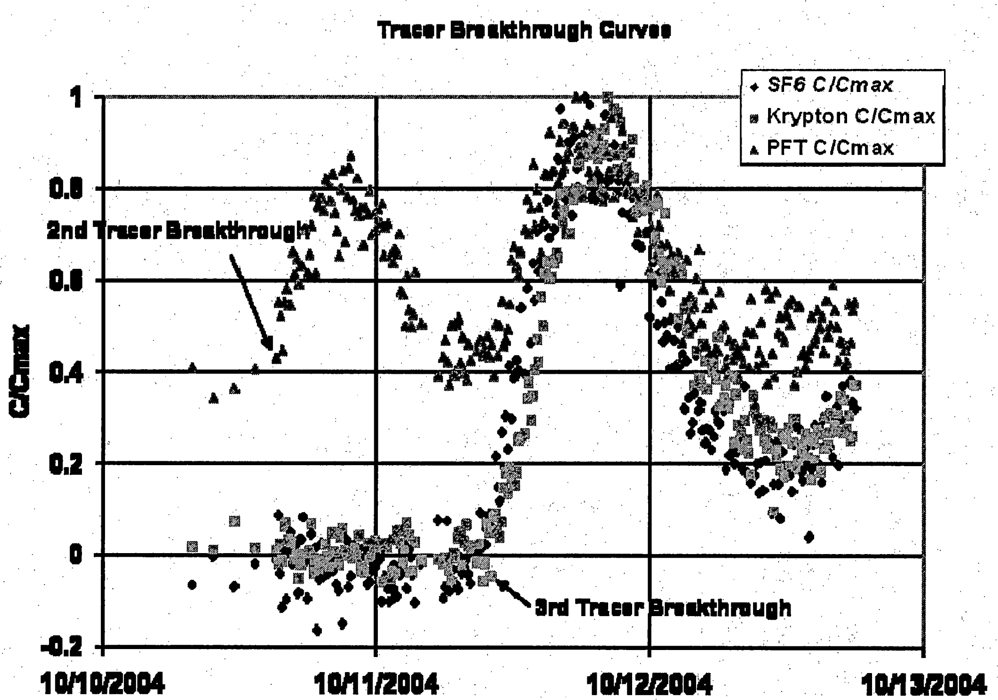


Figure 25. Tracer breakthrough curves after the U-tube became self-lifting. Prepared by Barry Freifeld, LBNL and Tommy Phelps, ORNL.

- One- to two-hour sampling continued on 24-hour shifts. In each test, changes accompanying detection of CO_2 "breakthrough" occurred in a number of stages. The earliest signal was slight warming. It is likely this is displacement of cooled brine near the wellbore by warmer formation fluids moving ahead of the CO_2. It is also possible that some warming by exothermic reaction of CO_2 and water is expressed. Cooling of the near well-bore is an effect of workover prior to injection using relatively cool surface temperature fluids. The second signal is drop in pH, indicating that dissolved CO_2 was increasing. It is not clear the extent to which this is a dissolved phase in the pores ahead of the immiscible supercritical Phase CO_2

as modeled, versus thick fingers of supercritical CO_2 reaching the perforations and dissolving in the wellbore fluids. The third change measured is increased concentration of CO_2 relative to methane in LBNL's quadrupole mass spectrometer (MS). The next change is recovery of supercritical CO_2 measured by density change in the U-tube weighing chambers. At the same time, temperature began to fall, as large volumes of cool CO_2 reached the observation well.

- In Frio I, this breakthrough sequence occurred over a short period. On October 6 at about 2:30 p.m., U-tube samples contained supercritical CO_2, and the produced fluid was bubbly. The ratio to the ambient gas (methane) was replaced by large amounts of CO_2 (Figure 26). Weighing sample chambers showed a change in the gas-water ratio produced from the U-tube as CO_2 filled the 37-ft (~ 11 m) "trap" in the wellbore above the perforations. During this period, the formation brine stored in the tubing was mostly displaced downward through the perforations as CO_2 accumulated in the tubing. This brine was in contact with CO_2 and steel tubing, and significant corrosion of the tubing likely impacted the geochemistry. Formation of ice created complications for U-tube operations, and sample volumes were reduced. In an attempt to get more water into the system, we opened flow at the wellhead at 3 a.m., producing a frac tank of CO_2. At 5 a.m. we shut the well in because large volumes of CO_2 were being produced. After the shut in, pressure in the observation well started to climb much more rapidly than before, until a new high pressure equilibrium was reached mid-morning. Small volumes of water could be obtained intermittently using the U-tube. The U-tube became self-lifting, meaning that gas flows to the surface, which allowed a shorter sampling cycle and samples could be obtained as fast as they can be collected, to add detail to the tracer recovery curves.

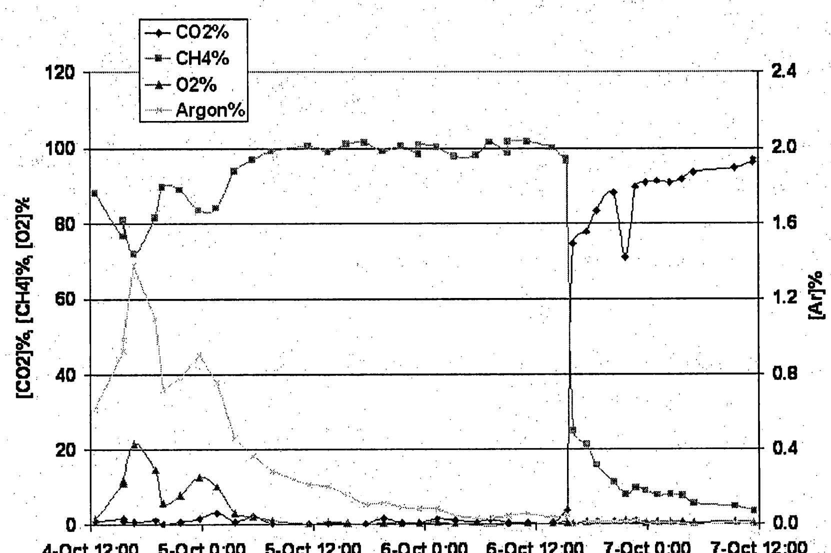


Figure 26. Ratios of gases recovered by the U-tube, followed by ambient methane, which is replaced at breakthrough by CO_2. Modified from Freifeld and others, 2005.

- In Frio I the PFT arrived with the CO_2, and a peak in concentration was obtained in the second sample. This shows compression of the first arrivals, indicating that significant CO_2 was dissolved. However, sample density is not sufficient to quantify how much dissolved at the plume front.
- Geochemical analysis shows a sharp change in chemistry at breakthrough. pH fell and stabilized. In Frio I, pH was measured in the field lab after pressure decrease. Alkalinity increased from 60mg/L prior to breakthrough to 2,100 mg/L after breakthrough. Increases in iron and manganese were apparent in brine samples, which changed from clear to coffee-colored at breakthrough (Figure 27).

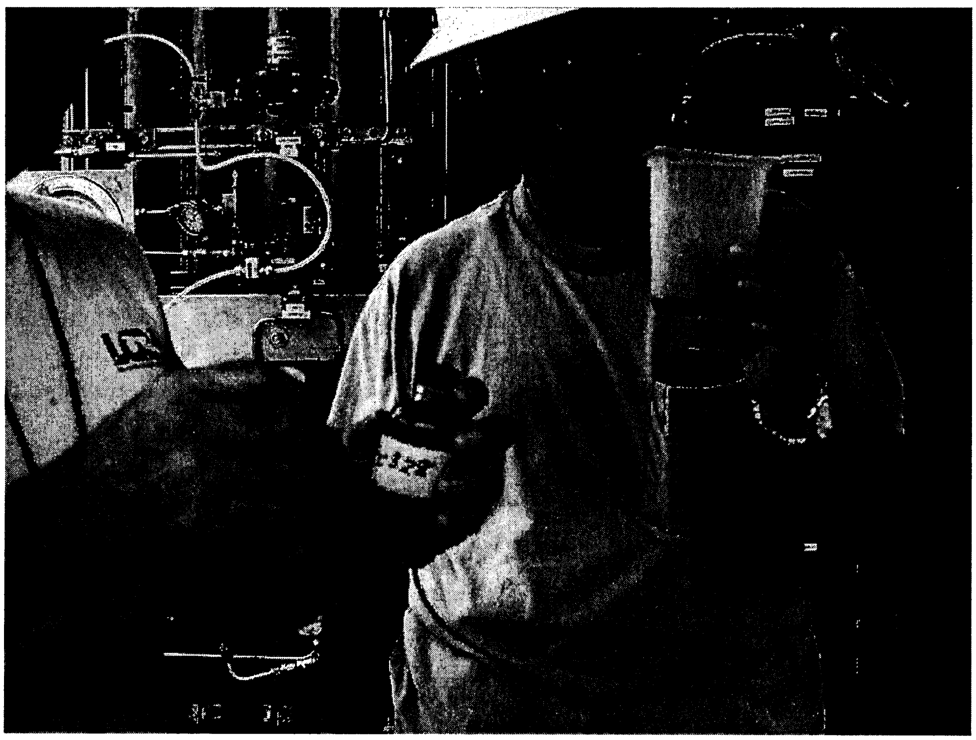


Figure 27. Increases in iron and manganese were apparent in brine samples, which changed from clear to coffee-colored at breakthrough.

- On Frio I, an intentional 30-hour pressure fall-off test started at 11:45 a.m. on October 7. Hydrologic analysis of this and the previous unintentional fall-off tests' data showed trends that were analyzed to confirm the reduction in relative permeability as a two-phase system replaced a single-phase system. A second fall-off test was conducted on October 12, 2004, from 6 p.m. until noon the next day with the addition of some 1-hour pulses. The pulse test consisted of a 1 hour injection cycle at 20 gpm (~0.011 m^3/min), 1 hour shut-in, 1 hour injection cycle at 20 gpm (~0.011 m^3/min), and a 3 hour shut-in period.
- During Frio I, RST was run shortly after breakthrough (October 8), and showed 12 ft (~4 m) of saturation in the "C" sandstone at the observation well (Figure 28).

This was run at the end of the first intentional fall-off test. The RST was run again at the end of injection in both wells, and it showed continued down-building during plume evolution. During the injection period when wells are at pressure and CO_2 is highly mobile, RST was run using a lubricator and grease head to control the wells. In addition, Schlumberger had to use a corrosion-resistant nickel-coated wireline. Pressure and temperature of tubing fluids (CO_2 and brine) from the RST tool were recorded on the trip in, and stational P/T data were collected at 1,000 ft (~305 m) intervals. Phase changes were noted at 814 ft (~248 m) from 0.14 psi/ft to 0.22 psi/ft at 82.5 °F (~28.1 °C). Second phase change occurred at 5,027 ft (~1,532 m), from 0.35 at 137 °F (~58 °C) to 0.45 psi/foot at 133.6 °F (56.4°C). This lower phase change is supercritical CO_2 over brine. The cool zone was highest in the uppermost 5 ft (~1.5 m) of brine below CO_2, but it extended about 50 ft (~15 m) total. Comparison of the pre-injection to during-injection RST log shows that significant change in sigma is found between 5,018 ft (~1,529 m) and 5,030 ft (~1,533 m). This change is attributed to CO_2 saturation in the rock pore system. The saturation appears variable, with the strongest change in 5,020 ft (1,530 m) to 5,023 ft (1,531 m), estimated by T. S. Ramakrishna at 70%. Top of brine in the borehole in near elastic ratio log appears at 5,029 ft (~1,533 m), and the CO_2 in the well annulus below the packer and the tubing to surface was clearly visible. Rerun of RST shortly after injection was restarted showed no measurable perturbations in saturation or water level resulting from short-term pressure change.

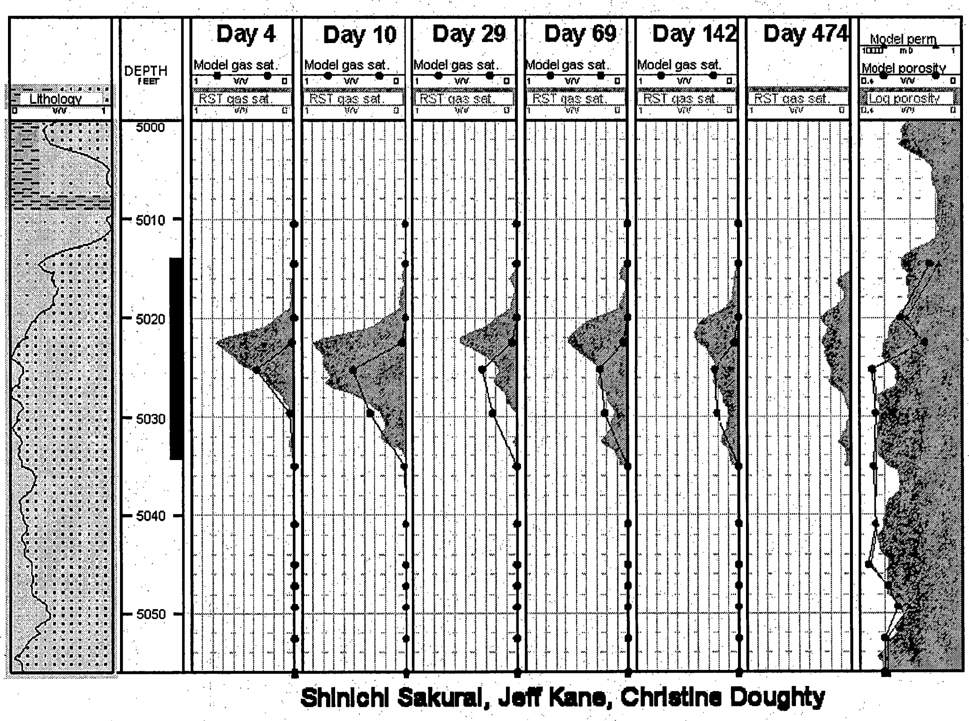


Figure 28. Interpreted changes in saturation with time shown by RST logs.

- In Frio I, a second suite of tracers was injected into the developing plume and arrived approximately 47.5 hours after the start of tracer injection (Figure 24). The arrival time of the initial PFT tracer (injected at the head of the CO_2 plume) is the same, within experimental error. This result is somewhat surprising as it is incompatible with the RST measurement of substantive plume thickening.
- The last Frio I tracers (PFT combination, noble gasses, and FS_6) were injected simultaneously on October 9, 2004, at 11:37, ending an hour later, to attempt to place them between the wells at end of injection. These tracers were never recovered, indicating either that mobility decreased such that they never migrated past the observation well or that post-injection sampling frequency was too low to catch them. Further tests of plume migration under gravity are needed.
- End of Frio I injection was at 2:30 p.m., October 14, 2004. CO_2 supply trucks stopped, and onsite storage tanks were emptied. This equated to 11 days of injection including fall-offs rather than the scheduled 14 days. We decided not to push on to put in the entire 3,000 tons because of large uncertainly in cost/benefit/risk issues. We felt we had achieved all of the during-injection goals and that the cost of 3 more days of injection to benefit cross-well and VSP was expensive and of uncertain benefit.

The third Frio I RST repeat at the end of injection showed that the CO_2 plume in the injection well thickened downward about 4 ft (~ 1.2 m). Maximum CO_2 saturation at the observation well is about 90%. The water level in the borehole has also fallen about 4 ft (1.2 m). In addition an RST log of the injection well was collected. For the injection well, no baseline RST log was recorded before injection. A baseline estimate was constructed using most of the RST run as well as $\sum$ from the multi-mineral log analysis program. At depths where no CO_2 intrusion was expected to occur immediately, the first RST log proved to be a good reference for reconstruction. A set of guide curves for variable water saturation was constructed using the same procedure as that for the observation well. Computed CO_2 saturation curves are labeled according to logging date. An approximately 30-ft (~9 m) thick CO_2 plume was observed in the injection well with a maximum CO_2 saturation of 100% of pore volume occurring within the 4-ft interval between 5,059 ft (~1,542 m) and 5,063 ft (~1,543 m). Because of the high CO_2 concentration during injection, formation water evaporated entirely in this interval. As predicted by the model, down-building of the CO_2 below the perforations and across the mid "C" high-permeability zone was observed. These additional runs were provided by Schlumberger as cost-share.

1.212 % Xenon
8.461 % Krypton
28.50% Neon
Balance nitrogen
3,370 L

Table 2. Noble gas composition (Frio I).

PFT Data for Frio Samples collected in April 2005

Location	Sample ID	[a]Press t_0 (psi)	[b]Press t_{an}(psi)	[c]Sample volume (μL)	PFT	Injection series	[d]Mean Area Count	[e]Mass/Volume (pg/100μL)
Surface (Injection well)	4/4/2005 16:40 (104)	8	-12	500	PMCH	1,3	bdl	bdl
					PTCH	1,3	bdl	bdl
					PMCP	2	bdl	bdl
					PDCH	2	bdl	bdl
C-Sand (Injection well)	4/5/2005 16:20 (106)	230	8	500	PMCH	1,3	600	1
					PTCH	1,3	bdl	bdl
					PMCP	2	1300	10
					PDCH	2	400	1
C-Sand (Injection well)	4/6/2005 9:55 (108)	250	178	500	PMCH	1,3	1600	9
					PTCH	1,3	< 200	< 0.5
					PMCP	2	7000	65
					PDCH	2	1700	7
B-Sand (Monitoring well)	4/6/2005 13:55 (109)	26	7	500	PMCH	1,3	4900	24
					PTCH	1,3	1000	3
					PMCP	2	< 200	< 0.5
					PDCH	2	< 200	< 0.5

[a] Pressure inside the sample cylinder at the time of collection (t_0).
[b] Pressure inside the sample cylinder just before GC analysis at ORNL. Note that sample cylinder 104 was under vacuum conditions.
[c] Volume of sample injected into the GC in microliters (μL).
[d] Mean area counts are calculated after a sample has been injected through the GC in triplicate.
[e] Mass/Volume is reported as pg/100 μL. This was done to directly compare this data with previously analyzed PFT data, which used 100 μL injections instead of 500 μL.

Table 3. Frio I PFT injection schedule (ORNL).

Post-Injection Monitoring

Several types of monitoring were conducted post-injection for the Frio I test. These include repeat RST and acoustic logs, repeat fluid and gas sampling, repeat cross-well seismic tomography, production test, two repeat surface tracer monitorings with Praxair Seeper Trace technology, geochemical sampling of the Frio "B" sandstone for leakage, and sampling of the behind-casing drilling mud looking for tracer with the Schlumberger Cased Hole Formation Tester (CHFT) (NETL). Most of these tests, except CHFT, were concluded prior to starting the Frio II test.

Post-injection repeat RST and acoustic logs

A fourth RST log in the observation well (Figure 29) was run on November 2, 2004, 20 days after the end of injection. Fluid density logging shows that in the borehole, the brine/ CO_2 interface is 4,990 ft (~1,521 m). The value of ∑ obtained with appropriate borehole corrections applied shows that the CO_2 plume has begun to dissipate noticeably, with gravity-driven migration further up-dip, resulting in counter-imbibition of formation water. No RST log was run in the injection well in this period.

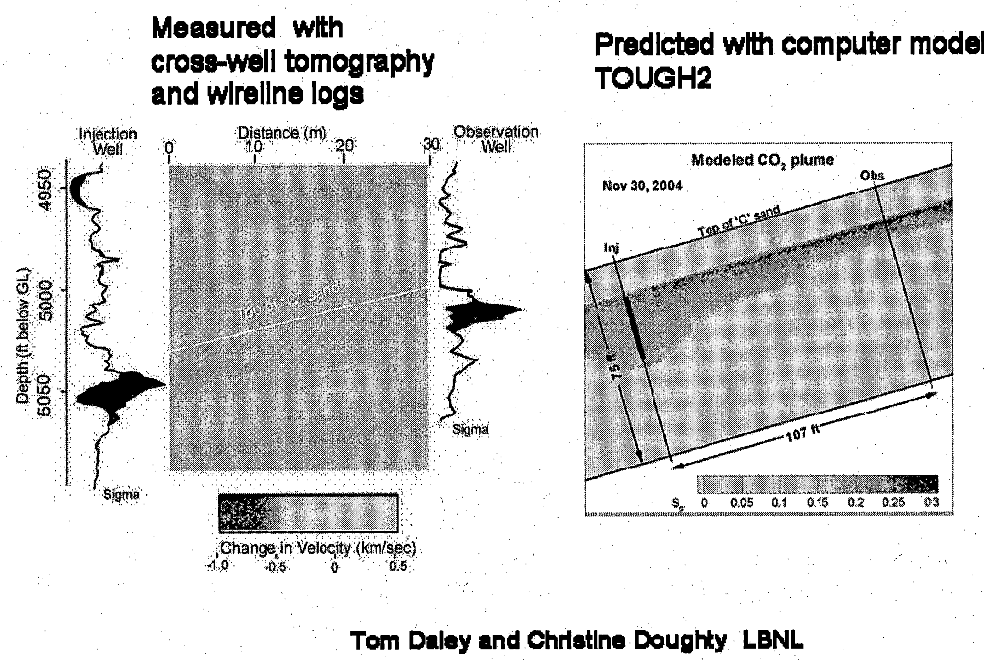


Figure 29. Subtraction of the pre-and post-injection data sets shows strong velocity changes in the area between the wells at approximately the same region as change measured with the RST (blue curves). Comparison of these observations with final TOUGH2 model for the same post-injection period shows a good match.

