The GEO-SEQ Project
Quarterly Status and Cost Report
September 1, 2000 – November 30, 2000

Project Overview:

The purpose of the GEO-SEQ project is to establish a public-private R&D partnership that will:

- Lower the cost of geologic sequestration by
  (1) Developing innovative optimization methods for sequestration technologies with collateral economic benefits (such as enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced coalbed methane production), and
  (2) Understanding and optimizing trade-offs between CO_2 separation and capture costs, compression and transportation costs, and geologic sequestration alternatives.

- Lower the risk of geologic sequestration by
  (1) Providing the information needed to select sites for safe and effective sequestration
  (2) Increasing confidence in the effectiveness and safety of sequestration through identifying and demonstrating cost-effective monitoring technologies, and
  (3) Improving performance-assessment methods to predict and verify that long-term sequestration practices are safe, effective, and do not introduce any unintended environmental effects.

- Decrease the time to implementation of geologic sequestration by
  (1) Pursuing early opportunities for pilot tests with our private sector partners and
  (2) Gaining public acceptance.

Technical work began in May 2000 with an initial focus on four tasks: A) development of sequestration co-optimization methods for EOR, depleted gas reservoirs, and brine formations; B) evaluation and demonstration of monitoring technologies for verification, optimization, and safety; C) enhancement and comparison of computer simulation models for predicting, assessing and optimizing geologic sequestration in brine, oil and gas, and coalbed methane formations; and D) improvement of the methodology and information available for capacity assessment of sequestration sites. Work continued on these four tasks during the second quarter. Technical progress and accomplishments are discussed below.

Highlights:

- Screening criteria were developed for selection of oil reservoirs for co-optimizing both CO_2 sequestration and oil recovery.
- Numerical simulations were carried out to study the geochemical interactions between sandstone and CO_2 containing H_2S mimicking a waste stream from a coal-gasification process. Results show that quartz increases in abundance, and two new minerals, chalcedony and dawsonite (a carbonate sink), form.
- Crosswell seismic and electromagnetic measurements were processed to produce tomographic images of the pre-CO_2 injection subsurface conditions at the Chevron Lost Hills oil field. Calculations were also made to assess the magnitude of changes in carbon

isotopes in CO_2 as it reacts with reservoir phases. The CO_2 pilot at Lost Hills is being used as a field scale test of monitoring technologies.

- As a first step in performing capacity-assessment simulations, mathematical models were developed, and capacity factors defined, to assess the relative contribution to sequestration in brine formations from CO_2 (1) in the gas phase, (2) dissolved in the aqueous phase, and (3) in the solid phase.

Papers Published and Presented:

Benson, S.M., Geologic sequestration of carbon dioxide: prospects and challenges, *EOS Transactions, American Geophysical Union*, 81(48), p. F246, November 28, 2000.

Benson, S.M., The scientific challenges of carbon sequestration, *EOS Transactions, American Geophysical Union,* 81(48), p. F283, November 28, 2000.

Daley, T.M., E.L. Majer, R. Gritto, and S.M. Benson, Borehole seismic monitoring of CO_2 injection in a diatomite reservoir, *EOS Transactions, American Geophysical Union,* 81(48), p. F3, November 28, 2000.

Gunter, W.D., The role of hydrostratigraphic and geochemical trapping in secure storage of carbon dioxide, *EOS Transactions, American Geophysical Union*, 81(48), p. F282, November 28, 2000.

Hovorka, S.D., M.L. Romero, A.G. Warne, W.A. Ambrose, T.A. Tremblay, and R.H. Trevino, Sequestration of greenhouse gases in brine formation– Possibilities and issues, *EOS Transactions, American Geophysical Union*, 81(48), p. F283, November 28, 2000.

Johnson, J.W., C.I. Steefel, and J.J. Nitao, Reactive transport modeling of subsurface CO_2 sequestration: Identification of optimal target reservoirs and evaluation of performance based on geochemical, hydrologic, and structural constraints, Abstract published and paper presented at Geological Society of America National Meeting, Reno, NV. – Subtask A-3, 2000.

Oldenburg, C.M., K. Pruess, and S.M. Benson, Process modeling of CO_2 injection into natural gas reservoirs for carbon sequestration and enhanced gas recovery, *Energy and Fuels*, in press.

Oldenburg, C.M., S.M. Benson, and K. Pruess, Effects of reservoir heterogeneity on carbon dioxide injection into depleted natural gas reservoirs, abstract #52377, *Geological Society of America Fall Meeting*, Reno, NV, Nov. 9-18, 2000.

Oldenburg, C.M., S.M. Benson, and K. Pruess, On CO_2 injection into depleted natural gas reservoirs for carbon sequestration and enhanced gas recovery, *EOS Transactions, American Geophysical Union*, 81(48), p. F271, November 28, 2000.

Pruess, K., T. Xu, J. Apps, and J. Garcia, Numerical modeling of aquifer disposal of CO_2, Paper SPE-66537, submitted to SPE and to be presented at SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, TX, February 2001.

Ramirez, A., R.L. Newmark, and W. Daily, Geophysical monitoring of carbon dioxide sequestration using electrical resistance tomography (ERT): sensitivity studies, *EOS Transactions, American Geophysical Union*, 81 (48), p. F282, November 28, 2000.

Task Summaries

Task A: Develop Sequestration Co-Optimization Methods

Subtask A-1: Co-optimization of carbon sequestration and EOR and EGR from oil reservoirs.

Accomplishments:

- Criteria tables for selection of depleted or inactive oil reservoirs for combined EOR and sequestration were completed.

Summary:

The objectives of this subtask are (1) to assess the feasibility of co-optimization of CO_2 sequestration and EOR and (2) to develop techniques for selecting the optimum gas composition for injection. Results will lay the groundwork necessary for rapidly evaluating the performance of candidate sequestration sites as well as monitoring the performance of CO_2 EOR.

Progress This Quarter: The initial focus has been to assess the feasibility of CO_2 sequestration in depleted or inactive oil reservoirs. Existing CO_2–EOR selection criteria were examined co in light of the need to maximize CO_2 storage in a reservoir. Criteria tables (see Table 1) considering reservoir engineering and surface facilities as part of combined EOR and sequestration were developed. Work continued on a draft report.

Table 1: Screening criteria for anthropogenic CO_2-EOR and CO_2 sequestration.