During November, both wells were recompleted to prepare for the geophysical data acquisition, which included seismic surveys and cross-well electromagnetic analysis. The packer and tubing were removed, and perforated intervals were resqueezed with cement. The injection well required several attempts to seal the perforations and large volumes of cement and fresh water were lost to the formation, which made following quantitative interpretation of later RST less certain, as multiple phases (fresh water and CO_2) were changing at once. Within the interval where higher $\sum$ values were recorded, no CO_2 saturation was computed, and the response was interpreted as an effect of salinity, not of CO_2.

After the geophysical measurements were completed in November 2004, 60 days after injection, RST logs were run in the observation well. The borehole was filled with fresh water and corrosion inhibitor so no gas-filled borehole correction was needed. The CO_2 saturation in the observation well was about the same as it had been 1 month before. The slightly increased CO_2 below 5,030 ft (~1,533 m) may have been caused by a shift in $\sum$ due to invasion of the squeeze fluid.

RST runs were acquired in both wells at the end of February 2005, 133 days after the end of CO_2 injection. Thickness and saturation of CO_2 resembled those of the

December run with a possible slight decrease, which was an indication that CO_2 remained in formation without measurable movement under gravity. The slight increase in CO_2 in the interval below 5,030 ft (~1,533 m) is probably due to further mixing of the fresh completion fluid within the formation.

During Frio I, a baseline log and repeat cased hole dipole sonic logs were run. These logs were used to observe changes in acoustic properties and to help interpret geophysical data. Baseline acoustic logs were run in the open hole of the injection well and in the cased hole of the observation well. Extensive environmental correction and careful processing were applied by Schlumberger to obtain both compressional and shear velocity values because of unconsolidated sediments and alterations around the borehole. After geophysical data acquisition was completed in November 2004, cased-hole sonic logs for the post-injection stage were run in early December. Slow compressional velocity was expected where CO_2 was present. The log response confirmed the interpretation of the RST and cross-well seismic tomography that CO_2 was retained in the "C" sand months after the end of injection, confirming the hypothesis that residual saturation is important. However, weak compressional arrivals over the perforated interval made quantification of interpretation of saturation impossible.

Post-injection repeat fluid and gas sampling

USGS staff conducted repeat fluid sampling following injection. Initially, no sampling was possible, as relative permeability to CO_2 was so high compared to brine that almost no water could be produced. Prior to removing the tubing, packer and U-tube completions for repeat cross-well data collection, a brine sampling event was completed, that showed that iron and manganese had dropped but not all the way to original concentrations. In January 2006, we deployed a gas production rig to attempt to produce back any CO_2. The RST showed that the CO_2 was still present in the "C" sandstone of both wells. However, it was essentially immobile. As predicted by modeling, the amount of CO_2 produced was well below saturation with water, showing that the CO_2 was immobilized. During the production test, additional fluid sampling was conducted by producing water to surface as well as using the USGS Kuster sampler on slickline to obtain samples. Post-injection samples showed partial reequilibration of fluids (Figure 30). It is not clear the extent to which this is a result of mixing and dilution or reequilibration and sorption of precipitation of iron hemi-hydroxides. Experiments involving reaction of representative aquifer rocks with CO_2 under laboratory conditions showed somewhat similar transient peaks in release of cations such as Fe, Mn, and Al (Lu and others, in prep). It is hypothesized that these metals are complexed with high surface area clays, and that mobilization is strongly pH dependent. More work is needed to understand these reactions.

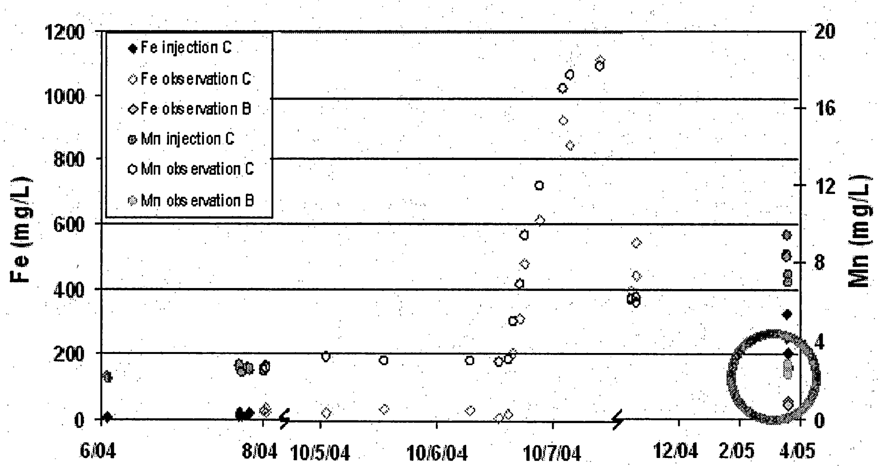


Figure 30. Possible slight elevation in Fe and Mn in the "B" sandstone brine post-injection compared to the "C" sandstone pre-injection. The metals are not as elevated as the post-injection "C" sandstone samples. Plot by Yousif Kharaka, USGS.

Repeat cross-well seismic tomography and vertical seismic profiling

Cross-well seismic and vertical seismic profiling (VSP) were selected to test the premise that measuring the extent of the plume across one or more azimuths can provide information on plume geometry with higher sensitivity and at a fraction of the cost of a 3-D survey. An LBNL orbital vibrator source provided P- and S- wave energy (in-line and cross-line source components) with frequency content of 70 to 350 Hz. A Paulsson Geophysical receiver string with 40 three-component sensors at 25 ft (~7.6 m) spacing was placed in five interleaved fans to produce a 5 ft (~1.5 m) sensor spacing over 250 ft (~76 m) of reservoir centered on the injection zone.

The pre-injection survey was completed before the wells were perforated; the post-injection survey required that the perforations in both wells be squeezed with cement to control the wells that were producing CO_2 gas to eliminate the noise of gas escape and to protect the downhole equipment from corrosive CO_2-charged brine.

Subtraction of the pre-and post-injection data sets (Figure 29) shows strong velocity changes in the area between the wells at approximately the same region as change measured with the RST. The relationship between compressional velocity and gas saturation is dependent on multiple factors, principally on the style of saturation (patchy versus homogeneous), and to a lesser degree on pore pressure, rock properties, and the gas properties themselves (Hoversten and others, 2003). Thus, while the velocity decrease may be attributed to the presence of CO_2, a quantitative conversion to gas saturation requires a rock physics model.

A time-lapse data VSP was collected along each of the three updip transects at the same time as the cross-well survey after the end of injection. The signal was normalized to a shallower reflection above the injection interval to remove changes not associated with injection such as shallow groundwater level and shot energy. A strong increase in amplitude was a measured, 70% to the north, 110% to the northeast, and 80% to the northwest. Estimating the plume edge requires estimating the reflection point offset, which is complex in an area of dipping strata and fault blocks. Making a simple assumption of a 15-degree ray trace and a 60% amplitude change for the plume edge yields a plume extent of 279 ft (~85 m) to the north and northwest, and 148 ft (~45 m) to the northeast. Good quality data suggest that stronger conclusions about plume migration could be obtained by collecting another VSP survey after 1 year to measure change over time, and that a surface seismic survey would be successful in defining the plume extent.

Repeat surface tracer monitoring with Praxair Seeper Trace technology

In the original Frio test design, we planned to have no near-surface monitoring, because we believed that injecting small volumes into high-permeability sandstones would have very little chance of leaking to surface. Moreover, the surface environment of the site is very complex, which would lead to complex ambient CO_2 baseline and complex discharge in the case of a leak to surface. At the request of the NETL COR, we considered the requests of the NETL research staff to host their near-surface monitoring pilot demonstration at the Frio site. We hosted three elements, the first being a request by Art Wells and Rod Diehl to repeat the PFT detection test that they had recently conducted at the West Pearl –Queen site, where they used sorbent pack Capillary Absorption Tube (CAT) hung inside shallow gas wells. These wells were made by hammering pipes into the soil, caulking with bentonite, and testing with a hand pump to make sure they were tight. CAT's were then allowed to passively collect PFTdata, which were then analyzed at Brookhaven National Labs. In addition, we agreed to host two researchers from West Virginia University to study fresh-water aquifers (Figure 31) and to look at seismic data and surface fracture pattern. In addition, Jennifer Lewicki (LBNL) and Ron Klussman (Colorado School of Mines) each collected soil gas before and after injection, using different techniques.

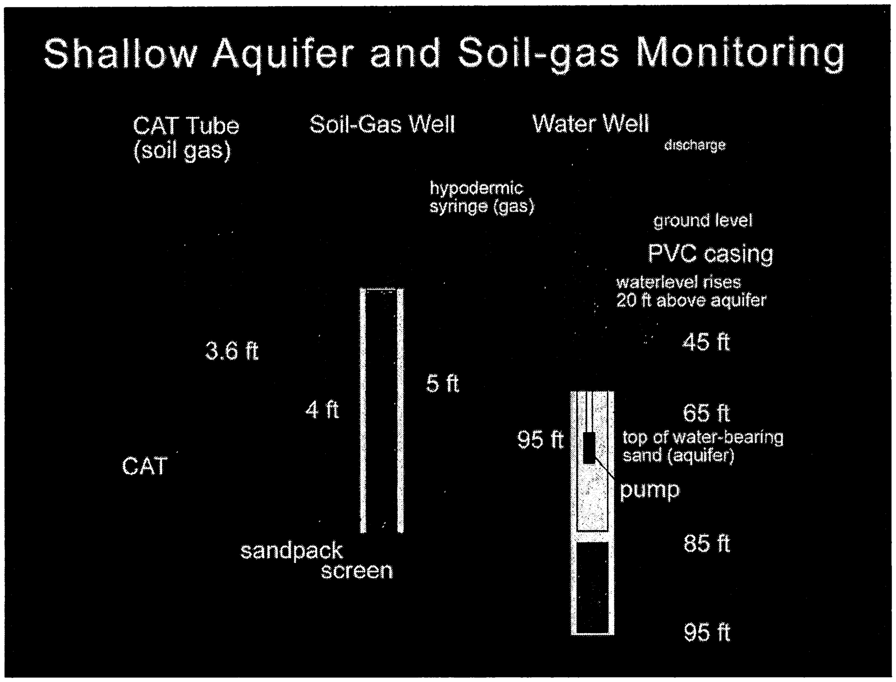


Figure 31. Near-surface monitoring program emplaced three types of wells: CAT tube access, shallow soil gas wells, and water wells. Figure prepared by Seay Nance.

The complexities of the Frio site for surface sampling are inventoried below:

- The subsurface test program required production of subsurface fluids (brine and supercritical CO_2) for analysis for aqueous and gas chemistry. About 26.4 gallons (~100 L) of fluid were produced each sample cycle. Samples were taken from the middle of the cycle, and the head and tail fluids were disposed appropriately; the brine in a frac tank and the gasses by release to atmosphere. This means that significant CO_2 and gas-soluble tracers were vented. This creates a useful setting for testing a tool because a controlled through-well "leakage" source was well quantified. However, the site is not suitable for detection of leaks from the subsurface, as this is not the expected or dominant leakage mechanism.
- The site is near the Houston heavy industry area and within an active oilfield; in this setting a large number of chemical perturbations would exist.
- The soil and aquifer at the site had obvious and significant impact by past oilfield practices such as spilled oil and unremediated mud-pits.
- The water table is high and variable. The site sits on the high terrace of the Trinity River. The river bottoms are seasonally flooded; the drainage in the uplands has been sufficiently disturbed by elevated oilfield roads that the water ponds in upland areas as well.

- The possible leakage scenarios are numerous. One can hypothesize flow paths on minor faults to major faults that reach the surface at various locations in the flooded river bottoms.
- The climate is warm, with high rainfall; there is no dormant season for vegetation or soil microbes in which to obtain a non-biogenic background.
- CO_2 from three different sources was injected by project end, so that no one compositional or isotopic signal can be assumed.

PFT was injected with CO_2 on October 4-11, 2004. Three research groups participated:

- ORNL (T. Phelps) had a focus on subsurface detection breakthrough times in zone.
- LBNL (Barry Freifeld) led the high-frequency sampling effort using the U-tube.
- NETL (Art Wells) had a soil gas detection experiment with CAT sorbents in metal pipes with detachable heads pounded into the ground and sealed at the top (Figure 32).

Figure 32. Soil gas detection experiment with CAT sorbents in metal pipes with detachable heads pounded into the ground and sealed at the top.

CO_2 + entrained PFT tracer was produced throughout the U-tube and then vented to air during injection at rates of about 26.4 gal/hour (~100L/hour). Larger volumes of CO_2 + brine through tubing were vented to the frac tank, where they could easily escape to air, at various times during injection and during post-injection sampling events. Spillage of minor amounts brine was minimized but probably occurred during trips in and out of the wells for recompletions logging, etc.

Significant aerosol release centered on the observation well was documented via CATs that sampled only air (Figure 33). A dominant southern transport is apparent. Soil gas PFT appeared very widely and quickly, which might be an expected effect of purging the atmosphere by frequent summer rain showers.

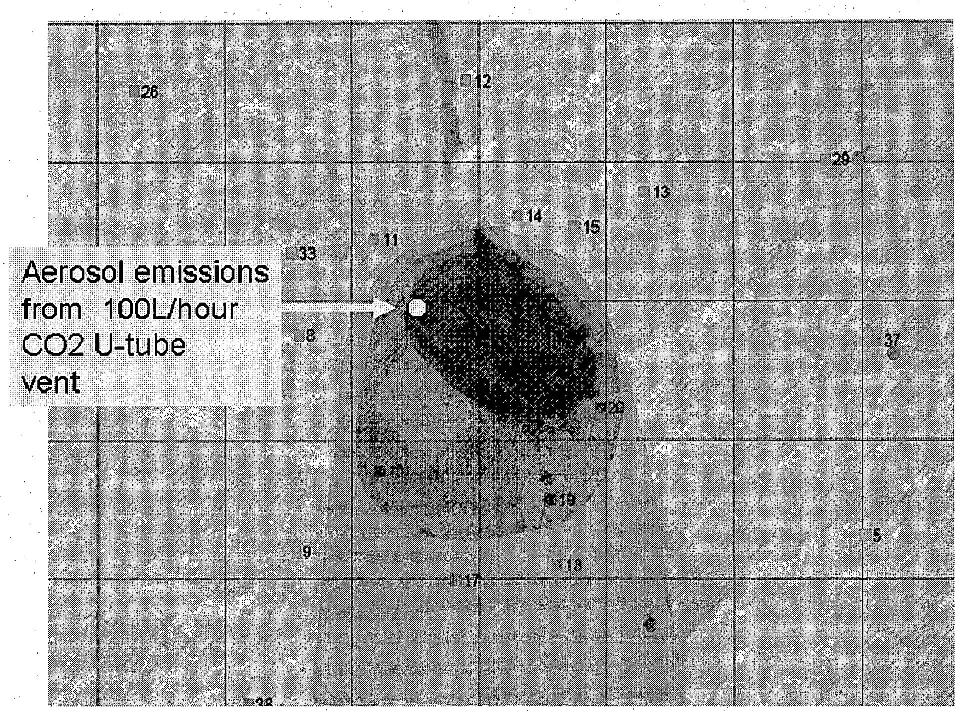


Figure 33. Significant aerosol release centered on the observation well was documented via CATs that sampled only air. Figure from Art Wells and others, NETL, 2005.

PFT was detected widely over the area in soil gas samplers which were deployed in three phases: (1) pre-injection baseline, (2) start injection to end injection, and (3) several weeks of post-injection. High concentrations were found in the soil, north of the test well pad, along the road, and near the well operated by Bill Hill northeast of the site (Figure 34). Slow turnaround on sample analysis as well as contamination by high water table were some of the drawbacks to this method. A subsurface leakage source for CO_2 is not considered a credible source for the soil PFT detections. Subsurface monitoring and modeling suggest that CO_2 with PFTs in the injection zone 5,000 ft (~1,520 m) below surface, had spread approximately radially a distance of < 330 ft (~<100 m) from the injection well at day 11, end of injection, through rock with permeability of >1 darcy. It is therefore not plausible that any of the possible leakage paths along faults, etc., could transmit fluids the greater distance vertically to the surface, a distance of 5,000 ft (~1,520 m) and to horizontal distances of many hundreds of feet (>30 m) where soil gas PFT is recovered. Therefore, it is unlikely that the widespread PFT detection in sample set 2 collected at the end of injection is from subsurface sources.

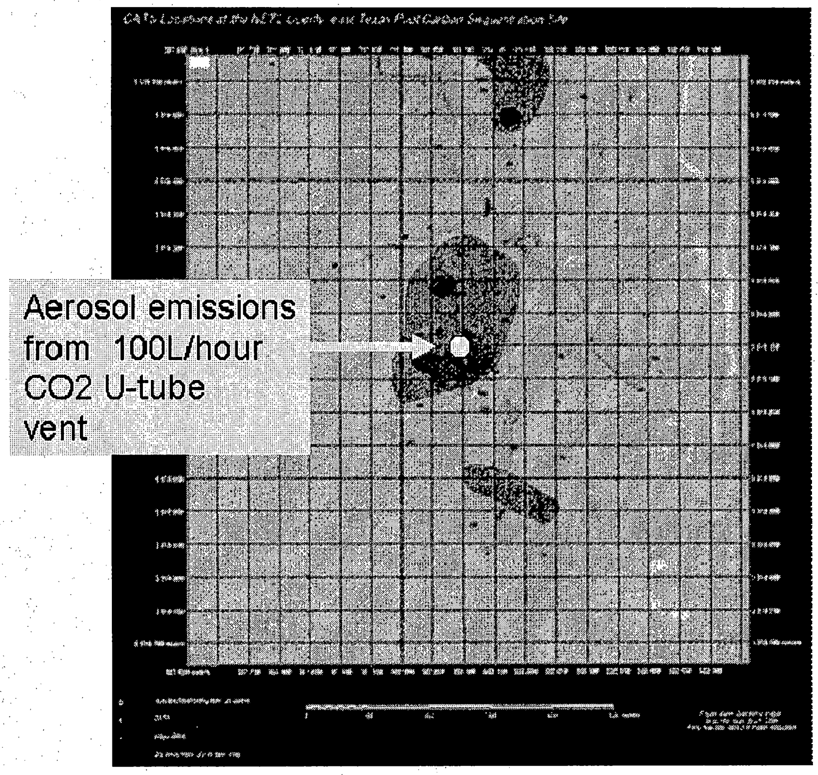


Figure 34. PFT was detected widely over the area in soil gas samplers that were deployed north of the test well pad, along the road, and near the well operated by Bill Hill northeast of the site. Figure from Art Wells and others, NETL, 2005.

Post-injection, the wells were produced to obtain geochemical samples and cement was emplaced during November so aerosol emissions of CO_2 continued. Azimuthal VSP suggests that plume migration is similar to modeled migration of <660 ft (~ <200 m). Thus, it is certainly possible that sample set 3 also reflects aerosol plus possible rain transport. It is highly unlikely that any subsurface transport is reflected by this sample event, and possible but unlikely that an excursion of CO_2 traveled far enough to encounter the Hill well, and then leaked through rock-casing annulus and up hypothesized flaws in the surface casing cement.

No detections were found at sites along surface fault traces. It can only be interpreted that the injection volume was too small and the sample period too short to test for leakage along faults.

When this result was presented, questions remained about possible leakage, so that we considered additional testing as a needed follow-on. In July 2006, Glenn Thompson demonstrated the Praxair "Seeper Test" equipment for PFT detection (Figure 35). This commercial technology, used for finding leaks in pipelines, uses a field-based version of the same sorbents used in the CATS and collects samples of air right above the soil (Figures 33 and 34). Analysis in the field with a tuned and semi-automated gas chromatograph allows scanning large areas for PFT "hits," which then can be verified and localized. The rapid turnaround allows quick response if needed to remediate leaks. High concentrations of PFT found on the road north of the site and at Bill Hill's well area during the NETL sampling were not found 20 months later. This suggests that earlier PFT load from an aerosol release at observation has evaporated and does not contaminate the area for repeat surveys when venting to atmosphere ceased. Concentrations of PFT were found near the injection and observation wells. These were tentatively attributed to drips from PFT-tagged fluids. A high-organic area near the closest producer, the "Brothers" well east of the test site, also produced a high PFT signal, but this is probably because of interaction of PFT and organics, not a leak.

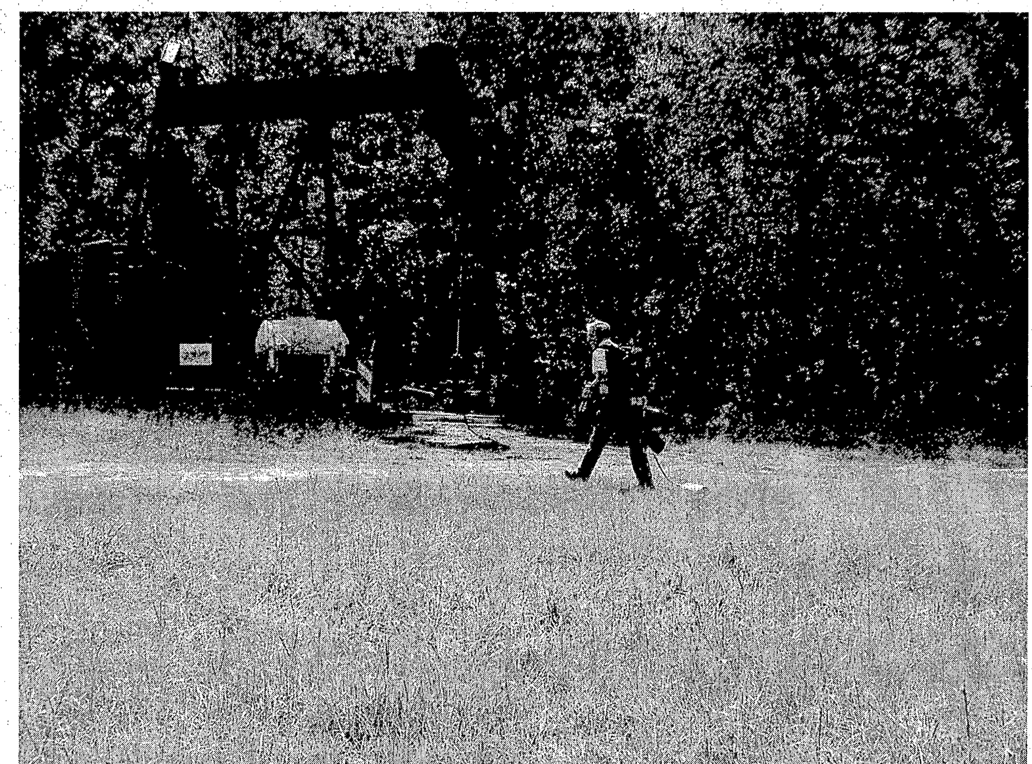


Figure 35. Testing Praxair "Seeper Test" equipment for PFT detection near the Hill well, June 2006. No PFT was detected with an above-ground survey.

A repeat survey on June 8, 2007, with the Praxair "Seeper Test" equipment was conducted after the wells had been idle for an extended period to avoid any contamination resulting from well tools drips at the surface. In this test we followed up the detections on the well pads, looking for increased signal deeper into the subsurface, which would be a leakage signal from the subsurface. PFT was all below detection limit, except for an emission that increased as the day grew warmer; it was traced to escape of heated atmosphere from the observation wellhead "Parker" brand 3/8" OD compression fitting, utilizing a tapered ferrule to affect a seal on the 3/8" OD tube. PFT sorbed onto a wellhead grease pack or metal was outgassing as it heated (Figure 36), showing the sensitivity of the approach and also the limits in an area where PFTs have been injected or produced.

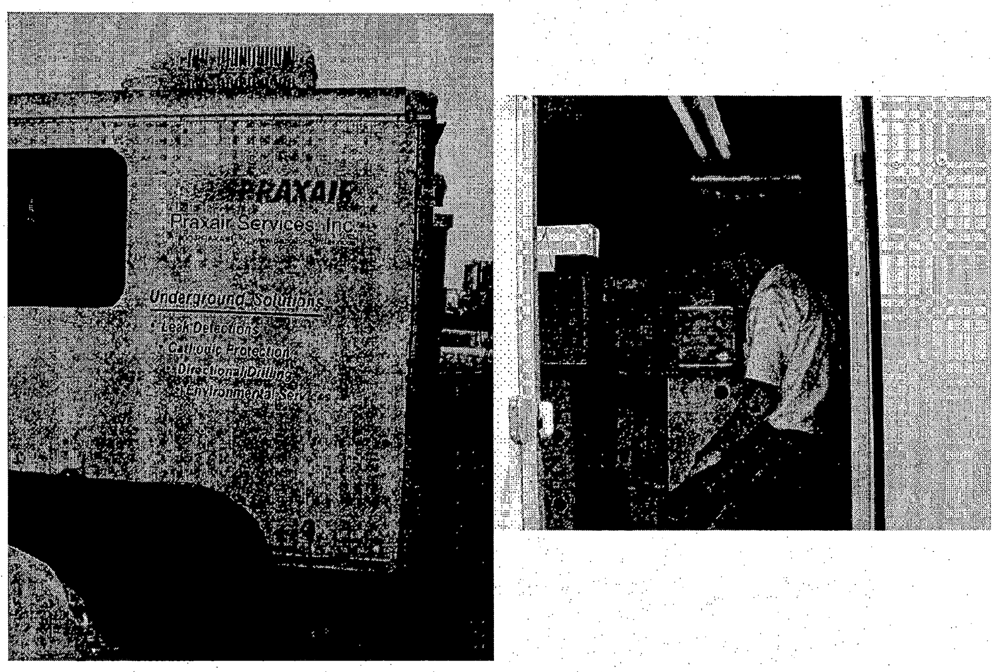


Figure 36. Portable lab for PFT determination in the field was helpful in removing measurements that were not leakage signal.

Geochemical Sampling of the Frio "B" sandstone for leakage

It is our hypothesis that the optimal location to monitor and document any unexpected escape from the injection zone is close to the injection zone, where signal would be strong. We therefore planned to monitor in the first sandstone above the injection zone.

The Frio "C" sandstone was selected as the injection interval, within the general permitted upper Frio injection zone. The top "C" is composed of about 50 ft (~15 m) of mudstone, shale, sandstone, and siltstone. This type of fine-grained zone commonly compartmentalized Frio hydrocarbon reservoirs; we therefore interpreted the top "C" as the effective seal of the injection test. The permitted confining zone for regulatory purposes is the Anahuac shale several hundred feet above the injection zone. Modeling showed that the maximum expected travel distance of 1,600 tons of CO_2 within high-permeability sandstone is a few hundred feet. Thus, we interpreted that the volume injected was too small to reach the Anahuac through porous media even if a flow path existed. The Frio "B," however, could be reached through a flaw in the seal, so we planned out monitoring program to focus on this zone. We note that the remedial squeeze to place cement behind casing (between the rock wall of the borehole and the 7 inch (~18 cm) long string production casing is the most likely leakage point from "C" to "B" (Figure 37). The repair was done to the best practices and standards, and tested first by holding pressure to document that the perforations sealed, then by running repeat USIT log post cement, and finally by conducting a radioactive tracer (RAT) test to determine cement bond. However, because the formation has very high permeability, the RAT might not be sensitive to small leakage behind casing.

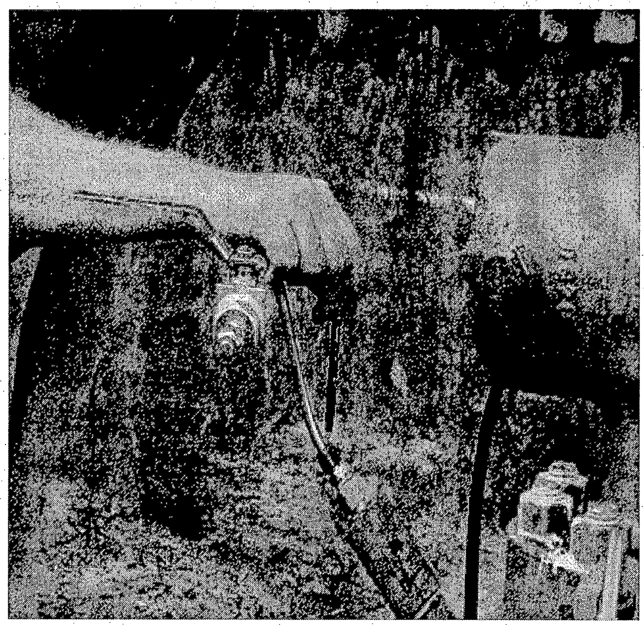


Figure 37. PFT measurement was found to be contaminated within the wellhead packing from earlier activities.

Initial design planned to monitor both "C" and "B" zones at the same time using a sliding sleeve completion. This design would allow sets of perforations to be opened using a tool on slick-line, and using pressure as the dominant monitoring tool, as well as geochemistry. It became apparent that this approach was costly and added risk of downhole component failure, for example, the sleeve sticking sanding up. In addition, the operation of the sliding sleeve would not have been fluid tight, so that contamination of the monitoring zone by fluids containing tracers from the injection zone would occur to some extent. We decided to leave the monitoring zone closed and until post-injection to reduce contamination risk. We attempted to collect baseline fluids under open-hole conditions; however, the "B" sandstone was too friable to allow the sampling tool to get a good sample.

The methods used to monitor the "B" sandstone for cross-unit leakage from the injection zone included RST logging and perforating this interval in the observation well to measure injected tracers, geochemical parameters, and direct collection of any CO_2 gas to look for any evidence of vertical migration of CO_2 and tracers at the end of the experiment 18 months of post-injection in early 2006. The observation well was selected for a proof-of-concept of above-zone leakage monitoring because of the possibility that the remedial cement was not completely tight to CO_2. The "C" sandstone perforation had been cemented shut in the fall of 2004 to collect the cross-well seismic tomogram. The non-corrosive brine in the wellbore was tagged with Rhodamine W-T and perforated at the "B" sandstone using 4,954 ft (~1,510 m) to 4,962 ft (~1,512 m). 28" (~71 cm) entry holes, and 19-inch (~48 cm) penetration, and the well produced by nitrogen lift backflow until tracer diminished to background and the conductivity stabilized. USGS sampled the produced fluid and ran the Kuster sampler to collect a sample at pressure, and analyzed the fluids. Sample splits were sent to ORLN for analysis of PFT.

Repeat passes of the "B" sandstone with RST (Figures 38 and 39) found no evidence of free phase CO_2 in the "B" sand. The sensitivity of detection in the "C" sandstone provides reason to believe that no significant CO_2 plume developed at any time in the "B" sandstone.

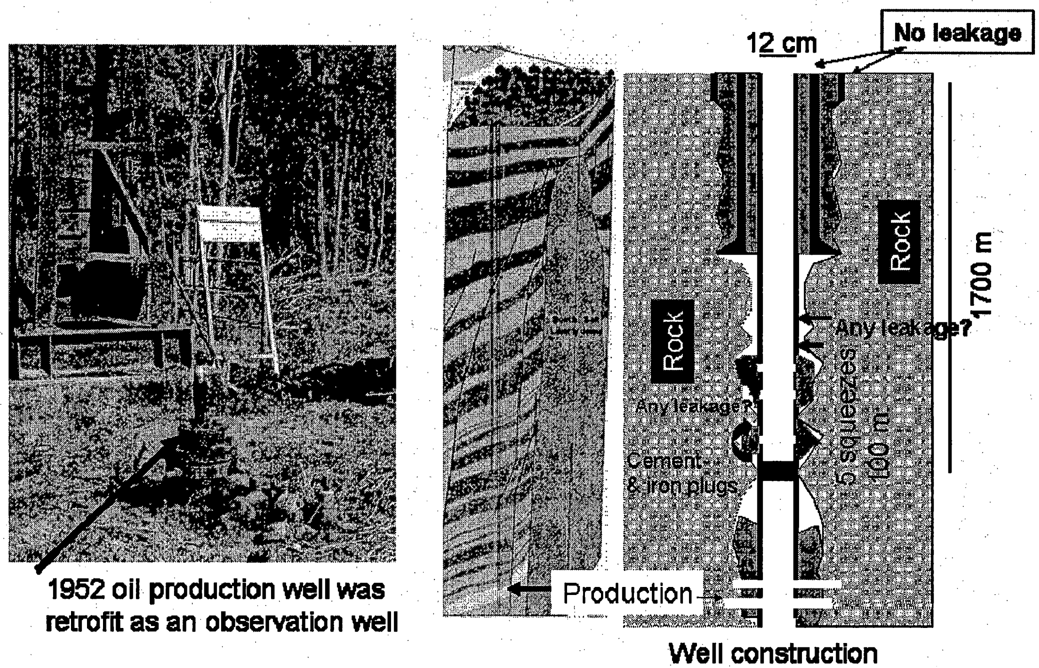


Figure 38. Schematic of possible leakage pathways related to remedial cement squeezes. PFT and possible geochemical evidence of leakage over the lowest blue pathway were identified, which is a proof-of-concept of the technique. Follow-up studies (upper blue arrows) with CHFT and surface measurements detected no PFT.

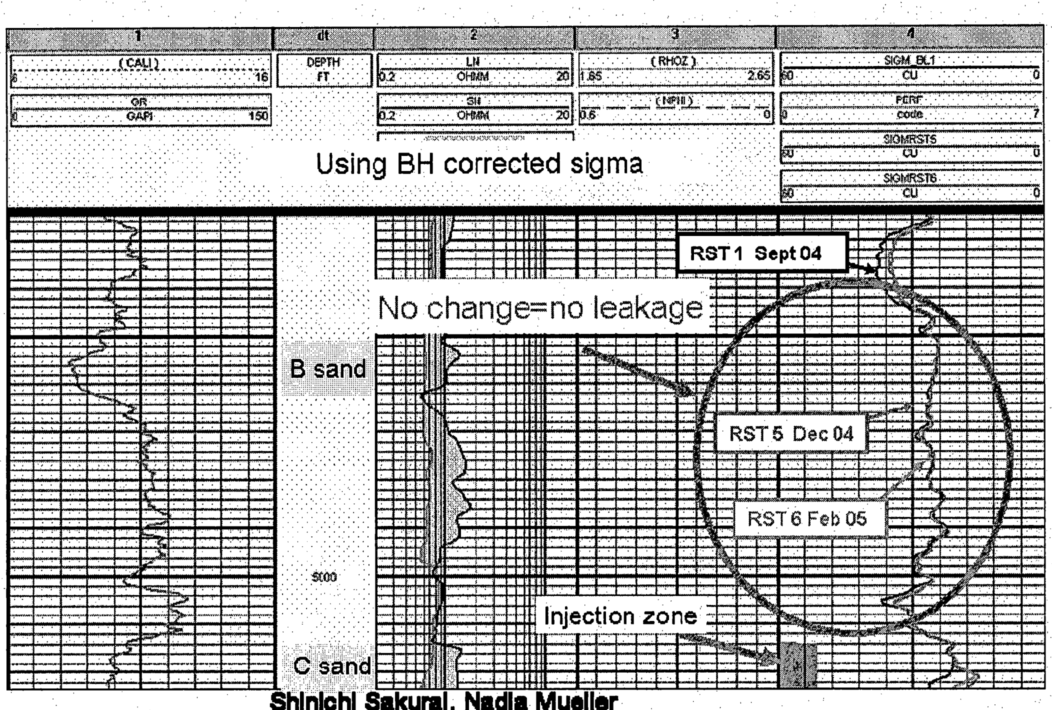


Figure 39. No change in RST was detected during multiple post-injection RST log runs. Data supplied by Shinichi Sakurai and Nadia Mueller.

However, USGS found that the chemistry of the "B" sandstone was slightly offset from the "C" sandstone in the direction that might indicate leakage of CO_2 or CO_2-reacted fluids (Figure 30). In particular, dissolved inorganic carbon and Fe was slightly higher. Since there is no baseline chemistry in the "B", the proposal that this is a leakage signal is based on an assumption that the "B" sandstone was originally geochemically identical to the "C."

Tracers became the most sensitive indicator. Analysis by ORNL used the following techniques. In order to decrease the background signal and increase the likelihood of detecting PFTs the GC was baked for over 30 hours and a GC injection sample volume of 500 µL was used. A 500 µL GC injection is 5 times larger than the volume used for PFT samples collected during the earlier test. The detection limit of the GC was approximately 200 peak area counts, which was > 2x above the baseline.

Sample 109 was collected from the "B' Sand at the observation well. This sample contained low concentrations of PFT, indicating that some type of fluid transfer occurred from "C" to "B". To eliminate the possibility that this leakage was concurrent with the test (from failed squeezed perforations in "C" sandstone), we set a bridge plug above the former perforation and repeated the test, and still recovered tracers, suggesting that the source of the tracer was, in fact, fluids in the "B". Tracer recovery was variable, but generally higher concentrations of the tracers PMCH and PTCH were identified for PMCP and PDCH. This is likely due to the fact that PMCH and PTCH were introduced in the first injection series at concentrations an order of magnitude larger volume than later injections.

Sample 108 collected at the same time from the injection zone in the injection well showed a 65 pg/100 µL PMCP concentration as the maximum reported value. Comparing sample 108 to the last sample collected during the Frio Test (10/12/04 at 4:00 p.m.) shows a PMCP concentration drop from 155 pg/100 µL to 65 pg/100 µL, which represents a 2.4 fold decrease. A second comparison of the PMCP concentration in sample 108 to the PMCP concentration of the breakthrough peaks identified during the Frio test shows over an order of magnitude drop in concentration. Therefore, the highest concentration for the Post-Frio samples is still lower by 2-10 fold compared to samples collected during injection, showing dilution.

The source or amount of the leakage cannot be uniquely determined. The high-risk area and reason for selection of this test area is suspicion that the remedial cement could be leaky to low-viscosity CO_2. However, it is possible that other leaks exist. For example, one can propose a cryptic, non sealing fracture pathway through the top "C" seal, or a conjectured cut-out of the seal by sandstone allowed leakage, or that CO_2 moved asymmetrically toward mapped faults to the east or west of the study area, and that this fault is not vertically sealing, and large amounts of CO_2 escaped to the "B" sandstone. No CO_2 was imaged in the B sandstone in the cross-well survey, so large amounts of free-phase CO_2 were not in this zone in the plane of investigation at the time of measurement. This is another case of how a small detection where detection was not expected can trigger a follow-on study. In a regulatory setting, such an in-depth assessment of the amount leaked might have been required. We could, for example, have tested the "B" sandstone chemical composition and tracer concentration at the injection well and conducted a hydrologic test to assess if any compressible fluids (free phase CO_2) were in the area of interest. However, such follow-on studies were not possible in the budget or required by the scope of this investigation.

If the leakage path was, as suspected, the remedial cement, we can bound the amount of CO_2 to a very small volume, enough to shift the composition of an unknown volume of water and add tracer to the "B", but below the detection limits of the RST. Because small amounts of tracer may have moved up outside the casing we were able to engage NETL researcher Grant Bromhal to conduct a follow-on test that also served as a test of concept. The Schlumberger Cased Hole Formation Tester (CHFT) provides a way to drill a hole in casing, sample a small volume of near well fluid, and plug the hole, bringing the sample to surface for additional analysis. Sampling behind-casing drilling mud the observation well was tested as a proof-of-concept. Samples of drilling mud from behind casing were recovered, and no tracers were detected in the fluid parts of the samples. However, the drilling mud did not yield fluid in some samples because of its design, and these could not be tested for tracer.

Outreach, publication and technology transfer

Public outreach and technology transfer were very important components of the project and were perused with vigor. Contributions include:

- Local outreach to public officials such as the major of Dayton, to Liberty County Commissioners, and to legislators via printed materials, and by an informational meeting hosted by the mayor (no attendees).

- Informal public outreach via informal news updates to local residents, phone conversations, speaking at the Rotary Club.
- Public Acceptance study executed by Rebekah Lee, Oxford University, as a student project.
- Press interviews were sought with the local media and through the Jackson School of Geosciences and UT media contacts. A sample of media coverage is included in Appendix 3.
- The Frio I test was recognized by Carbon Sequestration Leadership Forum (CSLF) because of the multinational research participation (Canada and Australia). This cooperation was in-kind, by hosting research funded internationally to participate in the experiment. This was beneficial because of the excellence of the contributed research, prestige it gave the project, and opportunities for reciprocal participation, mostly as review panelists with international projects.
- Hosting numerous site visitors, such as Don Sherlock, CSIRO, Tsuyoshi Ishida and colleagues (10/18/04), a group from Toyota working on GHD issues (10/19/04), and the geologic working group of the DOE regional partnerships (10/20/04). Press and public were invited to a briefing on carbon issues and a review of the Frio on October 29 at HRC and the site.

2006-2009 Frio II – Injection into the Frio "Blue" sandstone

The second field test was conducted in four steps: (1) pre-injection well work, baseline data collection, and permitting, (2) injection and during injection monitoring, (3) post-injection monitoring, and (4) plug and abandonment. The test also had significant outreach, publication and technology transfer efforts.

The overall goals of the Frio-II brine pilot experiment include studying storage permanence, quantifying residual saturation and dissolution, conducting post-injection monitoring under stable conditions, and studying buoyancy in a thick sand to validate the apparently significant two-phase capillary trapping mechanism. In the Frio II follow-up experiment, we attempted to create an unperturbed, gravity-dominated environment where this property can be better measured. Improvement of modeling capabilities to include full hysteresis of drainage and imbibition will also better reproduce physical processes.