	Positive Indicators	**Cautionary Indicators**
Reservoir Properties		
$S_o\varphi$	≥ 0.05	< 0.05 Consider filling reservoir voidage if capacity is large
kh	$\geq 10^{-14} - 10^{-13}$	$< 10^{-14}$ If kh is less, consider whether injectivity will be sufficient
Capacity (kg/m^3)	> 10	< 10
Seals	Adequate characterization of caprock, minimal formation damage	Areas prone to fault slippage
Oil Properties		
ρ (°API, kg/m^3)	> 22, 900	< 22 Consider immiscible CO_2 EOR, fill reservoir voidage if C is large
μ (mPa s)	< 10	> 10 Consider immiscible CO_2 EOR
Composition	High concentration of C_5 to C_{12}, relatively few aromatics	n/a
Surface Facilities		
Corrosion	CO_2 can be separated to 90% purity; development of epoxy coated pipe and corrosion inhibitors	H_2O and H_2S concentration above 500 ppm each
Pipelines	Anthropogenic CO_2 source is within 500 km of a CO_2 pipeline or oil field	Source to sink distance is greater than 500 km
Synergy	Preexisting oil production and surface facilities expertise	Little or no expertise in CO_2-EOR within a geographic region

Work Next Quarter: The report "Criteria for Selecting Oil Reservoirs Suitable for CO_2 Sequestration" will be completed and circulated for comments. Work will begin on an operational model for simultaneous EOR and sequestration that maximizes ultimate oil recovery and placement of CO_2 into oil reservoirs for carbon sequestration.

Subtask A-2: Feasibility assessment of carbon sequestration with enhanced gas recovery (CSEGR) in depleted gas reservoirs.

Accomplishments:

- Numerical simulation of CO_2 injection into a model gas reservoir showed that heterogeneity speeds up the transport of CO_2 in the reservoir, anisotropy affects density stratification, and the water table can be displaced by CO_2 injection to enhance repressurization of methane in other parts of the reservoir.

Summary:

The objectives of this subtask are to assess the feasibility of injecting CO_2 into depleted natural gas reservoirs for (1) sequestering carbon and (2) enhancing methane (CH_4) recovery. Investigation will include assessments of (1) CO_2 and CH_4 flow and transport processes, (2) injection strategies that retard mixing, (3) novel approaches to inhibit mixing, and (4) identification of candidate sites for a pilot study.

Progress this Quarter: Investigation continued on CO_2 injection into a model system based on the Rio Vista gas field in California. The focus this quarter was on studying variations of the model system, including reservoir heterogeneity, the variability of permeability anisotropy, and different locations of CO_2 injection. The heterogeneous permeability fields were generated using a simulated annealing method to produce heterogeneity reflecting horizontal sedimentary structures. Numerous realizations were used and compared against homogeneous permeability results. The breakthrough curves for all realizations of heterogeneous permeability show faster CO_2 breakthrough than for the uniform permeability base case. This occurs because high-permeability channels in the heterogeneous cases enhance the transport of CO_2 to the production well. However, even for the cases with strong permeability heterogeneity, simulations showed several years of potential production of pure methane prior to CO_2 breakthrough. Decreasing permeability anisotropy was observed to delay CO_2 breakthrough because CO_2 could more easily migrate to the bottom of the reservoir because of density effects (when vertical permeability is larger). In Figure 1 below, we present a simulation of the injection of CO_2 near the water table, which acts to depress the water table at the site of injection and raise the water table at the other end of the reservoir. This simulation shows that displacement of groundwater can act to repressurize the reservoir independent of CO_2 transport.

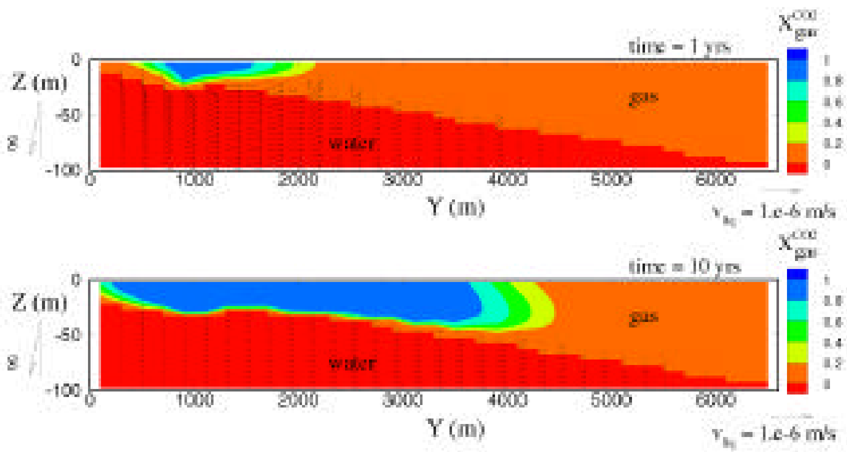


Figure 1. Simulated mass fraction of CO_2 in the gas phase and groundwater flow velocity for the case of CO_2 injection with water table displacement.

Work Next Quarter: More sophisticated equations of state for CO_2–CO_4–H_2O mixtures will be evaluated. The draft of the Energy and Fuels paper will be revised in response to reviewers' comments. Contact with Rio Vista operators will be initiated to discuss CSEGR and pilot test.

Subtask A-3: Evaluation of the impact of CO_2 aqueous fluid and reservoir rock interactions on the geologic sequestration of CO_2, with special emphasis on economic implications.

Accomplishments:

- Reaction-progress chemical thermodynamic and kinetic simulations representing batch type reactions were performed for evaluation of the impact of NO_2, H_2S, SO_2, and waste stream contaminants on injectivity and sequestration performance.

Summary:

Lowering the costs of the front-end processes can dramatically lower the overall costs of sequestration. One approach is to sequester less-pure CO_2 waste streams that are less expensive or require less energy to separate from flue gas. The objective of this subtask is to evaluate the impact of this impure CO_2 waste stream on geologic sequestration.

Progress This Quarter: During this second quarter of work, we continued the process of evaluating the impact of waste-stream contaminants (e.g., SO_2, NO_2, and H_2S) on injectivity and sequestration performance. This was accomplished by constructing a series of simulations. Last quarter we focused on the specific impact of SO_2 very near the well bore in a feldspathic-sandstone reservoir. This quarter we continued those studies by looking at the specific impact of adding (separately) NO_2 and then H_2S to the CO_2 waste stream and we broadened the scope to include an idealized carbonate reservoir. We constructed a series of simulations equivalent to batch-type (closed system) reactions, including full dissolution kinetics (that in turn included acid catalysis) for all of the mineral phases present in the reservoir rock. We used a rock composition and modal abundances appropriate for a feldspathic-sandstone reservoir containing clay and carbonate with and without a Fe-bearing phase, and a carbonate reservoir comprised of calcite, dolomite and siderite. Again, several approaches to dealing with setting initial fO_2 (f signifying fugacity) were investigated, as well as looking at the impact of assuming whether or not redox processes are in equilibrium. In these simulations, reaction progress was allowed to proceed for a time period of 30 years, appropriate for a real CO_2 sequestration process.

Figure 2 shows source of the results obtained this quarter. In this simulation we have reacted a reservoir rock comprised of 88.5% quartz, 9% K-feldspar, 1% calcite, 1% siderite and 0.5% muscovite (as a proxy for illite) with a gas phase that has fCO_2 = 80 b and fH2S = 10 b. This high fH2S mimics the waste stream from a gasification process (not unlike that being delivered to Weyburn). Conceptually, the aqueous phase is allowed to instantaneously equilibrate with the gas-phase in the absence of minerals, and then the minerals are added to the system and reactions proceed. After the initial equilibration with the aqueous phase, the gas-phase composition is also allowed to evolve as the aqueous phase evolves, always staying in equilibrium with it. The gas fugacities are not fixed. Redox processes have been effectively turned off in this simulation. The rock/water ratio is appropriate for a reservoir with 33% porosity, and the fluid is a simplified seawater-like brine consisting essentially of 0.7 m NaCl. Reservoir temperature is 60°C, with full-dissolution kinetics used in rate equations that account for acid catalysis.

The run lasts for 30 years. We expand the Y-scale to make the mineral evolution clearer. At the expanded scale results for the mineral quartz are not shown because it increases in volume by 3.9 cm^3 primarily as a result of K-feldspar dissolution. The main results are that under these conditions, K-feldspar dissolves initially in response to the low pH, a small amount of calcite dissolves (and even smaller amounts of clay and siderite dissolve), a new silica mineral (chalcedony) forms, and quartz increases in abundance, owing to K-feldspar and muscovite dissolution. Perhaps most importantly, the new mineral dawsonite appears as a carbonate sink.

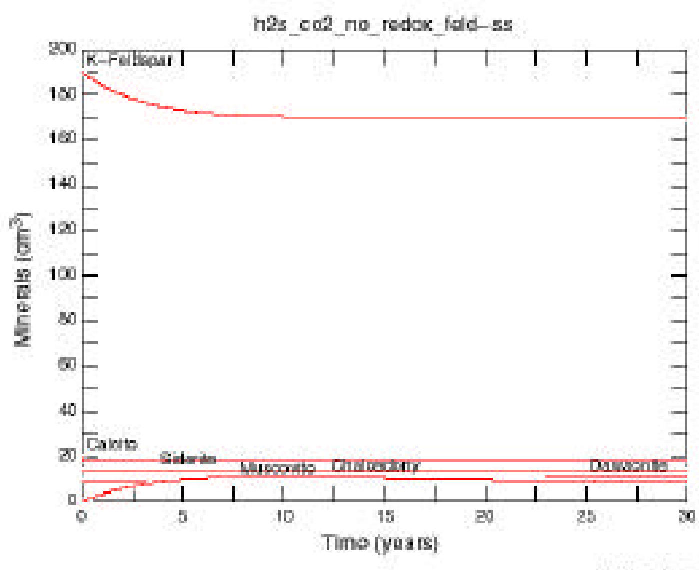


Figure 2. Results of geochemical simulations

Work Next Quarter: Investigation of the impact of other contaminants (SO_2, H_2S, NO_2, etc.) in the CO_2 waste stream will continue.

Task B: Evaluate and Demonstrate Monitoring Technologies

Subtask B-1: Sensitivity modeling and optimization of geophysical monitoring technologies

Accomplishments:

- Using reservoir simulations provided by Chevron, 2-D and 3-D seismic (elastic) and electromagnetic simulations were carried out for comparison with geophysical measurements prior to CO_2 injection at the Lost Hills Pilot.
- Using available borehole logs and rock physics models, transforms were developed to convert reservoir parameters to seismic and electrical parameters.
- A set of target scenarios was developed, indicative of realistic CO_2 injection projects for application of electrical resistance tomography (ERT), and numerical simulations were conducted to investigate the range of conditions and configurations under which ERT may be used to monitor CO_2 injection and migration.

Summary:

The objectives of this task are to: (1) demonstrate methodologies for and carry out an assessment of the effectiveness of candidate geophysical monitoring techniques, (2) provide and demonstrate a methodology for designing an optimum monitoring system, and (3) provide and demonstrate methodologies for interpreting geophysical and reservoir data, to obtain high-resolution reservoir images. Currently the Chevron CO_2 pilot at Lost Hills, California, is being used as a test case for developing these methodologies.

Progress this Quarter: The objective of the modeling work is to provide an understanding of the relationships between the reservoir parameters, the fluid and CO_2 saturations, and the observed geophysical data that will be used to monitor the injection process. The relationships developed through forward modeling will then be used to interpret the field data in terms of fluid saturations and CO_2 content. Forward and inverse modeling are in the initial stages. So far the pre-injection reservoir model is being used to explore the relations between the reservoir flow simulations and the geophysical data taken prior to injection. Future work will include modeling the geophysical response to CO_2 injection.

Work began with a flow simulation (provided by Chevron) that modeled the water flood of the area of the OBC1 and OBC2 wells up to the beginning of CO_2 injection. Figure 3 shows the well locations and the area of the field covered by the flow simulation.