Another uncertainty resulting from a conservative design for fast breakthrough is poor chromatography of dissolved phases. Lowered pH as a result of dissolution of CO_2 into brine in front of the immiscible CO_2 plume is predicted by transport models; however, the observed decline in pH was a complex function, which may be influenced by pauses in injection, by sampling inconsistencies, or by workover fluids. An inline method of measuring pH would improve the measurement of this indicator of dissolution. Tracer was not introduced at the front of the plume because of prediction of instabilities as CO_2 displaced brine in the wellbore and at the sandface, and no tracer was detected in the low pH brine produced before gas phase breakthrough. However, the PFT introduced near the front of the CO_2 plume revealed a sharpened front peak, providing evidence that the higher solubility CO_2 was dissolving into the brine. Slower breakthrough with high frequency sampling for a suite of partitioning tracers introduced at the front of the plume as well as within the devolved plume would help to further clarify the rate and process of dissolution of CO_2 into brine.

Additional research is needed to develop pragmatic methodologies for determining saturation from seismic methods to capitalize on the promise of these techniques for direct measurement of volumes injected.

The Frio experiment was designed to be conservative and to minimize both operation and research failures. Additional experiments to assess risks--such as the interaction of CO_2 and pressure increase due to injection near faults, fluid flow as a result of displacement of brine by CO_2, well completions and other heterogeneities that might serve as areas susceptible to leakage--are needed to move CO_2 storage to a larger scale. Monitoring in the above-injection zone worked well and is worthy of further implementation. As predicted, a more sophisticated surface monitoring system with a long period of pre-injection baseline measurements is needed to separate any potential leakage signal from the natural background and engineered variability.

Characterization

In 2006, the Frio II pilot program conducted a second CO_2 injection into the Frio "Blue" sandstone at a depth of about 5,410 ft (1650 m). The Blue Sandstone in an Oligocene fluvial sandstone that is thicker and more lithologically heterogeneous than the "C" sandstone used for injection in the Frio I test (Figure 40). The Blue Sandstone is high porosity (~34%), high permeability (3-4 darcys) (Figure 41), dipping (11-15 degrees), and has numerous overlying shale seals, including the thick regional confining system of the Anahuac shale at the top of the Frio Formation (Figure 42). Like the Frio I test, the Frio II injection zone is brine-only, no free-phase hydrocarbon or CO_2. The injection area is in a small fault block near the edge of a salt dome. The brine reservoir had pressure of about 2,390 psi (165 bars) and temperature of about 131°F (55°C).

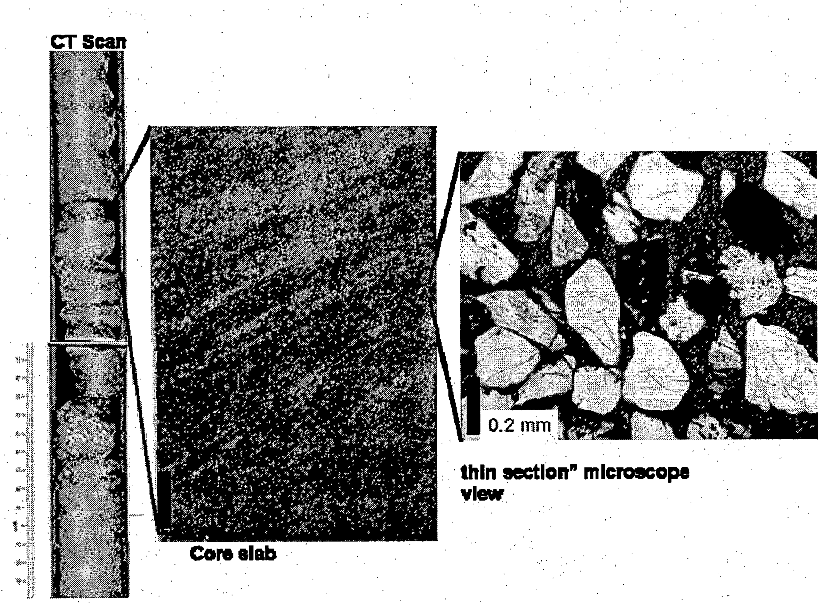


Figure 40. Frio "Blue" Sandstone is a thick and lithologically heterogeneous Oligocene fluvial sandstone. Cross-beds can be seen in CT scan and slabbed core. High permeability is evident in thin section.

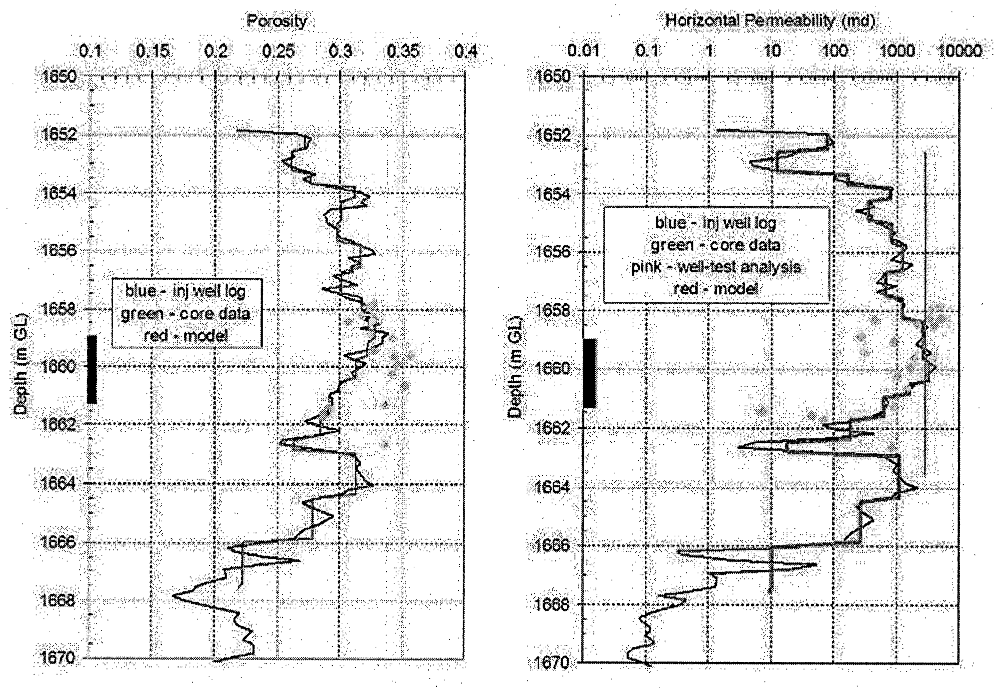


Figure 41. Permeability from log calculations and averages used in TOUGH2 simulation. Figure prepared by Christine Doughty from data provide by Shinichi Sakurai. Note that model inputs did not represent the heterogeneity of the system.

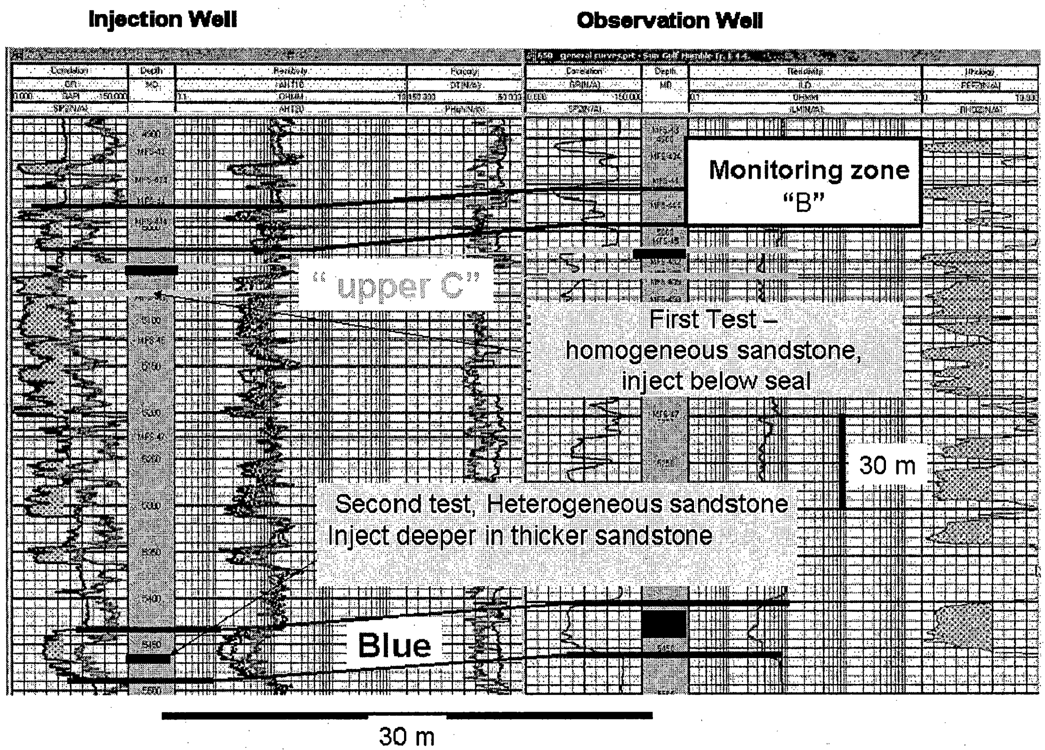


Figure 42. Log cross-section showing the relationship between the Frio "C" and Frio "Blue" Sandstones between the injection and observation wells. Figure modified from Mark Holtz.

Pre-injection well work baseline data collection, and permitting

Starting on July 8, 2006, Five J.A.B., Inc., well services staff working under the supervision of Sandia Technologies began preparation of the observation well and injection well for the deeper injection. The plan required three intervals to be squeezed - the open perorations in the observation well at the Frio "B" Sandstone, the open perforations in the injection well in part of the "C" interval, and leaking cement squeeze in the middle Frio of the observation well. This program required a number of repeat squeezes that had not been planned because cement failed to close perforations sufficient for the wells to hold pressure. Each repeat is a several-day effort: preparing the well and placing cement, allowing the cement to set up under pressure, and then drilling out cement inside the casing and retesting to see if the repair holds pressure. In addition, an unanticipated leak was found in the injection well, possibly related to the cement staging tool that required repair. The extended period of well repair caused cost overruns and set back the time that injection could take place to the very end of the fiscal year. The wells were perforated for an 8-ft (~2.4-m) interval deep in the "Blue" Sandstone in the injection well [interval at 5,458 ft (~1,664 m) to 5,466 ft (~1,666 m)], but over the full thickness in the observation well, because of uncertainty in the likely flow path.

Permitting required only a letter request for an extension on the duration of the Class V permit, which was granted by TCEQ. The Frio Formation had already been permitted for 3,000 metric ton injection, and the Frio "Blue" Sandstone, although a hydrologically separate zone for purposes of the test, was part of the permitted sequence.

Baseline data collection was kept to a minimum because of cost and time concerns. Sandia Technologies performed standard single-phase drawn-down and build-up test over 48 hours, and calculated a permeability of 3-4 darcys in the Frio "Blue" Sandstone between the wells. The samples were also produced to develop the perforations and to remove workover fluids contamination. Baseline RST was run after the wells were completed with tubing-conveyed instrumentation. Since the Blue Sandstone was near the lower part of the wells with only moderate rat-hole below the perforations, and because it is a poorly consolidated formation, we experienced recurrent trouble with sand falling into the wells and covering the perforations.

Injection and during-injection monitoring

A process similar to the one used in Frio I for ensuring safe site operation was used in Frio II. Sandia Technologies gathered contractors to update the Frio I HS&E documentation, and conducted safety reviews at shift starts. Figure 43 shows the timeline of the Frio II test.

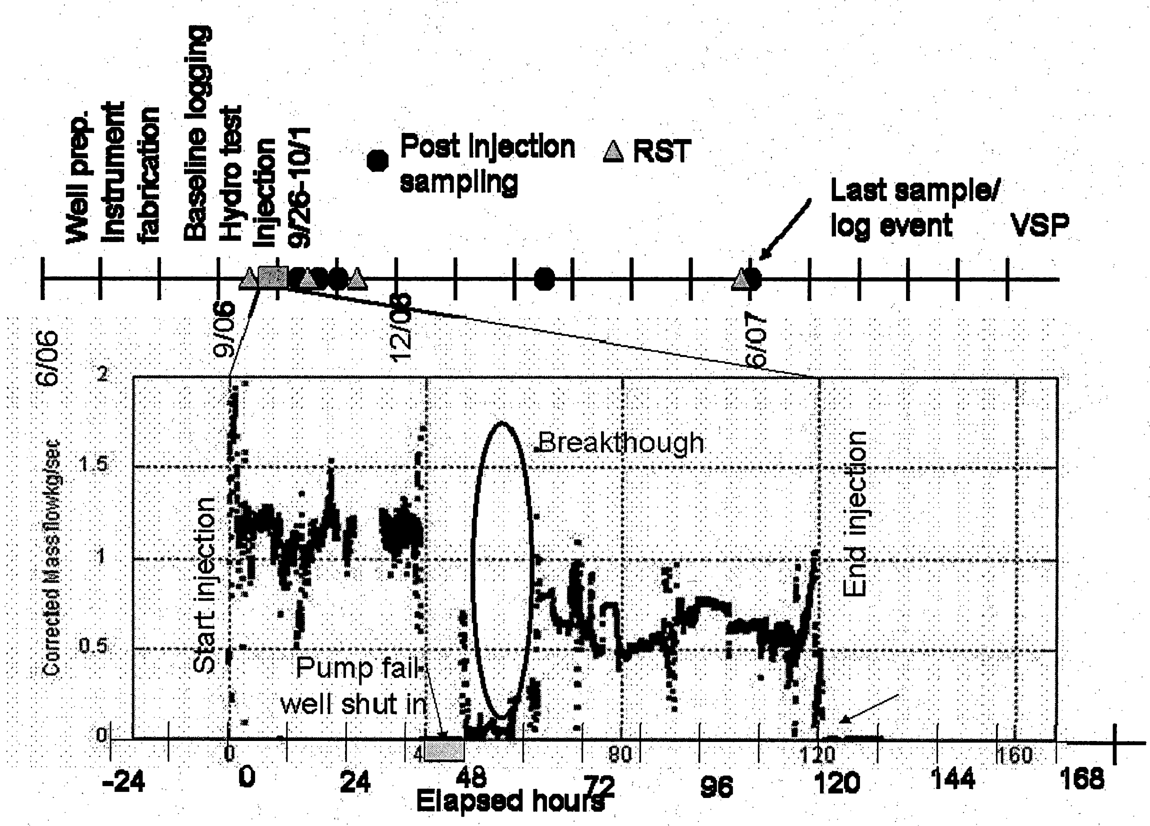


Figure 43. Frio II timeline, with detail of injection.

For the CO_2 injection, packers were set a short distance above the perforations in both wells to reduce attic storage where fluids could accumulate out of equilibrium with the flow system. Downhole Panex pressure and temperature sensors were installed in both wells in the tubing above the packers and open to the perforated intervals and were read-out continuously throughout the injection test. The Panex gauge in the observation well failed shortly prior to planned injection, and a pair of memory gauges on slickline was run into the observation well, and left during the injection period. The synchronization for the gauge is imperfect, as the clock and the time-intervals are not the same as the real-time read-out.

As in Frio I, CO_2 handling was modified from the operations used for conducting CO_2 reservoir stimulation by fracturing using commercial refrigerated liquid CO_2 trucked to the site and stored in insulated reservoirs. For Frio II, to reduce costs, the low bid CO_2 source used was Jackson Dome, Mississippi (a natural source), shipped by rail and overloading onto trucks, and Reliant Gasses provided storage and pumping services for Frio II. As in Frio I, the cold liquid was heated and compressed. For Frio II a coriolis flow meter was added to the gas flow line right before the wellhead. However, the calibration of the flow meter was damaged in the middle of the test because a sudden failure of the pump allowed a sharp pressure drop, freezing, and backflow from the well. Attempts to recalibrate the flow at test end were only partially successful, so that the volume in this test also has imprecision. The volume uncertainty is below the uncertainly of other model parameters in the interwell area (e.g., porosity, effective thickness), so that it does not make the results more uncertain.

As in Frio I Sandia Technologies deployed an Aspen Data Acquisition System for real-time monitoring and recording, and served the data to a password-protected website so that injection could be monitoring remotely. Monitoring downhole pressure and temperature and wellhead pressure in both wells continued until the downhole gauges were removed for cross-well repeat survey. The slow injection used for the Frio II test caused large volumes of CO_2 to be vented at the pump. The same manifold for tracer introduction used in Frio I was rigged up on the flow line a few feet before the wellhead. In Frio II, gas tracers were emplaced into an empty line, which was then filled with either nitrogen or CO_2 and swept into the tracer injection manifold. In all cases enough tracer was injected to get detection; however, a higher precision control on input signal for gasses would be desirable. The tracer tests were designed to have a sharp (1 hour) input, to observe travel time and changes in tracer concentrations at the observation well because of dispersivity.

Packers were inflated, and a high-pressure/low-volume injection pump was rigged up to the casing-tubing annulus to ensure that the 100 psi (~6.9 bar) minimum positive pressure on the annulus was maintained during injection and post-injection observation, using the same system as at Frio I. Near project end, the packer did deflate, and a drop in annular pressure signaled the need for maintenance. However, this occurred at the end of the monitoring period when no upward pressure was on the packer.

As in Frio I, the only evidence of injection was real-time changes in bottom-hole pressure and temperature displayed on the bottom hole gauges vs. real-time readouts. The events downhole could be traced by temperature and pressure responses. Prior to injection, downhole pressure in the injection well injection zone was 2,405 psi (~166 bar) and temperature was 143°F (~62 °C). As in Frio I, the arrival of CO_2 could be followed as temperature cooled when CO_2 reached bottom hole. Downhole pressure at observation well responded immediately, confirming the high permeability measured in single phase. Bottom hole pressure in the injection well increased a maximum of 40 psi (~2.7 bar) during the injection, reflecting the high permeability of the Frio "Blue" Sandstone injection interval

In the Frio II test, as in the Frio I test, a failed seal on a CO_2 compressor pump caused an extended pause during injection (Figure 42). Down-time for repair prior to breakthrough added complexity to the experiment. The timeline therefore includes a period when pumping under pressure stopped and migration continued under differential pressure and buoyancy. This is dealt with in modeling.

U-tube equipment and a crew from LBNL, led by Barry Freifeld and Paul Cook, were again successful in obtaining 26.4-gallon (~100 L) samples at reservoir pressure and temperature from the observation well. In Frio II we added a U-tube to sampler the injection well. During injection, samples from the injection well confirmed tracer saturation. Post-injection, it was planned for the injection well to serve as a second observation point, however the microfilter at the end of the U-tube fractured, allowing mud to be pulled into the U-tube, and clogged it early post-injection. Sampling started at low frequency, and then increased as indications (pH and CASSM) suggested that breakthrough was drawing closer. As in Frio II, real-time data on changing gas composition was collected with LBNL's quadrupole mass spectrometer (MS) in the field. For Frio II, we also deployed a GC supplied by Gary Pope, of UT Petroleum Systems Engineering to detect partitioning tracers, which were detected but with poor resolution. Gas samples are conserved for higher precision lab analysis by LBNL and ORNL. Brine samples were collected from most sampling events and field parameters, pH, alkalinity, and conductivity analyzed real time for evidence of breakthrough in dissolved CO_2. USGS also measured Fe^{+2} and Fe^{+3}, and Liquid samples were also conserved for additional lab analysis by USGS, including in Frio II additional analyses of organics.

The tracer program was conducted. The water soluble tracer injected in Frio II was fluorescein in brine in the injection well ahead of the CO_2 to investigate two-phase behavior near the well. Like Frio I, aqueous tracer was not recovered in this test either. The same tracer cocktails were injected, attempting to produce an hour-long "square" input signal. Combinations of tracers make each pulse unique, so that tracers could be repeated. Figure 44 details the tracer program.