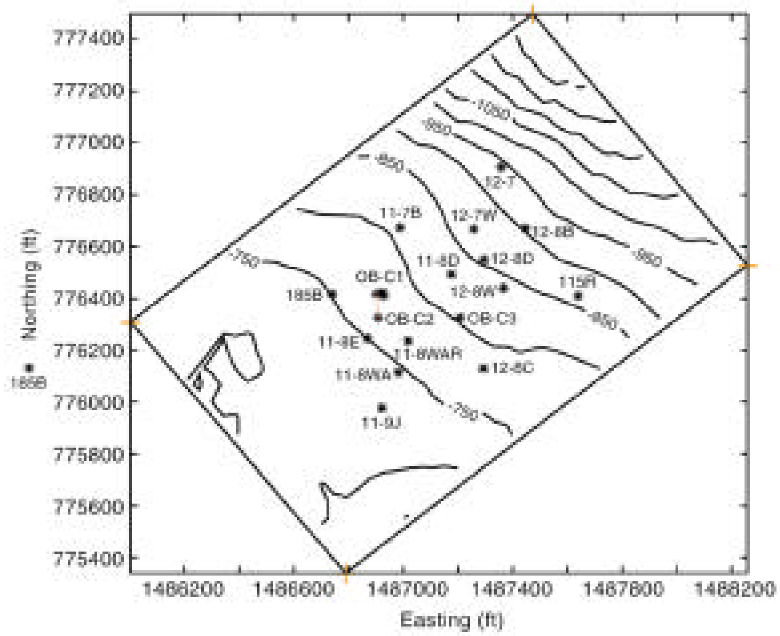


Figure 3: The area covered by the flow simulation is surrounded by the rectangle with crosses at the corners. The cross well seismic and EM data was acquired between OBC1 and OBC2 shown as the red line near the center of the figure. The W166 well used for developing the velocity model is to the west just below the vertical axis annotation. Contours show structure on the top of the reservoir interval.

The flow simulation parameters of interest for the geophysical modeling are porosity, pressure, and fluid saturations. To convert these to seismic velocity and electrical conductivity, log data from the W166 well was used for seismic velocities and data from the OBC1 was used for electrical conductivity. A model published by Dvorkin & Nur (1996) for unconsolidated sand grains coupled with Gassmann's equation (Gassmann 1951) was used to relate the porosity, pressure, and fluid saturations to velocity. A simple mixing law for porosity and fluid saturations is used to predict density. Although the Dvorkin & Nur model is not specifically for diatomite, it does a good job of predicting the observed p-wave velocity and density simultaneously for the available logs, given the logged porosity and saturations and assuming a hydrostatic pressure gradient. The velocities are not too sensitive to pressure and will be refined with pressure data from the flow simulations later. Figure 4 shows the regression fit for the W166 velocity and density logs.

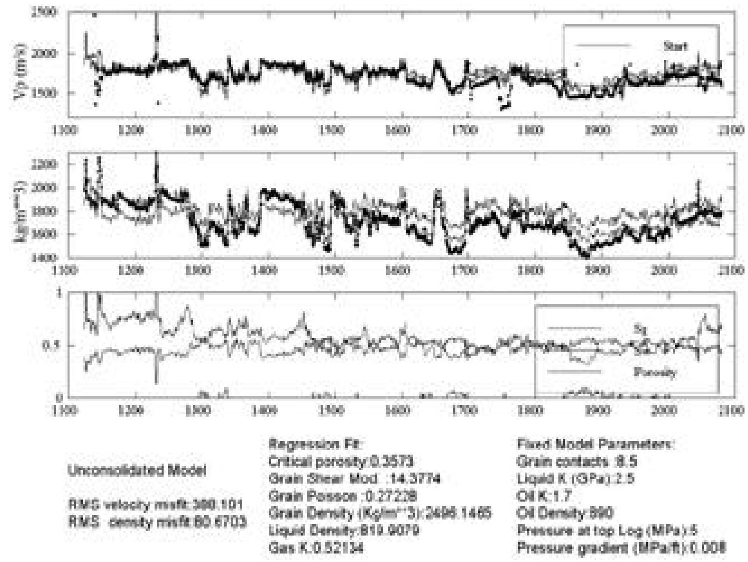


Figure 4: Log p-wave velocity, density, porosity, Sw and Sg used in multiparameter minimization for Dvorkin & Nur model parameters. Upper panel: observed Vp–red curve, starting Vp–blues curve, final Vp–magenta curve. Middle panel: observed density–red curve, starting density–blue curve, final density–magenta curve. Bottom panel: green curve–water saturation, light blue curve–gas saturation, black curve–porosity.

The largest errors in matching the W166 velocity log are found to occur where there is significant gas saturation. We are currently considering other models to address this and will be doing further modeling to determine a model with better performance in the presence of gas. This will be supported by ongoing laboratory measurements of sonic velocity and electrical resistivity in diatomite cores during CO_2 flood.

To calculate electrical resistivity in the 3-D model, the water saturation and porosity were used in an Archie's law regression. Figure 5 shows the results of fitting the OBC1 resistivity log.

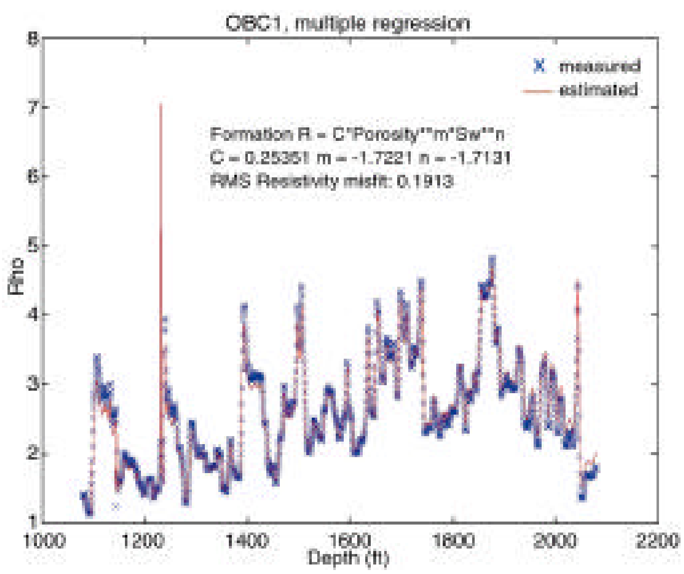


Figure 5: OBC1 deep induction resistivity log (RED) compared to the Archie's Law regresion (BLUE).

The models illustrated in Figures 4 and 5 were used to construct a 3-D velocity, density, and electrical resistivity cube. Figure 6 shows the porosity cube from the model.

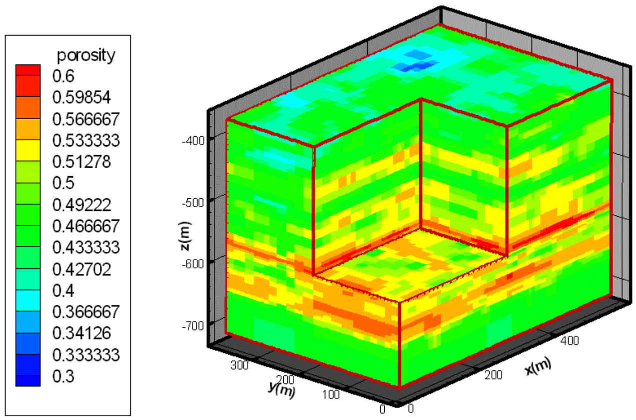


Figure 6. 3-D porosity cube viewed from the southwest. Northwest face of cutout section corresponds to approximate location of the OBC1 well.

A two-dimensional cross section between the OBC1 and OBC2 wells was extracted from the 3-D model for use in initial 2-D forward modeling. Forward 2-D and 3-D elastic and EM modeling has been done. As a first pass to check velocities, the 2D elastic simulation used a pressure source. The field data was acquired with an orbital vibrator so the wave fields are not the same. However, this comparison does show that model velocities are roughly 10% too low. Figure 7 shows the 2-D elastic response for a single shot at a depth of 567 meters compared to the field data for this shot location.

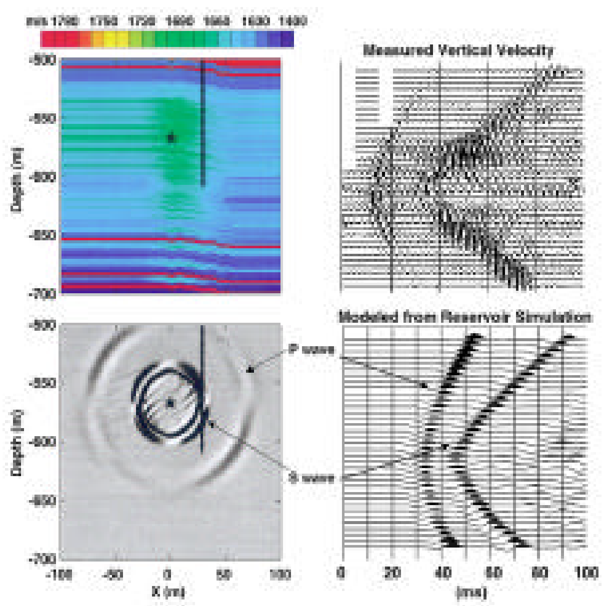


Figure 7. Two-dimensional elastic forward model based on reservoir simulation. Velocity was converted from reservoir parameters using the relations illustrated in Figure 2. The measured field data is compared to the calculated data showing a time shift that indicates our model velocities are on the order of 10% too low.

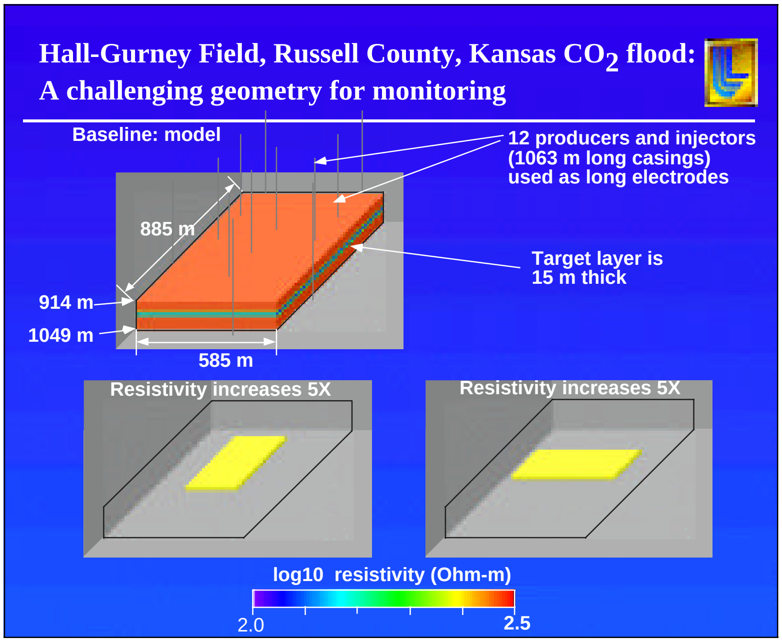
We are currently setting up the 3-D velocity model with the proper orbital vibrator source for simulation and examining why the velocities converted from the reservoir simulation are too low.

The pre- injection field data has been inverted using first-break travel-time tomography and 2-D electromagnetic inversion. The results are discussed in Task B2.

Under Subtask B-1, work also continued on assessing the sensitivity of the ERT method to detect the changes resulting from CO_2 migration. Previously, using published field data and unpublished information obtained through communication with industry researchers, a set of target scenarios, indicative of realistic CO_2 injection projects, were developed. A series of sensitivity studies was then begun to map the ERT performance envelope and evaluate the effectiveness of 3-D ERT as a potential monitoring approach for CO_2 sequestration. ERT resolution is affected by a number of factors, including resistivity contrast, anomaly location (proximity to electrodes), anomaly size and shape, noise level, and measurement configuration. Sensitivity studies were designed to explore all of these factors in a methodical manner, so as to permit quantitative evaluation of the relative influence of each. Using an initial model patterned after an oil field undergoing CO_2 flood, forward and inverse simulations of ERT surveys were run to test the sensitivity of the method to detect the changes resulting from CO_2 migration. This work was largely funded outside of GEO-SEQ.

This quarter, target scenarios were developed that reflect the expected conditions present at other fields in which CO_2 injection either is occurring or will occur: the Hall-Gurney field, in Russell County, Kansas, and the Sleipner project in Norway. Both projects pose challenging geometries for monitoring. In the DOE-funded Kansas project, CO_2 will be injected into a thin (~15 ft thick) unit at about 3,000 ft depth for enhanced oil recovery. This geometry is similar to having a change occur in the bottom sheet of a stack of paper over an inch high, with the detection instrumentation consisting of a pattern of thin vertical metallic pins penetrating the stack. It presents an extremely thin target for detection. An example of the Kansas results is shown in Figure 8. In this example, it is assumed that the only available electrodes are the vertical production and injection-well casings themselves; because of the measurement configuration, only lateral information is depicted in the reconstructed images. Although the general shape of the anomalous region can be detected, the magnitude of the change is greatly underestimated. Using this measurement configuration, potential vertical leak detection is problematic. In the Sleipner example, the target sands underlie a conductive silt layer (>300 m thick) beneath a 300 m thick sea layer. This structure poses field design problems as well as resolution issues. Initial field design involved point electrodes along the seabed. Both the magnitude and shape of the anomaly were well resolved in this configuration.