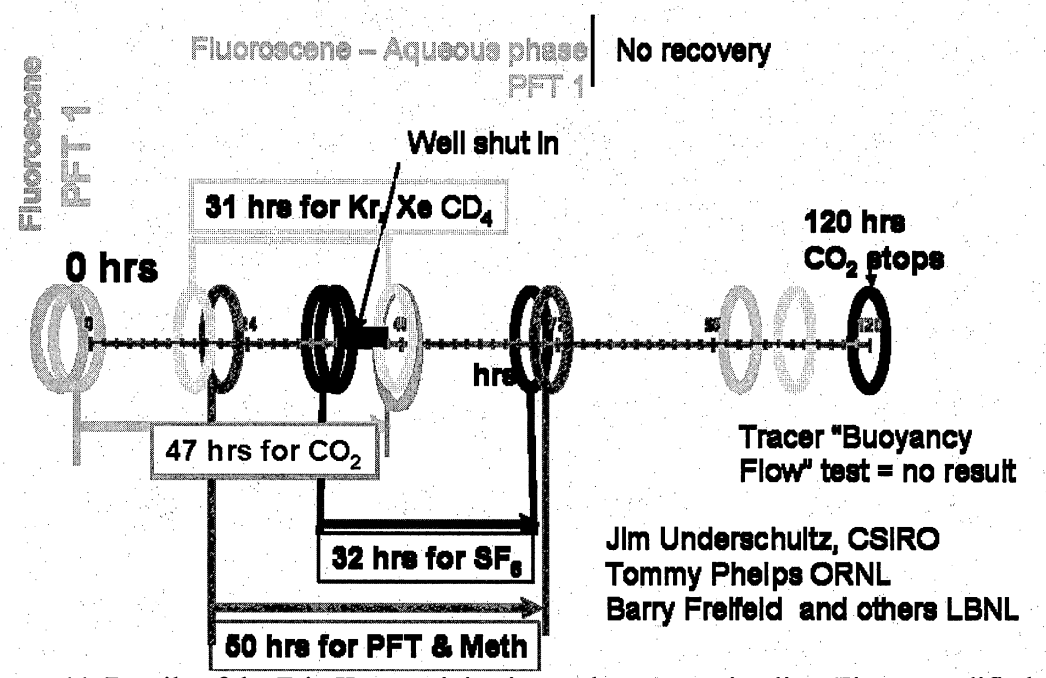


Figure 44. Details of the Frio II tracer injection and recovery timeline. Figure modified from a presentation by Jim Underschulz, CSIRO.

One to two-hour sampling continued on 24-hour shifts. As in the first test, changes accompanying detection of CO_2 "breakthrough" occurred in a number of stages. Frio II's breakthrough period was more prolonged than that of Frio I, and somewhat more complex because of coincidence of flow system with the sampling design. The first CO_2 arrival bypassed the upper perforations, and only after some plume growth by down-building was the supercritical CO_2 sampled. In order to obtain more liquid, the U-tube inlet was placed lower than in was in Frio I, but the Frio II plume remained thin, so that most of the CO_2 sampled was dissolved phase. Similar to Frio I, the earliest signal was warming attributed to displacement of cooled brine near the wellbore by warmer formation fluids moving ahead of the CO_2 and/or some warming by exothermic reaction of CO_2 and water. In Frio II, cooling was the second indicator of breakthrough, attributed to cool CO_2 reached the observation well (Figure 45). The next signal was a drop in pH, indicating that dissolved CO_2 was increasing (Figure 46). In Frio II, it was also unclear if this was (1) a dissolved phase in the pores ahead of or below the immiscible supercritical phase CO_2 as modeled, or (2) a wellbore mixing effect of initial droplets of supercritical CO_2 reaching the perforations and dissolving in the wellbore fluids. The third change measured is increased concentration CO_2 relative to methane measured by mass spectrometer. The next change is recovery of supercritical CO_2 measured by density change in the U-tube weighing chambers. Because of the U-tube placement, supercritical CO_2 was a minor constituent.

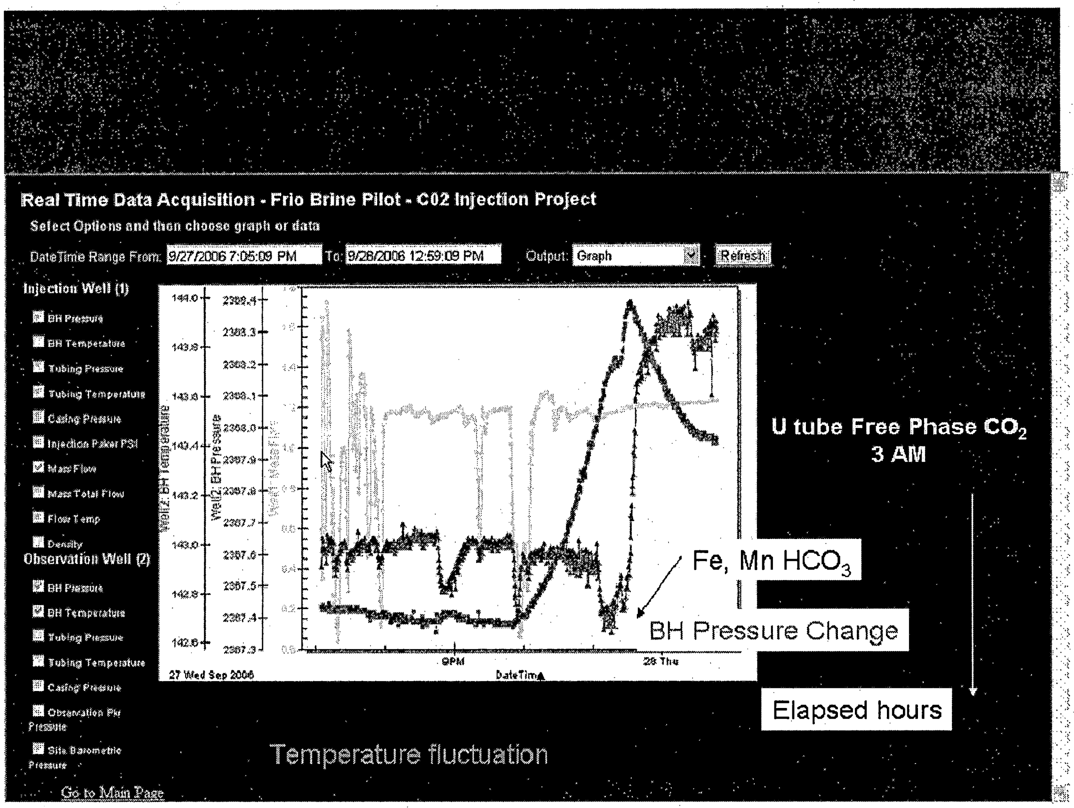


Figure 45. Real-time data acquisition system shows the ~1 degree temperature fluctuation that preceded other indicators of CO_2 breakthrough.

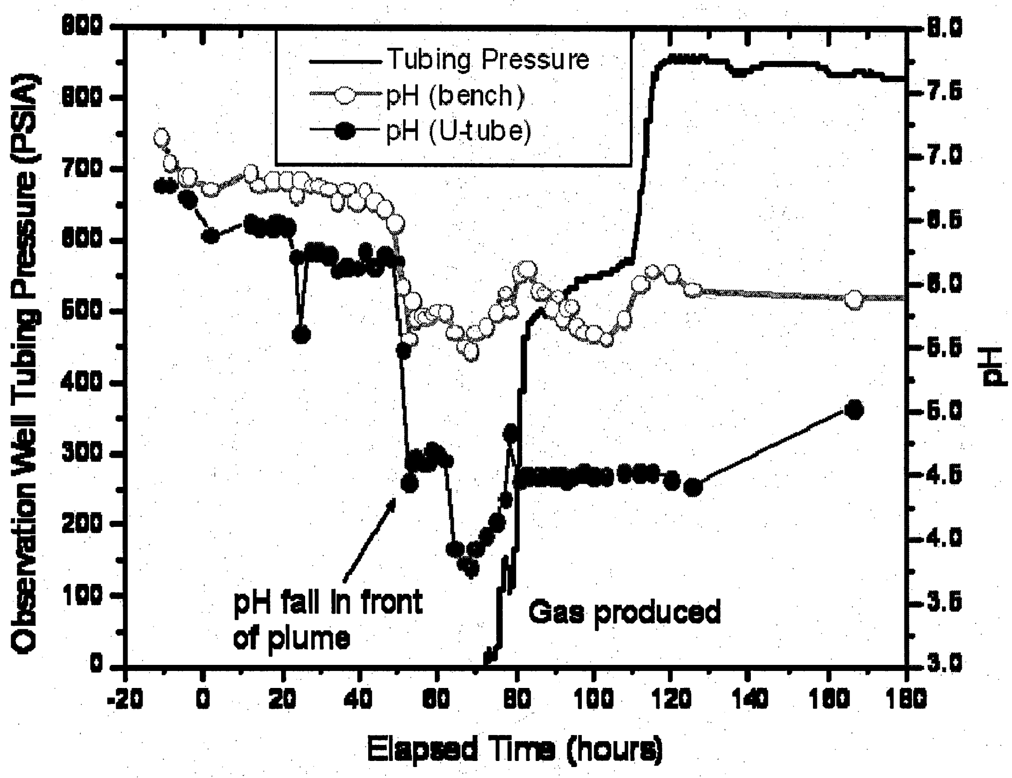
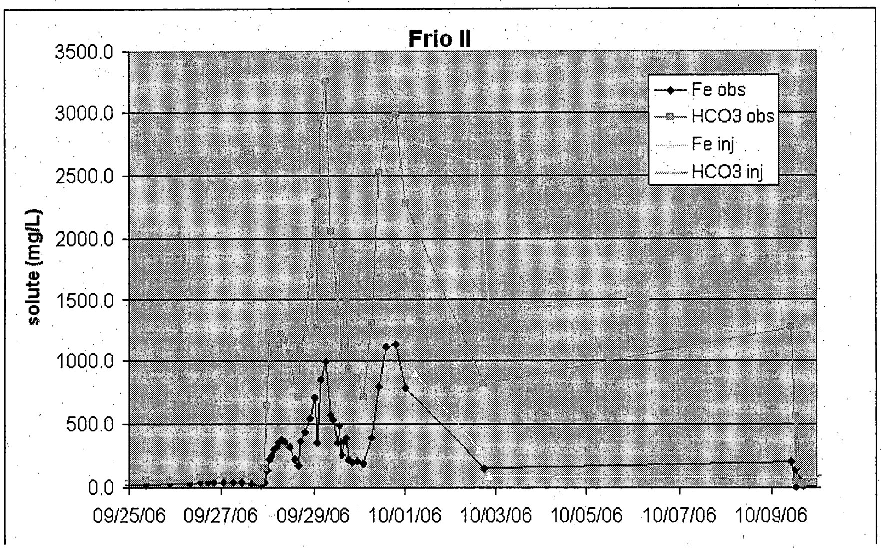


Figure 46. pH of fluids dropped below tubing pressure increases, indicative of free-phase CO_2 inside the wellbore. In line pH in the U-tube gave lower measurements than did out-gassed depressured samples tested in the lab. Plot by Yousif Kharaka, USGS.

In Frio II, the PFT placed at the front of the plume was not recovered, confirming that the first CO_2 bypassed the sampler. Following tracer recovery was good, but the uncertainty regarding how much CO_2 was dissolved was not reduced.

Frio II geochemical analysis showed a sharp change in chemistry at breakthrough similar to the one observed at Frio I, in that pH fell and stabilized. In the Frio II test, the USGS and LBNL purchased an in-line pH meter to make measurements of pressure. Quantification of pH is at pressure is not simple, and the meter showed significant fluctuation during each sample event. pH at pressure was 3.9 (Figure 46). Alkalinity and metals also increased (Figure 47). However, reuse of tubing also added contamination, evidenced in oxygen (from rust) and hydrogen (from reduction). Frio II results clarified the Frio I results, which had not been completely understood.



Yousif Kharaka, USGS

Figure 47. Alkalinity and Fe increased following breakthrough, and then decreased post-injection.

During Frio II, RST was run shortly after breakthrough The Frio II tracer program was similar to the Frio I programs in the use of the same PFT suite and noble gases, but Frio II was augmented by a test of a fully deuterated methane (CD4) conducted by CSRIO in order to support the deployment of this tracer planned for the Otway test in Australia. Figure 44 shows the suite of timing of tracer injected and the time of breakthrough.

We wanted to test the effect of buoyancy in moving the CO_2 through the rock volume and attempt to measure increased residual saturation and greater dissolution. We hoped injecting through a thin perforated zone in the lower part of thick sandstone would favor CO_2 risking through the rock mass during injection radially from the perforations and upward under buoyancy forces post-injection. This movement would maximize rock-water- CO_2 interaction that in turn should maximize a number of aforementioned factors that benefit sequestration. This concept has been developed by Steve Bryant. In addition to benefiting sequestration, maximizing rock-water- CO_2 contact would cause breakthrough to be slower. Because sample time is fixed by cycling of the U-tube, and distance between the wells is also fixed, the way to improve detail on geochemical and tracer indicators of dissolution and residual saturation is to increase the duration of breakthrough to allow better chromatography. We therefore injected slowly at 100 tons/day, in the thickest single flow unit in the interval.

However, heterogeneities within the permeability system offset these efforts, and caused rapid breakthrough. Interpretation of the CASSM ray path intersections and the RST saturation logs suggest that CO_2 first moved outward and upward rapidly along high-permeability flow paths. It then intersected a narrow 2-ft (~.6 m) high permeability unit in the upper part of the interval. Core was not recovered, but the setting, the high single-phase (4 darcy) permeability, and lack of distinctive character on well logs suggests that this is a gravel stringer. The CO_2 then flowed laterally along this narrow zone and arrived rapidly at the observation well with only modest and decreasing rock-water- CO_2 interaction. Further testing should be done to determine how common this tendency is for low viscosity CO_2 to seek preferential flow paths in injection settings. However, it would seem to be a dominant mechanism at plume edges, where large plume circumference leads to low local flow rate.

The CASSM experiment (Daley and others, 2007) was a unique design developed by LBNL that required development of novel instrumentation (including the "piezo-tube" seismic source). LBNL has applied for a patent on this source. The continuous monitoring of cross-well seismic response provided information on the spatial and temporal variation of the CO_2 plume as it migrated. A seismic monitoring experiment such as the Frio-II CASSM generates gigabytes of data, which were processed and analyzed in various ways. The initial and primary data set is cross-well travel time change (delay time) as a function of calendar time (Figures 48 and 49). The CASSM data, with 15-minute sampling, combined with U-tube fluid sampling on 1-2 hour intervals, provide key constraints on CO_2 flow in the brine reservoir at scales not previously measured.

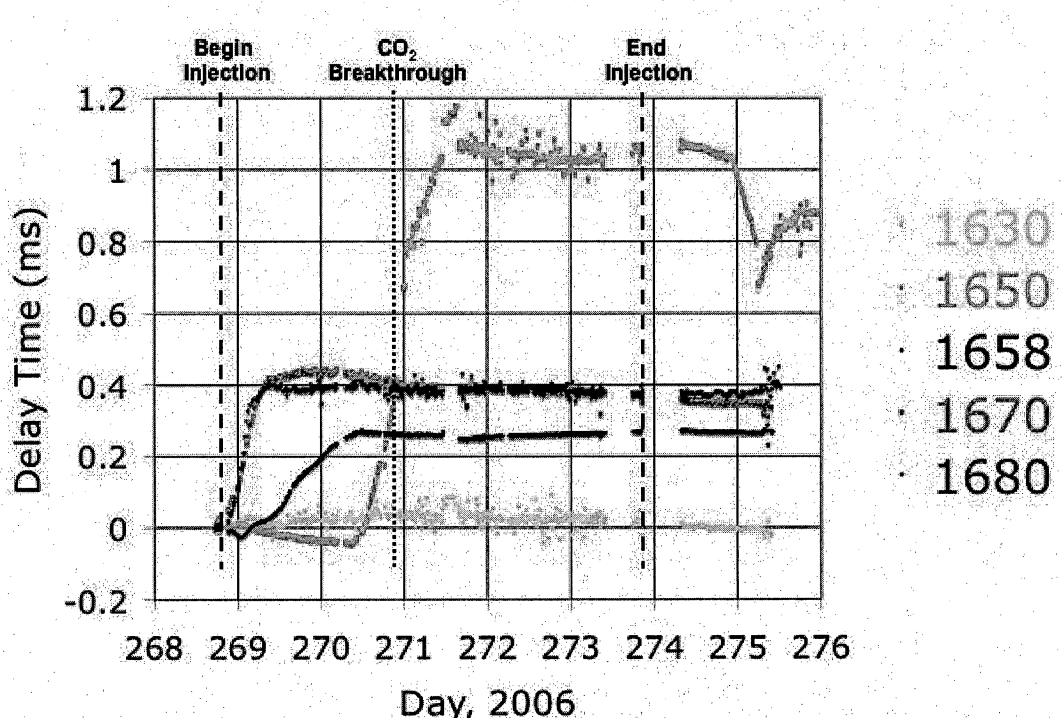
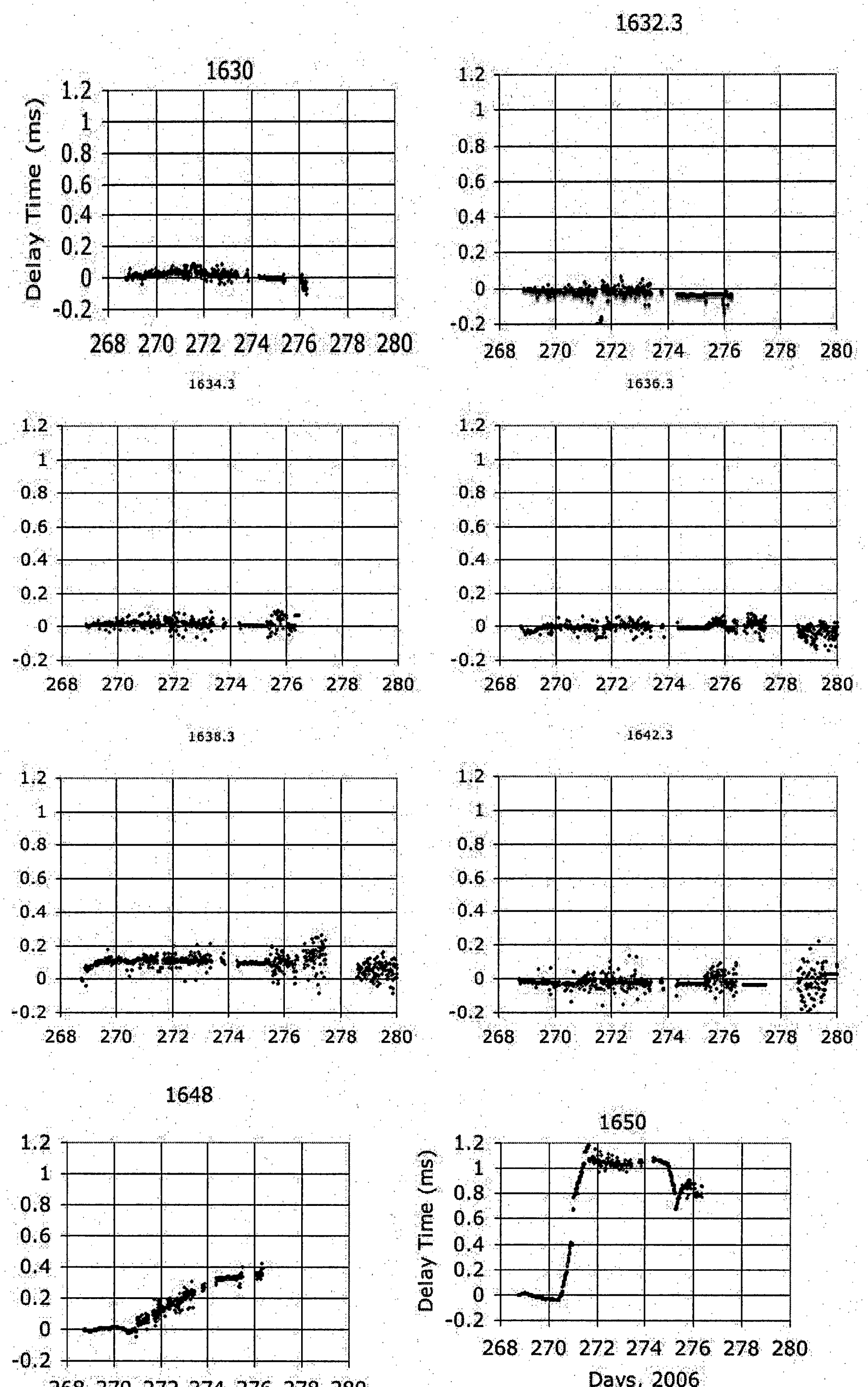


Figure 48. Delay time measurements for five sensor depths. Change in delay time is assumed to be caused by the change in CO_2 saturation and/or plume thickness. No change is seen at the shallowest control depth 5,348 ft (~1,630 m), whereas the other depths show progressively later increase in delay time with decreasing depth, thereby monitoring the upward movement of the CO_2 plume.