Work on applying ERT to the Chevron Lost Hills Pilot has just initiated. Both well logs and laboratory results will be used in modeling efforts. The baseline well logs were obtained during the summer. Independently funded laboratory measurements are being made on Lost Hills core to determine the changes in electrical properties resulting from CO_2 flood.



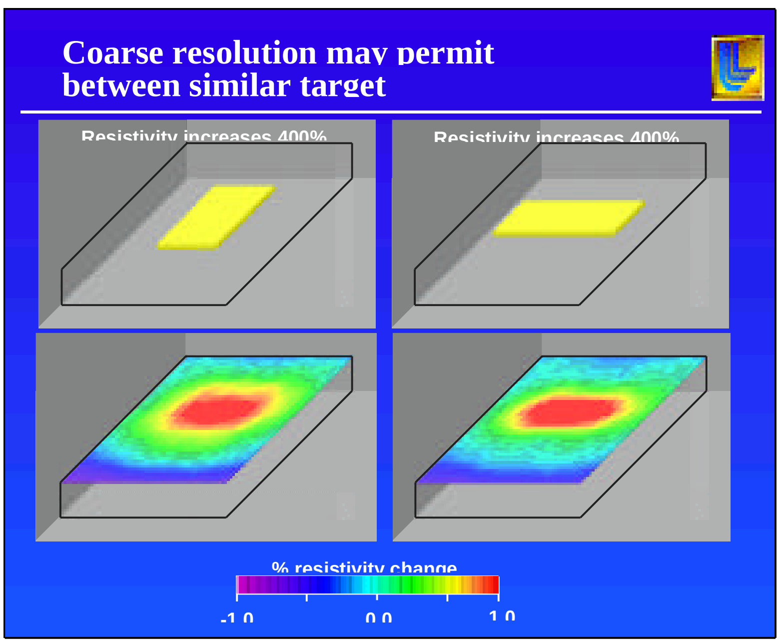


Figure 8. Results of ERT modeling.

Work Next Quarter: An improved rock physics model will be sought for diatomite partially saturated with gas. Results of reservoir simulation runs provided by Chevron for CO_2 injection will be converted to electrical resistivity and velocity and used to compute the expected geophysical responses. A 3-D velocity model with an orbital vibrator source will be simulated. The computed responses will be compared to the observed data and used to update both the geologic and petrophysical models to improve the fit between observed and calculated data.

Work will also continue on investigating the potential for using ERT, with a focus on finding a site for a field test.

Subtask B-2: Field data acquisition for CO_2 monitoring using geophysical Methods

Accomplishments:

- 2-D tomographic images of velocity were computed for baseline (pre-injection) crosswell seismic measurements obtained at Chevron Lost Hills CO_2 injection test site.
- Initial inversion using only the vertical component of the magnetic field was carried out on crosswell EM data provided by Chevron

Summary:

The goal of this subtask is to demonstrate through field testing the applicability of single-well, crosswell, surface-to-borehole seismic, crosswell electromagnetic (EM), and electrical-resistance tomography (ERT) methods for subsurface imaging of CO_2.

Progress This Quarter: During the previous quarter, pre-injection crosswell seismic measurements were performed at the Chevron CO_2 injection pilot site. A high-frequency piezoelectric source (1-5 kHz) and a low-frequency orbital source (50-400Hz) survey were performed between wells OB-C1 and OB-C2 (see Figure 3). This quarter, preliminary 2-D tomographic images of velocity for both the low frequency and high-frequency pre-injection seismic crosswell experiments were obtained. These results are shown in Figure 9 with an interpreted cross section provided by Chevron USA shown in between. The high-frequency piezoelectric data set has higher resolution, as expected. A low-velocity zone is seen between 1,600 and 1,700 ft. in the high-frequency data. The apparent dip of this zone may be indicating the faulted offset seen in the cross section. Lower velocities are measured from the longer wavelength orbital vibrator data, which may be an indication of different scales of heterogeneity being measured in the diatomite. It is not unusual to see frequency dependent measurements of seismic velocity. No sonic logs are yet available in these wells; however, sonic logs, which are about 10,000 Hz, often have higher velocities than surface seismic data, which are about 100 Hz. Borehole tomogography falls in between these scales of measurement. The most important aspect of these data sets is that they represent a baseline measurement of reservoir properties before CO_2 injection. The complexities of the diatomite reservoir make direct measurement of one property (such as CO_2 concentration) very difficult. However, time-lapse changes measured against this baseline survey should be controlled by CO_2 injection and flow properties.

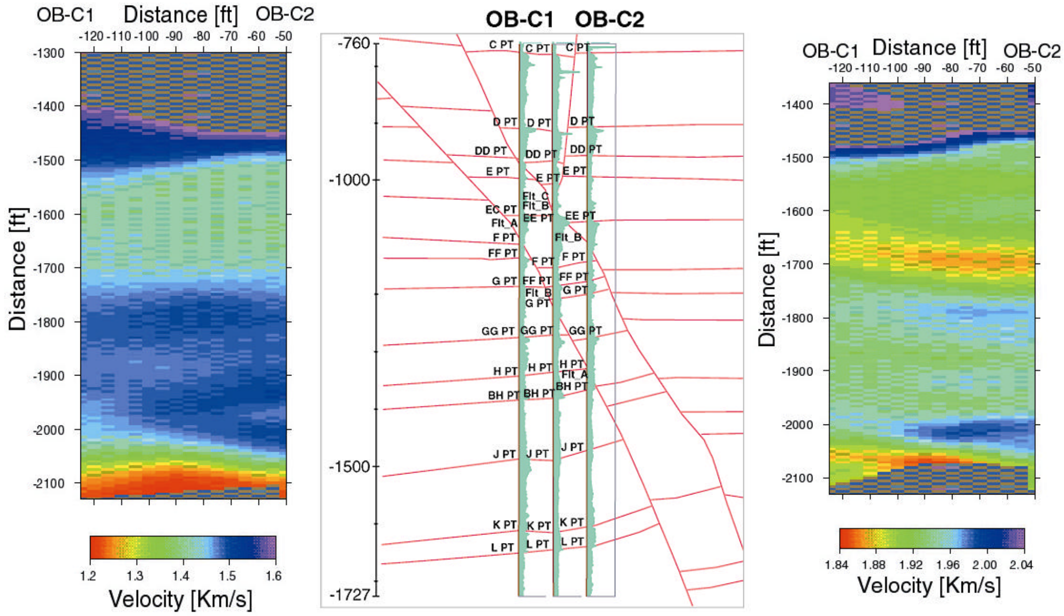


Figure 9. Initial velocity tomograms using low and high frequency sources.