1630
1632.3
1634.3
1636.3
1638.3
1642.3
1648
1650
Delay Time (ms)
Days, 2006

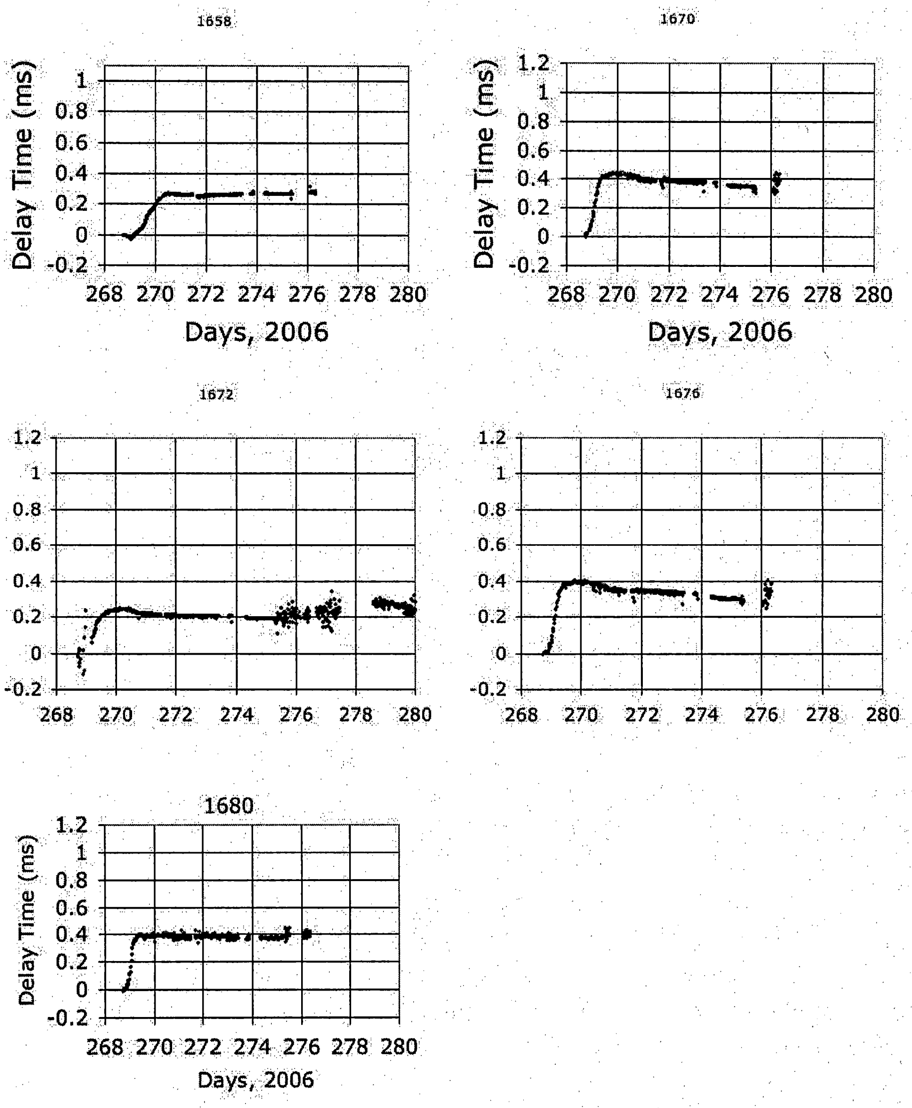


Figure 49. Plots of delay time (change in seismic cross-well travel time), in milliseconds, for the CASSM experiment over about 8 days in 2006. Depth of sensor in meters is labeled at top of each plot.

The response for each sensor is affected by heterogeneity along the source-sensor raypath with the amount of delay time observed being affected by CO_2 saturation and thickness of the CO_2 plume along a raypath. Nonetheless, sensors above the reservoir 5,348 ft (~1,630 m) to 5,387 ft (~1,642 m) have essentially no change, while the top reservoir sensors 5,407 ft (~1,648 m) and 5,413 ft (~1,650 m) have later and larger change, and deeper sensors have earlier change. Notable events, as shown in Figure 49, are beginning injection at day 268.8, observed breakthrough (via U-tube sample) at day 270.9, and end of injection at day 273.8.

Gas splits were collected and a portion was analyzed onsite using a quadrupole mass spectrometer (MS) (Omnistar, Pfeiffer Vacuum Systems) (Freifeld and Trautz, 2006). Qualitative breakthrough elution curves for PFTs, Kr, and SF_6 were also analyzed using the field mass spectrometer. Gaseous splits were collected on site by Jim Underschultz from CO2CRC.

During Frio II, CD_4 was used for the first time to our knowledge as a tracer in the subsurface. Perdeuterated methane ($^{12}CD_4$) is the end-member isotopologue of $^{12}CH_4$ and, as such, offers the best gas chromatographic (GC) resolution from methane. CD_4 is GC baseline-resolved on a molecular sieve GC capillary column when doped in CH_4 with a GCMS detection limit of 0.05 part per billion volumetrically (ppbv) (signal-to-noise ratio of 2 for m/z 20.06 at 1,000 resolution), which is similar to the sensitivity achieved by MS-MS (Mroz and others, 1989a). CD_4 has been used sparingly in airborne-based studies (Mroz and others, 1989b; NPS, 1989) where the extremely low natural level of CD_4 at $1.3*10^{-16}$ volumetrically (Mroz and others, 1989a) offers minimal "background" in mass spectral detection. Sixteen hours after the commencement of the CO_2 injection, CD_4 (27 g) was injected as a front to ~100-fold excess of Kr and Xe. At the monitoring well, 30 m up-dip of the injection well, Xe unexpectedly arrived with CO_2 breakthrough 48.3 hours after CO_2 injection began, but only 31.9 hours after the injection of the tracers (Figure B4). The first gas sample for CD_4 analysis was taken after another 9.4 hours while the last sample was taken at 207.2 hours after CO_2 injection. Maximum CD_4 concentrations (up to of 92 ppbv) were observed between 57.7 and 69 hours. The CD_4 concentration elution profile follows closely that of Kr and Xe (not shown), suggesting very similar migration pathways for CD_4 and the noble gases between the injection and the monitoring wells. Despite the narrow injection pulse for CD_4, it was still detectable 1 week after introduction at concentration levels of a few to sub-ppbv, indicating dispersion.

Initial modeling with TOUGH2 was used to guide the design of the Frio II experiment (Figure 50). The expected plume growth, based on well log and core information from the injection well did not capture the true response of the injected plume. A semi-quantitative inversion (Figures 51-53) designed by Sally Benson shows a likely flow path through highly heterogeneous rock volume.

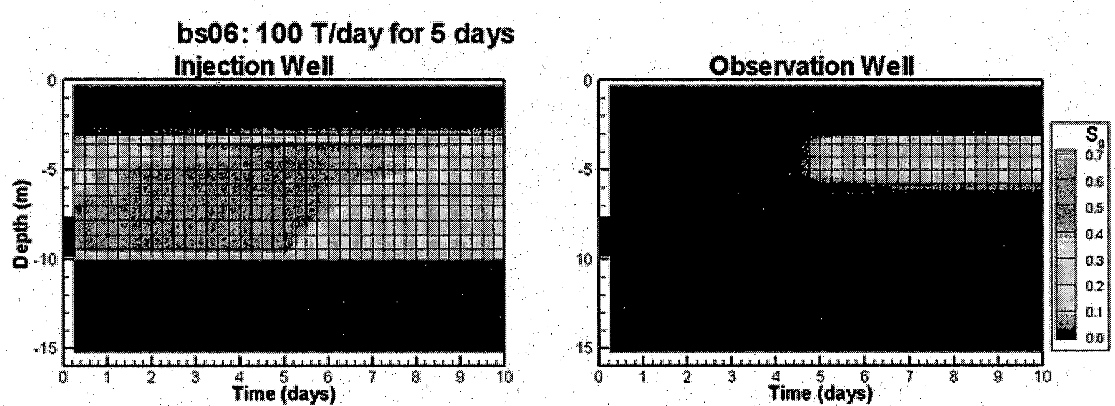


Figure 50. Pre-injection TOUGH2 model by Christine Doughty predicted that vertical flow would be important and that significant volumes of rock would be contacted to give a 5-day breakthrough time and a thick saturated interval.

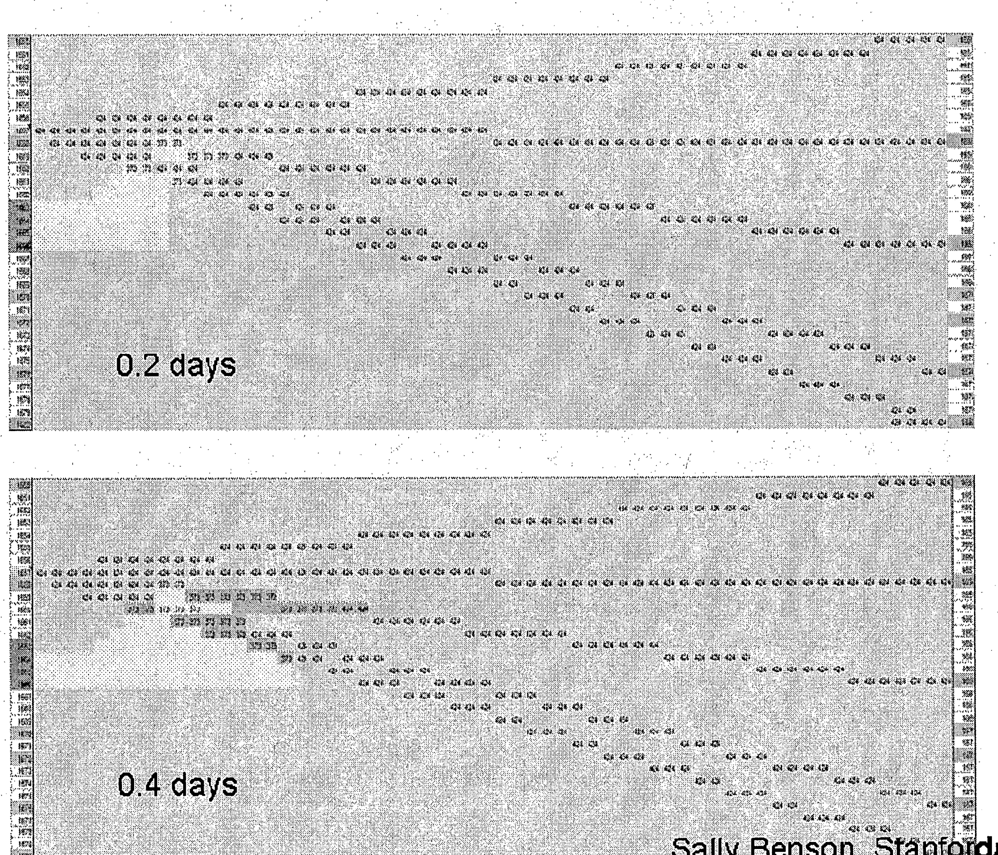


Figure 51

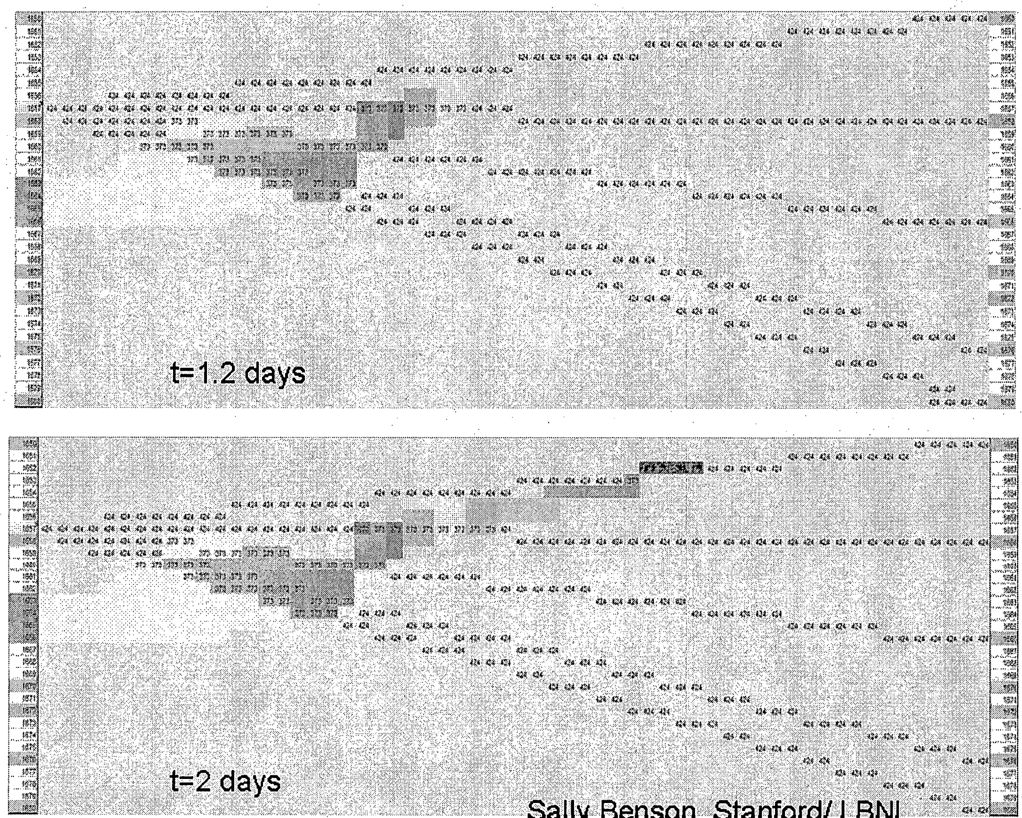


Figure 52

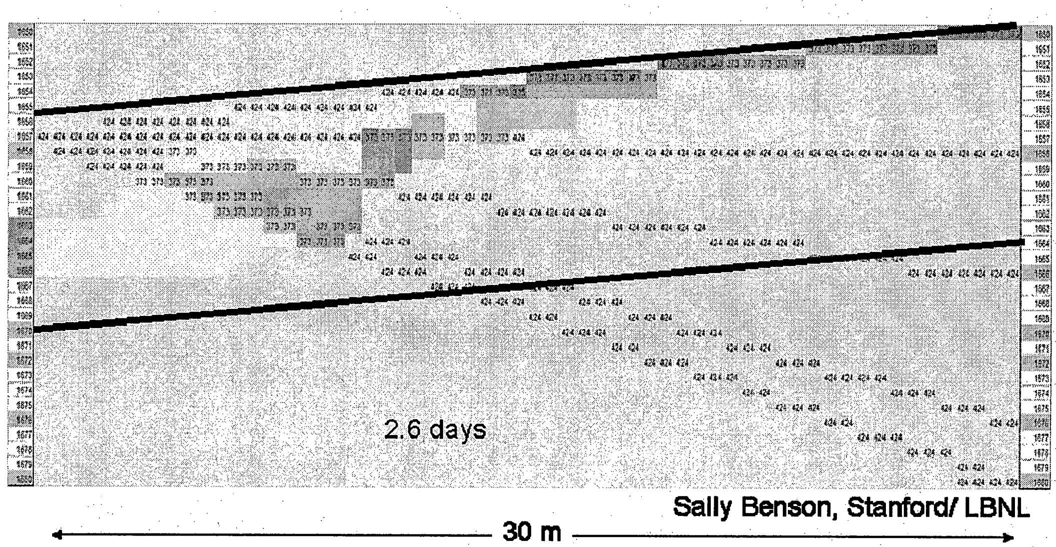


Figure 53

Figures 51, 52, 53. Time slices through a semi-quantitative inversion that matches volumes and times of breaking the cross-well CASSM raypaths. Slices show a likely flow path through a highly heterogeneous rock volume that matches the observed fast breakthrough. Figures by Sally Benson.

Post-injection monitoring

Post-injection monitoring of the Frio II injection followed the same general pattern as that of the Frio I, with sampler frequency diminishing over time. The number of RST runs was curtailed because of cost overruns, and the final runs were incomplete because of sand that would not allow tool access in the injection well and packer failure in the observation well that contaminated the zone with fresh water. The receiver string of the CASSM developed electrical shorts to ground and gradually stopped working shortly after the end of injection, so that the hoped-for long stabilization was not observed. On October 26, 2006, LBNL shut down the acquisition and brought the computer and acquisition system back to the lab. The source and receiver array were left in the wells, rather than being immediately retrieved, to allow long geochemical and saturation equilibration.

Geochemical sampling of Frio II fluids

Starting on June 19, and ending late on June 21, 2007, David Freeman (Sandia), Lynco personnel (operators), and Jim Thordsen and Yousif Kharaka (USGS) obtained five good water and gas samples from the injection and observation wells. Because of fluid mixing due to possible failure of the packers in the injection well, we monitored the water chemistry while swabbing. We took our surface sample after the chemistry was constant and after about 50 bbls of water were produced. The well continued to flow, driven by the CO_2 pressure, but was killed by shutting it down, and ultimately slowly releasing the gases at well head. We obtained a Kuster sample from the observation well on June 19 as well, then we swabbed about 12 bbls of water and sampled it again (Kuster) on June 21. As expected, the specific conductance and alkalinity were a little higher for water from the injection well; the specific conductance was comparable before and after swabbing for the observation well, but alkalinity was about 5% higher for new formation water after swabbing.

Well integrity and equipment durability

The Frio test was designed to be a short-duration study, so ordinary materials, including steel casing and tubulars, Class H cement, and a retrofit 1952 production well, were used. In order to collect minimally perturbed data, we did not use any of the commercial corrosion inhibitory methods that are available. In effect, we considered the well and equipment expendable. The experiment was extended to a second injection and a sustained period of monitoring. As a result, we have an inventory of corrosion and equipment failure data that can be used in other studies and risk assessments.

Data include:

(1) USIT before and after Frio I and post Frio II USIT:

(2) Sondex 36 arm caliper tool log during pre Frio I workover

(3) Data on tubing corrosion at the end of Frio I that developed under idle conditions between January and May 2006 - photographs, mechanical data.

(4) Data on additional corrosion of used tubing in May 2007, after 3 years of hard service (many reentries, production, etc). The elastomers in inflatable packers were damaged by contact with high CO_2, and we will try to use mechanical packers for future experiments because of greater durability. This shows that the durability of standard materials even in wet, high-CO_2 environments is substantial. Longer integrity could likely have been obtained by well management, and even longer durability by seeking corrosion- resistant materials, which we are doing in following experiments planned for longer duration.

The observation well U-tube was fully operational and facilitated sampling throughout the course of injection (at 1-2 hour intervals) and in the weeks and months following. Shortly after the conclusion of the active injection phase of Frio II, the injection well U-tube had a downhole failure. This was initially noted because coarse sand was able to travel up the U-tube, indicating that the sintered metallic inlet filter had experienced a failure. While an exact cause of this failure has not been determined, other observations of deterioration indicate that the CO_2/brine environment may have contributed to premature failure of the weld that attaches the sintered metallic filter inlet to the solid sampling tube. The other observations of deterioration include a 0.2 inch (~.5 cm) hole in the injection tubing at a 3,640-ft (~1,110-m) depth, along with 12 pinholes discovered in the observation well stainless steel U-tube sampling lines between 4,490 ft (~1,370 m) and 5,479 ft (~1.670 m).

The CASSM experiment ended about a week after injection ceased due to failure of a downhole electrical connection within the sensor string (deployed in the observation well). Additional information regarding the response of the instrumentation material to long-term deployment was obtained when the system was removed from the wells in July 2007. The sensor cable's downhole electrical connection used a buna-N (nitrile rubber) O-ring, which was the likely cause of failure. Another potential cause is small nicks in the O-ring sealing surface that were observed before installation. The cable itself was polyurethane which survived; however, part of the hydrophone outer mould, which was not polyurethane, had significant damage, apparently due to long-term exposure to CO_2-rich fluids. The seismic source cable was a standard coaxial cable with an additional polyurethane outer jacket. Upon removal from the injection well, a cut was observed in the outer jacket that allowed well fluid, including CO_2, to penetrate between layers. However, the source cable maintained its electrical integrity during the injection and this cut may have occurred during removal.

Closure

The Frio test was designed to be an early success for the DOE program. Several factors aided in completion of this success. The test was designed as an experiment, not designed to continue at this site to full scale. Completion of this experiment would then accelerate deployment in many other sites in the US as well as promote advanced utilization of similar Frio and other Gulf Coast sandstones in the region, which it has done.

The site was selected to allow the experiment to be conducted rapidly and at low cost. Cost containment led to selection of experiments that could be done with a small volume of CO_2 injected. We also selected to work within an oil field setting, where roads, well pads, and wells were available, and to use a shallow injection zone above production, so that the reused observation well would not have to be deepened. We selected a small, steeply dipping fault block adjacent to a salt dome, where CO_2 could move under gravity so that stabilization could be tested. These characteristics, desirable for this experiment, make the site undesirable for a large-volume sustained injection. In a large test, the area of pressure increase and area of the CO_2 plume would include many historic wells that penetrate the Frio test interval; each of these wells would have to be assessed to determine that they would not leak. Further, the compartment is sealed to pressure on at least three sides, and might become overpressured relatively quickly, making it a relatively non-ideal setting. Large volumes of CO_2 would migrate to the top of the structure against the salt. Oil, but not gas, was produced from the Frio at this setting, raising a question of whether the updip seal was transmissive to gas. This uncertainty would require relatively difficult site characterization. At the time of the experiment no long-term source of CO_2 was in the in the immediate area, so CO_2 had to be shipped by truck. After the experiment ended, the Denbury CO_2-carrying Green line was sited nearby.

The Frio wells were constructed for a 2-year lifetime, and they were actually used for 5 years. We did not design to protect the steel casing and standard Class H cement from corrosion by CO_2-saturated brine because this would perturb and complicate interpretation of experimental results. Such protection is standard in commercial CO_2 production and injection wells. However, at the end of the experiment, we felt that damage to the steel probably prohibited further use.

Plugging and abandonment of the observation well was delayed by a hurricane that came through the site area, but following resumption of normal activities, the well was completed on September 29, 2008. Texas American Resources completed a plugging and abandonment report to the Texas Railroad Commission. Plugging and abandonment of the injection well was deferred until completion of the final research tasks, collection of a third repeat VSP by LBNL, which was started on May 11, 2009, and completed on May 19, 2009. Analyses of these results are reported separately by LBNL.

The injection well was plugged and abandoned to TCEQ specifications and site returned to landowner specifications on May 22, 2009. Sandia Technologies submitted a closure report to TCEQ on June 17, 2009. TCEQ completed the review of the closure report on October 6, 2009, and noted, "The UIC staff has found that the closure has met all the requirements of 30 Texas Administrative Code (TAC) Chapter 331 including the Class V well plugging standards of 331.133" (written communication, Bryan Smith, UIC Permits Team, October 6, 2009).

Discussion

The Frio Brine Pilot experiment was a first-of-its-kind field investigation into the feasibility of modeling and monitoring CO_2 injected into brine-filled sandstone to assess the permanence of the storage. The experiment differed from the geosciences and engineering communities' extensive previous experience in injection of CO_2 and other fluids into the subsurface in that it was, from inception to completion, focused on assessing monitoring strategies. An important product of this study is a list of recommendations to the next generation of developers of geologic CO_2-injection-pilot projects, which is summarized in this paper.

To provide a strong test of the capability of monitoring, we assembled a diverse team of experts from the GEO-SE consortium (Lawrence Berkeley, Oak Ridge, Lawrence Livermore National Labs), National Energy Technology Lab, U.S. Geological Survey, Schlumberger, Alberta Research Council, CO2CRC-CSIRO, Core Labs, University of West Virginia, and The University of Texas at Austin, Department of Petroleum Engineering and the Bureau of Economic Geology, the lattermost serving as the Texas State Geological Survey.

The pilot site was selected to be a pragmatic demonstration from which results could be scaled up to support very large injection projects. The area chosen was the Tertiary age Frio Formation of the Gulf Coast of Texas, USA, which is a large-volume, regionally extensive sandstone that underlies many industrial and power plant sources of CO_2. This geology is generally typical of clastic wedges on the trailing margins of many continents. The Frio Formation has the additional advantage of being well studied as a result of a century of exploration for oil and gas and decades of successful use as a waste-injection horizon. The high-permeability (more than 2 darcy), high-porosity (as high as 35%), mineralogically immature, marine-reworked, fluvial sandstone unit selected has a steep dip of 16°, with multiple shale seals to ensure permanence of storage.

Successful monitoring strategies we consider worthy of duplication in future demonstrations and large-scale injection are: (1) high-quality characterization prior to injection, (2) numerical modeling integrated with all phases of the project, (3) cross-comparison of multiple types of measurements, (4) use of wireline logs for monitoring plume movement, (5) data collection focused on selected azimuths, (6) above-zone monitoring for leakage, and (7) traditional groundwater monitoring for leakage.

Characterization was essential in providing qualitative data to models (Hovorka and others, 2000; Vendeville and others, 2003). We used mostly traditional oil-reservoir and disposal-well reservoir characterization techniques. However, some innovative approaches, such as extensive pre-injection hydrologic characterization, proved informative (Trautz and others, 2005; Freifeld and others, in press).

Numerical models of flow guided site selection, well design, and tool selection and were integral to designing a successful project, as was analyzing interpretations of results. Input of predicted reservoir conditions after injection from TOUGH2 (Hovorka and others, 2004) was used in calculations to test tool performance. Model predictions also resulted in revisions of engineering design and experimental timelines. Redesign eliminated tools with low probability of success or those that could not be effectively implemented under experimental conditions and substituted tools that could accomplish required tasks.

Cross-comparison of measurements made using different techniques provides a critical check on precision and accuracy of measurements. For example, we measured plume evolution using direct sampling of fluids (Kharaka and others, 2007, 2009) and breakthrough of a suite of gas-phase tracers having different solubilities (Sakurai and others, 2005) with saturation logs, cross-well seismic, and VSP (Daley and others, 2005). However, it was impossible to create optimal conditions for each instrument in a single test; compromises were made and success depended on making thoughtful compromises.

Geochemical issues- new results and future tests

Fluids injected into subsurface environments must be assessed to determine how they interact with the pre-existing rock-water system. Therefore, for CO_2 rock-water-CO_2 interactions must be critically assessed to ensure that the net effect is acceptable in terms of favoring long-term storage and isolation of resulting CO_2-brine fluid systems from groundwater resources and from the atmosphere. Major rock-water- CO_2 interactions include dissolution of CO_2 into brine, dissolution and sorption of CO_2 into any organics such as coal or oil that are present, dissolution of existing minerals, especially calcite and precipitation of new minerals. Most of these processes strongly favor trapping the CO_2 to retain it in the subsurface. However, mineral dissolution caused by acidic pH values could under certain conditions lead to scenarios that might increase leakage risk. US regulations for Underground Injection Control (UIC) require characterization of the rock-brine system coupled with geochemical modeling to ensure that interactions are understood and that adequate assurance can be provided that injectate will be retained within the injection zone.

Dissolution of CO_2 into brine is the limiting step that controls how strongly geochemical interactions favor trapping. Solubility of CO_2 into brine at subsurface temperatures and pressures is well-known. However, the contact area between the CO_2 and brine that controls the amount of dissolution is poorly quantified in rock pore systems. The contact area evolves through three phases of development of the plume: a highly dynamic phase during injection, a moderately dynamic phase as the plume migrates to a stable geometry, and a sluggish phase of long duration when the plume is stable except for dissolution into water and mineral precipitation. Rock pore systems, formation geometry, basin hydrology, and injection strategies can alter the contact area and must be considered in assessing the role of geochemistry. Results of recent field tests at the Frio brine pilot provide a first look at the rates and processes by which these phases and reservoir properties interact.

Fluids sampled from the Frio "C" sandstone injection and observation wells during the Frio I test (2004-2006) showed the expected rapid decrease in pH and rise in alkalinity. However, an unexpected rapid increase in the concentrations of Fe (from 30 to 1,100 mg/L), manganese, and other metals following CO_2 breakthrough needed to be explained. Geochemical data (Knauss, personal communication, Figure 54) coupled with laboratory studies and modeling indicate that the increases likely resulted from rapid dissolution of Fe-oxyhydroxides (Figure 55) caused by lowered pH (~3.9 initially) of the Frio brine in contact with the injected CO_2, but contamination of the samples by formation brine that was stored in the tubing is certainly a factor. Repeat tests were carried out during the Frio II test. For Frio II, USGS installed online pH, EC, and temperature probes, conducted field determinations of Fe^{2+} and Fe^{3+}, and carried out analyses of a larger number of metals using ICP-MS.

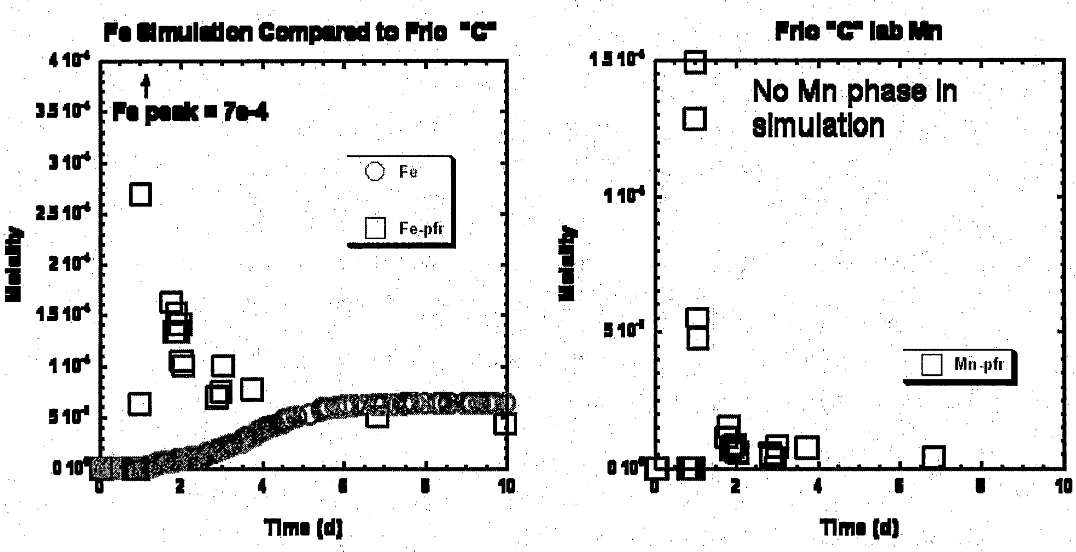


Figure 54. Laboratory reactions of Frio "C" samples with CO_2 and artificial brine (Kevin Knauss, LLNL) show release of unexpectedly large amounts of Fe and Mn compared to what was expected based on modeling. This result shows that not all the high Fe and Mn observed in the field was contamination.

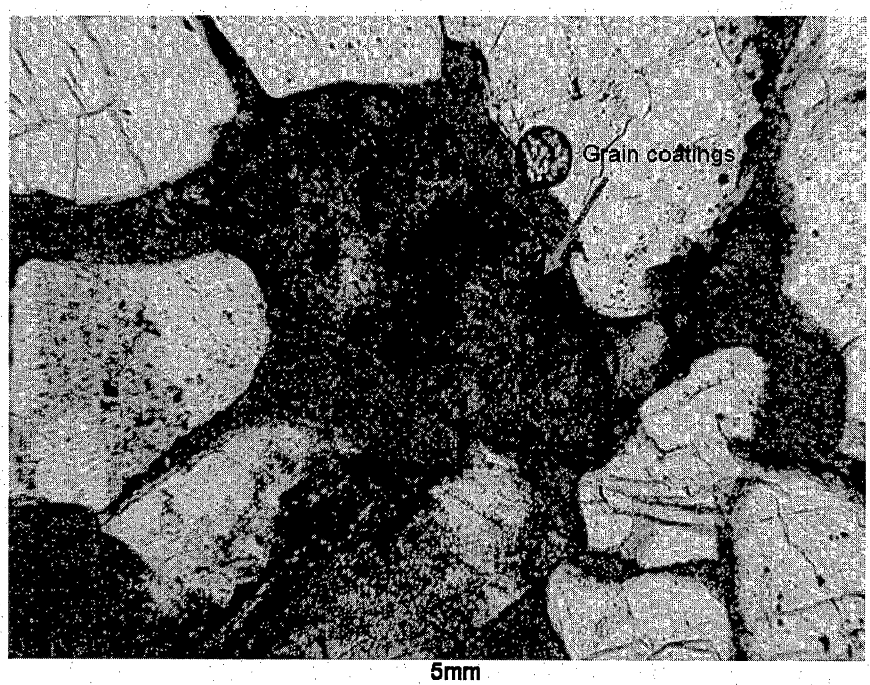


Figure 55. Minor amounts of high surface area Fe-oxyhydroxides on clays coating Frio "C" sand grains are possible sources of Fe and Mn released when pH is lowered. Recovery of the fluids suggests that only small volumes of reactant are present.

Results show higher maximum concentrations for Fe, Mn, Zn, Pb and other metals compared with those obtained from Frio I. Fe increases could be caused by: (1) a combination of reactions, (2) dissolution of the observed Fe-oxyhydroxides, and (3) corrosion of now-rusty tubing in contact with low-pH brine.

$$2Fe(OH)_3(s) + 4H_2CO_3^0 + H_2(g) = 2Fe^{2+} + 4HCO_3^- + 6H_2O \quad (1).$$

$$Fe(s) + 2H_2CO_3^0 = Fe^{2+} + 2HCO_3^- + H_2(g) \quad (2)$$

Similar reactions may be written for Mn, Zn, and Pb, which are associated with Fe-oxyhydroxides, but they could also be present in the low-carbon steel pipe used in wells.

Follow-on testing is underway and includes additional rock-water CO_2 interactions (Lu, in prep.) and further testing at a large-volume, long-duration injection at Cranfield, Mississippi (USGS). The Cranfield test will be conducted in coated tubing, so that contamination from pipe is minimized.

Introduced and Natural Tracers

U-tube samplers located in the perforated intervals of the injection and observation borehole collected uncontaminated aliquots of reservoir fluids. The arrival of CO_2 in the observation borehole was noted by a significant decrease in pH and the arrival of various tracers. Krypton tracer arrived at the observation borehole at the same time as the CO_2, despite its injection 16 hours after the start of the CO_2 injection, highlighting the rapid dissolution of CO_2 in the brine. The co-location of the disparate monitoring tools was highly successful, although refinements to the system for future deployments are needed to maximize data collection.

Seismic monitoring- progress and next advances

LBNL analysis of Frio experiment data has made progress toward development of a rock physics model relating seismic velocity to CO_2 saturation. The estimation of CO_2 saturation from seismic measurements affords one of the only monitoring techniques capable of detecting CO_2 movement beyond the zone immediately surrounding the borehole. Rock physics models capable of predicting the change in geophysical properties induced by CO_2 provide a link between multiphase flow simulation and seismic modeling. Analysis of the Frio I dataset (Daley, 2007) relied on application of the heuristic model proposed by Brie and others (1995); this model suffers from several limitations, the most serious of which is the use of an *ad hoc* fitting parameter with no physical basis.

One of the recurrent problems in seismic data interpretation is to select the appropriate model to predict the properties of rocks partially saturated with CO_2 in order to calculate the relationship between change in velocity and change in saturation. The elastic properties of the rock matrix can be determined reasonably well from selected log and core information. For example Daley (2007) estimated that the Frio "Blue" Sandstone has a base V_p of 2700 m/s, base V_s of 1200 m/s and permeability of 2 darcys.

CO_2 and brine properties can be calculated for reservoir pressures and temperatures (P = 15 MPa, T = 55 °C) in the Blue Sandstone. However, the seismic response is highly variable in conditions where the CO_2 is well-mixed with brine on the pore scale as compared to where the CO_2 occurs in patches of different sizes. Measurements made with CASSM in the Frio II experiment show, for the first time, unexplained changes in the signal that may be tied to properties of the flow system. Other constraints are needed, however. Additional input needed could come from calibration experiments (on the core or log scale) or from the field scale measurement of secondary properties such as electrical resistivity changes. A follow-on experiment is planned at SECARB Phase III early at Cranfield to test combining CASSM with electrical resistivity tomography to further explore better quantification of CO_2 with seismic data.

RST logging as a tool to measure changes in saturation

Earlier studies of CO_2 monitoring include those of Gould and others (1991) and Butler and others (1993). They showed induction resistivity and neutron logs run through fiberglass casing and saturation of three phases monitored in West Texas carbonate reservoirs. The wireline reservoir saturation tool (RST) used pulsed neutron capture to determine changing brine saturation as brine was displaced by CO_2. Sigma (Σ), the parameter collected by the RST tool, is derived from the rate of capture of thermal neutrons (mainly chlorine). The high value of Σ for formation water derived from brine conductivity allows estimation of Sw and the inverse, CO_2 saturation (Sakurai and others, 2005). A time-lapse series of five logs in the observation well and three in the injection well was collected. Logs required extensive correction for borehole conditions because fluids and completions were changed to accommodate other instrumentation. The biggest change (and the most incomplete correction) was after the wells were prepared for collection of the post-injection seismic data (month 3) which required injection of a small volume of fresh water in order to place a cement squeeze across the perforations. Pre-injection wireline density and sonic logs using the dipole sonic imager (DSI) were used to calculate shear and compressional wave velocities. In early December 2004, after the geophysical survey was completed, DSI logging was repeated for both wells (Fig. 2).

BEG and Schlumberger researchers have substantively increased confidence in use of Schlumberger RST to monitor changes in CO_2 saturation. The high porosity in the "C' and Blue sandstones and the large contrast in Σ between CO_2 and saline formation water were ideal conditions for RST time-lapse measurements. At experiment start it was predicted but not known that the tool would perform well under sequestration conditions. We also had some concern that near-wellbore artifacts would be so important that the measurements would not be representative of the plume. In the Frio I test, Σ was used rather simply and was force corrected because borehole corrections for the changing conditions related to placement of allochthonous fluids and cement (in order to collect cross-well seismic) were complex and poorly constrained. Nevertheless, RST proved to be the most quantitative method for monitoring changes as CO_2 displaced the formation water and then post-injection as CO_2 spread and saturation decreased toward residual saturation. Maximum CO_2 saturations were estimated as 80% (local drying); the residual saturation in zones of high initial saturation was about 20%. TOUGH2 model saturations agree that these are reasonable endpoint saturations, although the solution is not unique.

The Frio II test was designed to provide simpler wellbore conditions to optimize quantitative, in-reservoir observation of the changes in saturation near the wellbores. It was planned that no perturbation in fluids would be introduced, and the fluid stabilization would proceed unperturbed. Several factures prevented this data collection from being ideal. First, the Blue Sandstone is highly heterogeneous and includes gravels, so the residual saturation is a complex function of grain size compared to the rather homogeneous fine sandstones of the Frio "C." The saturation history in the Frio "Blue" Sandstone in the injection well was complex, and a component of upward near-well flow through disturbed sediments may play a role. The zone of saturation in the Frio "Blue" Sandstone of the observation well is thinner than ideal for obtaining a log-based measurement, and because of fast preferential flow it is suspected of being course grained. Cost overruns prevented collection of interim RST measurements, and the final measurements were lost, because of sand covering perforations in the observation well and packer failure adding allochthonous fluid. The Frio II RST measurements, however, are quite significant, in that they show substantial residual trapping even in very coarse-grained sediments, in that where CO_2 was measured over the year-long monitoring period, it was retained and did not flow-up dip. Apparent increase in saturation toward the top of the interval shows subtle relative permeability effects not completely modeled.

In both tests, the RST measurements show reasonable although not unique or highly quantitative convergence with cross-well techniques, suggesting that the near wellbore fluids are reasonably representative of the larger rock volume. An attempt in Frio I to duplicate saturation change measurements using cased hole sonic logging failed, because the change was to large to be quantified. Follow-on tests to enhance confidence in the quantification of saturation using RST are needed, and several tests are planned at Cranfield.

Conclusions

This study pioneered research into the geologic sequestration of CO_2 into unused, deep-subsurface, brine-bearing sandstones. This technique is proposed as a method for permanently storing CO_2 produced by combustion of fossil fuels, preventing its atmospheric release. Prior to this study, geologists and engineers had extensive experience with subsurface injection of CO_2 for Enhanced Oil Recovery (EOR) that provided confidence that the process would be successful. EOR can only accept a small fraction of the CO_2 produced by combustion, so that increasing CO_2 injection experience to include brine-bearing formations increases in importance. It is also important to gain improved understanding of the validity of flow model and monitoring tools, so that the effectiveness of the process of geologic sequestration can be documented. EOR is a highly complex setting dominated by (1) continuing perturbations such as production and water flood, and (2) the miscible interaction of CO_2 and oil. These complex conditions make it difficult to rigorously test the performance of monitoring tools and flow and geochemical models, which therefore became the focus of this study.

In this 10-year study, we started with an assessment of the information needed to evaluate the feasibility of large-volume injection into brine-bearing formations, selecting two well-known, high-volume units, the Frio and Woodbine Formations, as test cases. We then extended the study to 19 other formations across the on-shore United States.

This regional study documented the correctness of the initial assumptions that the Frio and Woodbine were typical but higher-volume sequestration targets. We therefore focused the field study on these units.

The Frio test site was selected from about six sites considered. Frio was the only test site that negotiations espoused in the surface and subsurface owners a willingness to host the experiment. The selected site is in a small, steeply dipping fault block, on the flanks of the South Liberty salt diapir. The site is in a field that produces oil from the Yegua Formation at depths of 9,000 ft (~2,700 m) to 10,000 ft (~3,000 m). The site itself is probably not suitable for large-scale sequestration because of the small compartment and uncertainly about sealing properties of the upper closure, which is in a highly faulted area close to the diapir. However, large volumes of similar Frio sandstones in areas between salt structures proved to be one of the major US sequestration targets. We therefore named the test site "Frio Pilot Test" to emphasize the regional significance, not the local setting in South Liberty oil field, which hosted the experiment.

The Frio Pilot Test site was ideal for a small-volume injection, in that structural compartmentalization reduced the number of possible CO_2 interactions, existing roads and wells provided access, the local community was experienced with subsurface work, a recent 3-D seismic survey was made available by the operator, abundant logs through the Frio existed, and Yegua production history provided dense data needed to support the study. Steep dips and high permeability created conditions in which fluid mobility would be maximized, allowing two full cycles, from injection to stabilization, to be completed in 4½ years.