An initial inversion (Figure 10) was completed of crosswell EM data obtained by Chevron between the same wells. Interpretation of these various images has just begun.

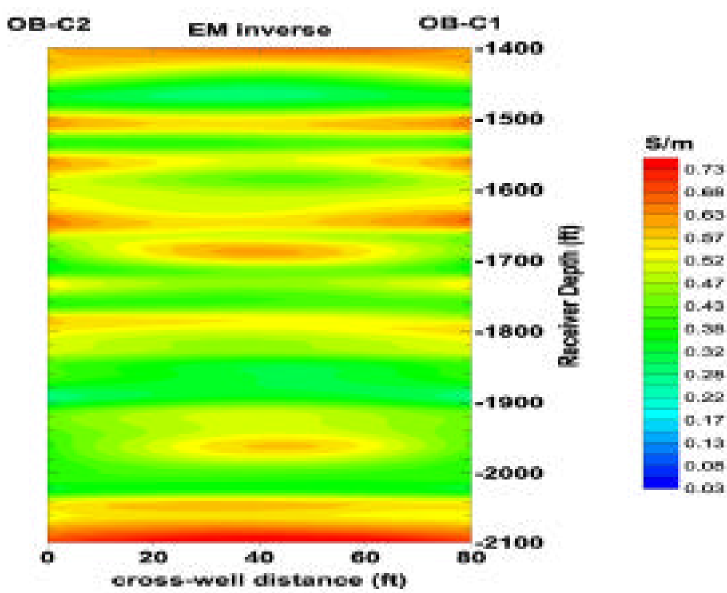


Figure 10. Initial EM tomogram

Work Next Quarter: Processing modeling, inversion, and interpretation of the cross-well seismic and EM data sets will continue. Preparations will be made for the post-injection time-lapse surveys.

Subtask B-3: Application of natural and introduced tracers for optimizing value-added sequestration technologies

Accomplishments:

- Model calculations were performed to assess the magnitude of carbon isotope change in CO_2 interacting with various reservoir phases (e.g., brine, calcite).
- Selection was made of an appropriate suite of gas tracers for use in conjunction with CO_2 injection.
- Design of a flow-through system for testing the interaction of the gas tracers with a range of reservoir materials was carried out.

Summary:

The overall goal of this effort is to provide methods that utilize the power of natural and introduced tracers to decipher the fate and transport of CO_2 injected into the subsurface. The resulting data will be used to calibrate and validate predictive models used for (1) estimating CO_2 residence time, reservoir storage capacity, and storage mechanisms; (2) testing injection scenarios for process optimization; and (3) assessing the potential leakage of CO_2 from the reservoir.

Progress this Quarter: Model calculations were conducted to assess the magnitude of carbon isotope change in CO_2 as it reacts with potential reservoir phases. The calculations assumed reaction in a closed system where CO_2 is allowed to interact (in varying portions) with either a HCO_3-bearing brine, calcite, or hydrocarbon-rich rock (HC; Lost Hills) of unspecified composition. Equilibrium isotope fractionation is assumed in all calculations except one set, where we used experimental sorption isotope partition data obtained in the last quarter on Lost Hills core. Calculations were conducted for 20 and 100°C except for the sorption process, which was based on our 20°C data. The initial carbon isotope value ($\delta^{13}C_{PDB}$) of the CO_2 was set at – 35‰, typical for CO_2 generated from coal-burning power plants. The initial carbon isotope values for the HCO_3-fluid and calcite were set at -5 and 0 ‰, respectively, and are typical of what is observed in carbonate-hosted brine reservoirs. The HC carbon isotope value (-23%) is based on what we measured for the Lost Hills core (vertical core sample 1706).

The results of these calculations are shown in Figure 11 where the $\delta^{13}C_{PDB}$ values for CO_2 are plotted against the atomic percent carbon ratio between CO_2 and the interacting phase of interest (i.e., HCO_3^-, calcite, HC). In a simplistic way, one can think of the extreme left-hand side of the figure as the injection point for the CO_2, which undergoes reaction with progressively more and more of a particular carbon source during transport through the reservoir (left to right across the figure). In all cases, the carbon isotope values of CO_2 become less negative through reactions with either aqueous HCO_3, calcite, or HC. The carbon isotope trajectory is determined by temperature that fixes the fractionation factor between CO_2 and any coexisting phase and the relative proportion of carbon in CO_2 to the carbon in the interacting phase. All of the cases shown are for binary systems (e.g., CO_2 – calcite; CO_2 – HCO_3^-). However, carbon isotope trajectories for CO_2 interacting with both HCO_3^- and calcite would lie between the respective binary curves for any given temperature scenario. Note that the carbon isotope trajectories for CO_2 interacting with HC-bearing rock vary considerably, depending on whether the process is controlled by equilibrium isotope exchange or sorption. Sorption is perhaps more realistic for low temperatures involving CO_2 injection into EOR or CBM systems.

After evaluating the results of published laboratory and field tracer studies, we have selected a suite of gas tracers that appear to have the physical and chemical properties that would make them appropriate for field tracking of injected CO_2. The important selection criteria include: (a) low to zero concentration in the subsurface; (b) detectable at very low concentrations (parts per trillion or less); (c) stable under reservoir conditions; (d) environmentally safe; (e) subject to some of the same mass transfer processes as the injected CO_2; and (f) amenable to analysis using a single sample and a single method for the entire suite. Based on published studies, we have selected SF_6 and a suite of perfluorocarbons for our initial column studies. Results of these studies will be the basis for final determination of the tracers to be used for the field-scale CO_2 injection test and evaluation of the results of that test. Additionally, we have completed the basic design for a flow-through column apparatus that will allow us to test the relative interactions of the gas tracers with a variety of reservoir materials and under a range of pressure and temperature conditions appropriate for proposed injection scenarios.