A preparation period of about 2 years (2002–2004) was required to complete contract negotiations, build a research and engineering team, iterate our experimental designs, and complete required NEPA documents for leasing and permitting for well drilling, injection, and seismic monitoring. Texas has primacy for all UIC program classes. The permitting strategy was negotiated prior to site selection through discussion with Richard Ginn, then UIC supervisor for the Texas Railroad Commission (RRC), and Ben Knape, UIC department director for the Texas Commission on Environmental Quality (TCEQ). It was determined that permitting for injection and the injection well for the experiment was somewhat unusual, in that the site was within an oil field, which is traditionally regulated under the Texas RRC. However, the injection did not fall under the Class II hydrocarbon-related activities, as it was planned to inject into a brine-only reservoir, failing to meet the specifications in CFR 144.6 for Class II. We then discussed permitting the injection through TCEQ as a Class I non-hazardous project, but Texas has an extended process for all Class I wells that seemed inappropriate for short-duration, small-volume tests. TCEQ proposed to use the Texas version of Class V "other" wells that allows experimental wells to be constructed under Class V, which was appropriate for the test purpose.

The final design moved the injection well closer to the observation well than was originally proposed, moving it from 400 ft (~122 m) to 300 ft (~91 m). This was done to reduce experimental and operational risks by reducing the amount and cost of CO_2 while also allowing for construction of a new injection well with well-documented fabrication. Construction of an observation well also added significant research value because it allowed collection of new open-hole logs and core from three intervals. An existing oil production well was plugged back to create an observation well, allowing use of existing well pad and roads. Significant cost to emplace cement behind casing and uncertainty as to performance resulted from this reuse; we suggest that new wells would give higher value in future tests. The wells were designed with long "rat holes," open borehole below the test interval. Use of this open hole allowed us to conduct a second test in a deeper interval. If we had known in advance that two tests were possible, considerable costs could have been saved by conducting the deeper test first and setting a bridge plugs to separate the first test from the second. Since the second test was deeper, we experienced cost overrun trying to restore well-bore integrity past the zone where the first test was conducted.

The first test (September 2004) injected about 1,600 tons of supercritical CO_2 into the Frio "C" sandstone over a period of 10 days. The top of the perforated interval was at 5,050 ft (~1,540 m), just below a sealing mudstone within the upper Frio Formation, this design was based on pre-injection modeling that showed that using the seal to guide the CO_2 would reduce risk that breakthrough of the CO_2 to the observation well would not occur within the budgeted amount of CO_2 and injection time. The upper part of the Frio "C" sandstone was relatively homogeneous, massive bedded, well sorted, unconsolidated fine sandstone. Pre-injection characterization of core and a dipole hydrologic test with introduced fluorescein tracer showed high permeability of over 1 darcy, so that CO_2 moved rapidly through the formation. Ending injection after a relatively short period while continuing injection was also an important design element, as it allowed observation of a relatively long period post-injection. Post-injection is the time of greatest uncertainty with regard to long-term storage. Observations continued for 18 months, after which preparation began for the second test in the Frio "Blue" sandstone at a depth of 5,400 ft (1,600 m).

The first experiment was successful in measuring multiple time-lapse techniques with different methods of detection. Measurements were taken of changes in subsurface properties indicative of movement of supercritical CO_2 injected into high permeability sandstone. Tools used include a novel design fluid sampler, the U-tube, developed for the experiment by LBNL to measure changes in brine and gas phase geochemistry and to recover an array of diverse introduced gas-soluble tracers, a first application of Schlumberger's pulsed neutron reservoir-saturation tool (RST) in a brine - CO_2 fluid system, and a first use of cross-well acoustic tomography to image the change in velocity over time as CO_2 replaced brine in the pore system. In addition, a number of other tools were tested. These measurements document a reasonable match with predictive numerical models of CO_2 flow and geochemical reactions with in-situ brine and minerals. Saturation evolution at the trailing edge of the plume suggests that two-phase processes leading to CO_2 permanently retained in the pore space because of low relative permeability was correctly conceptualized and significant. In addition, as predicted, dissolution of CO_2 into brine was rapid and is likely to have been a volumetrically significant process that drove rock-water reactions. These results increase our confidence in the validity of conceptual and numerical models for CO_2 storage and in the feasibility of testing the permanence of storage using available monitoring strategies in settings where there is no history of hydrocarbon accumulation and production.

The successful results of the Frio monitoring project demonstrate, however, the limits of precision and accuracy in tracking a plume of injected CO_2. Tool resolution and complexity of the natural environments are components that lead to uncertainties which need to be considered as CO_2 storage, permitting, and verification systems evolve.

The Frio experiment demonstrated the effectiveness of employing a number of relatively low-cost monitoring techniques in concert to build a strong case demonstrating the performance of the subsurface in retaining CO_2. High-quality characterization was used to build predictive models, which were then used to design a parsimonious but effective selection of tools. The performance of a number of tools was demonstrated, and comparison among the measurements increased confidence in the monitoring by showing the magnitude of uncertainty.

The second test was conducted in October 2006, using the same two wells 100 ft (~30 m) apart, but in a perforated interval at 5,600 ft (~1,700 m), in one of the many fluvial sandstones of the lower part of the middle Frio Formation. We wanted to test the effect of buoyancy in moving the CO_2 through the rock volume and attempt to measure increased residual saturation and greater dissolution. We hoped that breakthrough would be slower.

The Frio II Brine Pilot was conducted using the same injector/monitoring well pair developed and characterized for the 2004 Frio Brine Pilot CO_2 sequestration experiment. The CO_2 injection occurred in the Frio "Blue" Sandstone, a hydrologically isolated sandstone, 390 ft (~120 m) below the previously investigated "C" sandstone tested during the initial Frio Brine Pilot. The Frio II injection consisted of a small volume (about 300 tons) of CO_2 over 5 days (September 26–October 1) into the lower part of a 33-ft (~10-m) thick flow unit in a heterogeneous fluvial sandstone. A program of wireline logging, cross-well seismic monitoring, geochemical sampling with a U-tube and Kuster sampler, and hydrologic testing with water-soluble and gas-soluble partitioning and non-partitioning tracers, was used to analyze the fate of the injected CO_2.

During injection, the CO_2 traveled vertically near the injection wall and laterally through a thin, high-permeability zone and was detected near the top of the "Blue" Sandstone at the observation well 100 ft (~30 m) away. Comparison between the first and second injections illustrates interactions among injection rate, injection strategy, and heterogeneity of the injection interval and their impact on plume evolution. Both experiments illustrate the utility of combining several monitoring tools with modeling assessments to describe plume evolution. Monitoring continued through summer 2007 to measure the stabilization process of this small plume.

An important product of this study is recommendations to the next generation of developers of geologic CO_2 injection pilot projects. We highlight the value of interactive modeling before and during project development. Numerical simulation of flow strongly guided site selection, well design, and tool selection, and was integral to designing a successful project. The two-well design was effective in reaching project goals. We directly detected CO_2 breakthrough at the observation well, sampled formation waters as CO_2 interacted with rock and brine, and recovered tracers to quantify CO_2 saturations and CO_2 dissolution. We used two-well hydrologic approaches for evaluating multi-phase flow parameters and cross-well EM and seismic imaging. The observation well provided access during injection for logging CO_2 saturation and "ground truthing" indirect geophysical methods for monitoring. Research team integration is critical but time and labor intensive, and it required vigorous e-mail communication, phone conferences, in-person meetings, and field coordination. Effective data exchange within the research team was challenging. Engineering designs and the experimental timelines had to be redone to reduce conflicts between optimal conditions for each instrument, risk of failure, and cost. Redesign eliminated tools with low probability of success or those that could not be effectively implemented under experimental conditions and substituted tools that would accomplish the required tasks. Even if cost were not an issue, it is impossible to create optimal conditions for each instrument in a single test; compromises must be made, and success is dependent on making thoughtful compromises.

Results include demonstration of the new seismic monitoring methodology incorporated in a unique instrumentation deployment with the recently developed U-tube geochemical sampling methodology. Geochemical sampling included aqueous chemistry (pH, EC, Eh) and organic and metal analysis as well as gaseous analysis. Gas analysis included CO_2 concentration (showing breakthrough in the monitoring well), tracers (PFTs, KR and SF_6, Xe and Kr) in addition to the unique use of CD_4 as a tracer. Both seismic and sampling data sets can be used to provide fundamental input and constraints to flow and transport modeling. Modifications to the Frio flow model, using seismic monitoring as a constraint, are being incorporated in a methodology aimed at iterative inversion. Additionally, recent work developing the petrophysical relationships governing the seismic response demonstrates the sensitivity of seismic monitoring in a brine aquifer, including the possibility of joint-analysis of attenuation and velocity to improve saturation estimates.

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References Cited

Altunin, V.V., Thermophysical Properties of Carbon Dioxide, 1975 Publishing House of Standards, p. 551 (in Russian).

Batzle, M., and Z. Wang, Seismic Properties Of Pore Fluids, 1992, Geophysics, 57, No.11, p. 1396-1408.

Bergman and Winter, 1995, Disposal of Carbon Dioxide in Aquifers in the US, Energy Conversion and Management 36(6-9),p. 523-526.

Brie, A., F. Pampuri, A.F. Marsala, and O. Meazza, Shear sonic interpretation in gas-bearing sands, 1995, SPE Annual Technical Conference and Exhibition, p. 701-710.

Carcione, J.M., S. Picotti, D. Gei and G. Rossi, Physics and Seismic Modeling for Monitoring CO_2 Storage, 2006, Pure and Applied Geophysics, Vol. 163, p. 175-207.

Code of Federal Regulations, 2002, Title 40, Volume 19, From the U.S. Government Printing Office via GPO Access [CITE: 40CFR144.6] Title 40 – Protection of Environment, Chapter 1 – Environmental Protection Agency, Part 144 – underground injection control program, section 144.6 Classification of wells.

Daley, T. M., Myer, L. R.., Hoversten, G. M., and Majer, E. L, 2005, Time-lapse monitoring of CO_2 injection with vertical seismic profiles (VSP) at the Frio Project, online at http://www.beg.utexas.edu/mainweb/presentations/2005_presentations/2005co2seq.htm .

Daley, T.M., Myer, L.R., Peterson, J.E., Majer, E.L., Hoversten, G.M., 2007, Time-lapse cross-well seismic and VSP monitoring of injected CO_2 in a brine aquifer, Environmental Geology, DOI 10.1007/s00254-007-0943-z.

Daley, T.M., R.D. Solbau, J.B. Ajo-Franklin, S.M. Benson, 2007, Continuous active-source monitoring of CO_2 injection in a brine aquifer, Geophysics, v72, n5, pA57–A61, DOI:10.1190/1.2754716.

Doughty, C, Freifeld BM, Trautz RC (2007) Site characterization for CO2 geologic storage and vice versa: the Frio brine pilot, Texas, USA as a case study. Environmental Geology, DOI 10.1007/s00254-007-0942-0.

Dutta, N.C., and A.J. Seriff, On White's model of attenuation in rocks with partial gas saturation, 1979, Geophysics, Vol. 44, p. 1806-1812.

Freifeld, B. M. and Trautz, R. C., 2006, Real-time quadrupole mass spectrometer analysis of gas in borehole fluid samples acquired using the U-tube sampling methodology. Geofluids 6 (3), 217–224. doi:10.1111/j.1468-8123.2006.00138.x.

Freifeld, B. M., and Trautz, R. C., 2006, Real-time Quadrupole Mass Spectrometer Analysis of Deep Borehole Fluid Samples Acquired Using the U-tube Sampling Methodology, Geofluids, in press.

Freifeld, B. M., Trautz, R. C., Kharaka, Y. K., Phelps, T. J., Myer, L. R., Hovorka, S. D., and Collins D. J., 2005, The U-tube: A novel system for acquiring borehole fluid samples from a deep geologic CO_2 sequestration experiment: Journal of Geophysical Research-Solid Earth, v. 10, B10203.

Freifeld, B.M., Trautz, R.C., Yousif K.K., Phelps, T.J., Myer, L.R., Hovorka, S.D., and Collins, D., The U-tube: A novel system for acquiring borehole fluid samples from a deep geologic CO_2 sequestration experiment, J. Geophys. Res., 110, B10203, doi:10.1029/2005JB003735, 2005.

GEO-SEQ, 2009 (access date) Geologic Storage research http://esd.lbl.gov/CO2GeoStorage/research/geoseq/geoseq.html .

Holtz, M. H., 2002, Residual gas saturation to aquifer influx: a calculation method for 3-D computer reservoir model construction: Society of Petroleum Engineers, SPE Paper No. 75502, 10 p.

Holtz, M. H., 2005, Reservoir Characterization Applying Residual Gas Saturation Modeling, Example from Starfak T1 Reservoir, Middle Miocene gulf of Mexico, The University of Texas at Austin, Master's thesis, 111 p.

Hoversten, G. M., R.Gritto, J. Washbourne, and T. M. Daley, 2003, Pressure and fluid saturation prediction in a multicomponent reservoir using combined seismic and electromagnetic imaging: Geophysics, 68, 1580-1591.

Hovorka, 2005, Monitoring saturation changes of CO_2 sequestration: Petrophysical support of the Frio brine pilot experiment: Society of Petrophysicists and Well Log Engineers 46th Annual Logging Symposium, New Orleans, LA.

Hovorka, S. D., Doughty, Christine, Benson, S. M., Pruess, Karsten, and Knox, P. R., 2004a, The impact of geological heterogeneity on CO_2 storage in brine formations: a case study from the Texas Gulf Coast, in Baines, S. J., and Worden, R. H., eds., Geological storage of carbon dioxide: Geological Society, London, Special Publications, 233, p. 147–163.

Hovorka, S.D., Holtz, M.H., Sakurai, S., Knox, P.R., Collins, D.J., Papadeas, P., and Stehli, D., 2003, Frio pilot in CO_2 sequestration in brine-bearing sandstones: The University of Texas at Austin, Bureau of Economic Geology, report to the Texas Commission on Environmental Quality to accompany a Class V application for an experimental technology pilot injection well. GCCC Digital Publication Series #03-04. http://www.beg.utexas.edu/gccc/bookshelf.php .

Hovorka, S. D., Romero, M. L., Warne, A. G., Ambrose, W. A., Tremblay, T. A., Treviño, R. H., and Sasson, D., 2000, Sequestration of greenhouse gases in brine formations: The University of Texas at Austin, Bureau of Economic Geology, hypertext publication at http://www.beg.utexas.edu/environqlty/co2seq/dispslsaln.htm .

Kharaka, Y. K, Cole, D. R., Thordsen, J. J., Kakouros, Evangelos, and Nance, H. S., in press, Gas-water-rock interactions in sedimentary basins: CO_2 sequestration in the Frio Formation, Texas, USA: Geofluids.

Kharaka, Y. K., and Hanor, J. S., 2004. Deep fluid in the continents: I. Sedimentary basins, in Treatise on Geochemistry, v.5, Surface and Ground Water, Weathering, and Soils, Elsevier Pergamon, p. 499–540.

Kharaka, Y.K., D.R. Cole, D. R., Thordsen, J. J., and Kakouros, Evangelos, 2007. Application of isotopes to understanding anthropogenic CO_2-brine-rock interactions in sedimentary basins: Results from the Frio brine pilot tests, Texas, USA. Proc. Intern. Sympos. on Advances in Isotope Hydrology and its role in Sustainable Water Resources Management, IAEA, Vienna, Austria, May 21-25, 2007 (in press).

Kharaka, Y.K., J.J. Thordsen, D.R. Cole, S.D. Hovorka, and T. D. Bullen, Potential environmental issues of CO_2 storage in saline aquifers: Geochemical results from the Frio Brine Pilot tests, Texas, USA, Goldschmidt Conference in Cologne, Germany, 19-24 August, 2007.

Kharaka, Yousif K. Bullen, Thomas D, Hovorka, Susan D. Cole, David R. Knauss, Kevin G. Freifeld, Barry M. 2007, Mobilization of metals as a result of CO_2 injection into sedimentary basins: Results from the Frio-II Brine test, Texas, USA. Abstract, CCS-6, Pittsburgh, PA, May 7-10, 2007.

Kharaka, Y.K., Thordsen, J.J., Hovorka, S.D., Nance, S.H., Cole, D.R., Phelps, T.J., and Knauss, G.K., 2007, Subsurface monitoring of anthropogenic CO_2 injected in sedimentary basins: Results from the Frio-I brine test, Texas, USA. Proc. 12th International Symposium on Water-Rock Interaction (WRI-12), T.D. Bullen and Y. Wang, eds., Taylor & Francis, v. 1, p. 597-601.

Knauss, K. K. Johnson, J. W., and Kharaka, Y.K, 2005, Preliminary reactive transport modeling and laboratory experiments conducted in support of the Frio Pilot Test, Fourth Annual Conference on Carbon Capture and Sequestration, online at http://www.gulfcoastcarbon.org .

Knox, P.R., Paine, J.G., and Hovorka, S.D., 2003, Environmental assessment: optimal geological environments for carbon dioxide disposal in brine formations (saline aquifers) in the United States--pilot experiment in the Frio Formation, Houston area: The University of Texas at Austin, Bureau of Economic Geology, draft report prepared for the U.S. Department of Energy (DOE), Contract DE-AC26-98FT40417 Modification A008, April 2003. GCCC Digital Publication Series #03-05, http://www.beg.utexas.edu/gccc/bookshelf.php .

Lemmon, E.W., M.O. McLinden, and D.G. Friend, Thermophysical Properties of Fluid Systems, 2005, NIST Chemistry Web Book, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, ed. P.J. Linstrom and W.G. Mallard.

Mroz E.J., Alei M., Cappis J.H., Guthals P.R, Mason A.S. and Rokop D.J. (1989a) Detection of multiply deuterated methane in the atmosphere. Geophysical Research Letters, 16, 677-678.

Mroz E.J., Alei M., Cappis J.H., Guthals P.R., Mason A.S. and Rokop D.J. (1989b) Antarctic atmospheric tracer experiments. Journal of Geophysical Research Letters, 94, 8577-8583.

Pruess, K., C.M. Oldenburg, and G.J. Moridis, TOUGH2 user's guide, Version 2.0, 1999, Rep. LBNL-43134, Lawrence Berkeley National Laboratory, Berkeley, CA.

Quan, Y., and J.M. Harris, Seismic attenuation tomography using the frequency shift method, 1997, Geophysics, Vol. 62, No. 3, p. 895-905.

Sakurai, Shinichi, Ramakrishnan, T. S., Boyd, Austin, Mueller, Nadja, and Hovorka, S. D., 2005, Monitoring saturation changes of CO_2 sequestration: Petrophysical support of the Frio brine pilot experiment: Society of Petrophysicists and Well Log Engineers 46th Annual Logging Symposium, New Orleans, LA.

Trautz, Robert, Freifeld, Barry and Doughty, Christine, 2005,Comparison of single and multiphase tracer test, results from the Frio CO_2 pilot study, Dayton, Texas, in Fourth Annual Conference on Carbon Capture and Sequestration, online at www.beg.utexas.edu/mainweb/presentations/2005_presentations/2005co2seq.htm .

Vendeville, B. C. Fouad, Khaled; Knox, P. R., 2003, Radial Faulting Above Salt-Diapir Overhangs: Natural Example and Physical and Kinematic Models: Transaction of the Gulf Coast Association of Geological Societies, October 2003, v. 53, p. 828-835.

Vendeville, B. C., Fouad, Khaled, and Knox, P. R., 2003, Radial faulting above salt-diapir overhangs: Natural example and physical and kinematic models: Transaction of the Gulf Coast Association of Geological Societies, 53, 828-835.

Wang, Z. and A.M. Nur, Effects of CO_2 Flooding on Wave Velocities in Rocks with Hydrocarbons, 1989, SPE Reservoir Engineering, Vol. 4, No. 4, p. 429-436.

Wang, Z., M.E. Cates and R.T. Langan, Seismic monitoring of a CO_2 flood in a carbonate reservoir: A rock physics study, 1998, Geophysics, Vol. 63, No. 5, p. 1604-1617.

White, J.E., Computed seismic speeds and attenuation in rocks with partial gas saturation, 1975, Geophysics, Vol. 40, p. 224-232.

Appendices

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TEXAS COMMISSION ON ENVIRONMENTAL QUALITY

Protecting Texas by Reducing and Preventing Pollution

October 6, 2009

Dr. Susan Hovorka
Bureau of Economic Geology
The University of Texas at Austin
University Station, Box X
Austin, TX 78713-8924

Re: Closure of Class V Injection Well Authorization
TCEQ Authorization 5X2500071; Tracking No. 12724081-1
CN601097413 / RN104859731
Sun-Gulf Humble Fee Tract 1
CO2 Sequestration Injection Well

Dear Dr. Hovorka:

The Underground Injection Control (UIC) staff has completed review of the June 17, 2009 closure report for the injection well system. UIC staff has found that the closure has met all requirements of 30 Texas Administrative Code (TAC) Chapter 331 including the Class V well plugging standards of §331.133. No further injection is authorized in the injection wells; a new authorization is required for any future well construction and injection operations.

If you have any questions regarding this matter, please contact me at (512) 239-6075. If you will be corresponding by mail, please use mail code MC-130.

Sincerely,

Bryan Smith
Underground Injection Control Permits Team
Radioactive Materials Division

BS/fp

cc: Mr. David Freeman, Sandia Technologies, LLC, Houston

P.O. Box 13087 Austin, Texas 78711-3087 512-239-1000 Internet address: www.tceq.state.tx.us