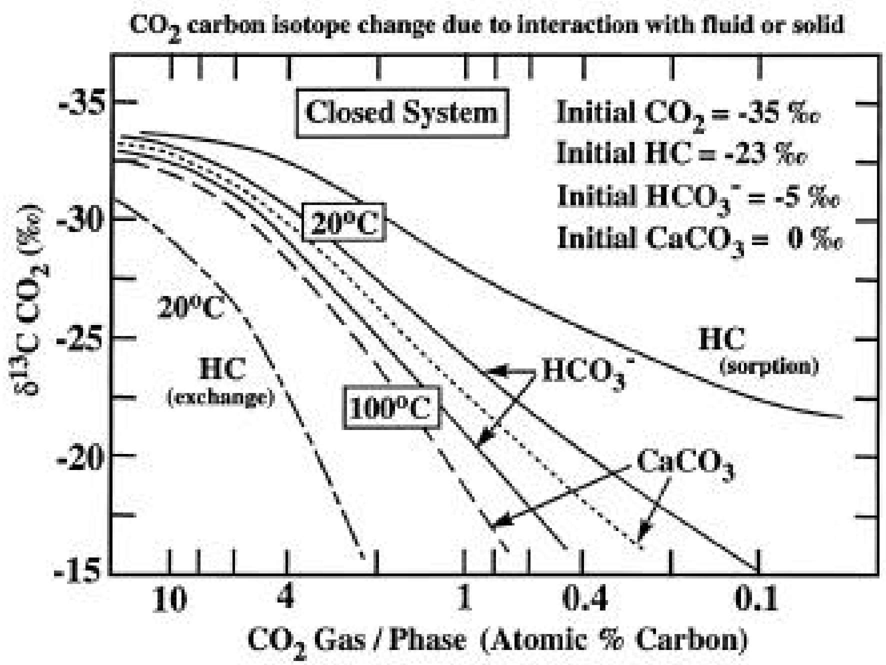


Figure 11. Results of numerical calculations

Work Next Quarter: Efforts in the next quarter will focus on three main areas:

a) Construction of flow-through column tracer apparatus and its initial testing using a select group of rock types and gas tracers. Initially, we will evaluate just the gas tracers to measure the relationship between variations in breakthrough behavior and specific transport processes. In later experiments, we will combine the injection of tracers and CO_2 to quantify the relationship between CO_2 partitioning and gas tracer partitioning.

a) Continuation of core-gas-fluid isotope exchange experiments, emphasizing both the Lost Hill samples and more generic minerals representative of common reservoir lithologies, such as quartz (sandstone analogue), calcite (limestone analogue), and montmorillonite (mudstone analogue)

a) Continuation of model isotope calculations involving more complex reaction-path scenarios. This activity will also involve an assessment of isotopic studies of gas-bearing reservoir systems that may qualify as analogues for various CO_2 injection scenarios (e.g., brine formations, EOR, CBM, etc.).

Task C: Enhance and Compare Simulation Models

<u>Subtask C-1</u>: Enhancement of numerical simulators for greenhouse gas sequestration in deep, unminable coal seams.

Accomplishments:

- Testing of two sets of numerical simulation problems using CMG's STARS and GEM was completed.

Final design of ARC website–to document problem sets and post solutions and discussion was completed.

The CBM numerical simulator, GCOMP, was evaluated in cooperation with software developers at BP-Amoco

Summary:

The goal of this subtask is to improve simulation models for capacity and performance assessment of CO_2 sequestration in deep, unminable coal seams.

<u>Progress This Quarter</u>: Testing of two sets of relatively simple numerical simulation problems have been completed using CMG simulators STARS and GEM. The first problem set is a single-well test with CO_2 injection into a coal seam; the second problem set is an ECBM process with CO_2 injection in a 5-spot well pattern. At this stage, instantaneous gas diffusion between coal cleats and matrix was assumed such that CBM simulators with single porosity model only can be evaluated.

ARC staff worked with BP-Amoco software developers to evaluate and modify the CBM numerical simulator GCOMP.

Testing of the problem sets using BP-Amoco's simulator GCOMP and CSIRO's simulator SIMED II is ongoing.

An ARCs website to document problem sets and post solutions and discussions has been designed.

<u>Work Next Quarter</u>: Prepare a report on the significant mechanisms for sequestration of CO_2 in coal seams that should be included in the ideal CBM numerical simulator. Enable ARC's website and link to GEO-SEQ site. Complete testing of the two problem sets using BP-Amoco's GCOMP and CSIRO's SIMED II. Post the benchmark problems at the ARC's website. More complex problem sets, in which several important mechanisms such as mixed gas diffusion (using a dual porosity model) and coal shrinkage/swelling occur, will be developed.

Subtask C-2: Intercomparison of reservoir simulation models for oil, gas, and brine formations

Accomplishments:

- Development of a first set of test problems for an international intercomparison study of codes for CO_2 sequestration in oil, gas, and brine formations was completed.

Summary:

The objective of this subtask is to stimulate the development of models for predicting, optimizing, and verifying CO_2 sequestration in oil, gas, and brine formations. The approach involves: (1) developing a set of benchmark problems, (2) soliciting and obtaining solutions for these problems (3) holding workshops of industrial, academic, and laboratory researchers, and (4) publishing results.

Progress this Quarter: Several new test problems were added that include chemical interactions, analysis of CO_2 injection at a site similar to Sleipner, and miscible and immiscible displacement of oil by CO_2. Guidance for the code intercomparison project from the GEO-SEQ Advisory Committee was obtained. A laboratory report giving the approach for the intercomparison study and detailed specifications of the first set of test problems (see Table 2) was revised and completed. The coalbed methane test problems included in an earlier draft were removed, because simulation technology in this area was judged to be too immature at this point. A "First Announcement and Call for Participation" was also drafted, so that all materials are on hand for actually starting the public phase of the comparison project.

Simulation studies of some of the test problems were started.

Process	Problem Title
Carbon sequestration with enhanced gas recovery	1. Mixing of stably stratified CO_2-CH_4 gases by diffusion with gravity effects 2. Advective-diffusive mixing of CO_2-CH_4 due to lateral density gradient
Aquifer disposal of CO_2	3. Radial flow from a CO_2 injection well 4. CO_2 discharge along a fault zone
Hydro-mechanical coupled processes	5. Caprock deformation, uplift, and permeability change during CO_2 injection in an aquifer
CO_2 sequestration in coalbeds	6. Single well CO_2 injection test 7. 5-spot CO_2 injection process

Table 2. First set of test problems for code intercomparison study.

Work Next Quarter: The report mentioned above would be distributed to interested groups worldwide to solicit their input and participation in the intercomparison study. These materials will also be placed on the GEO-SEQ web site. Simulations of the first test problem set will be continued. Additional test problems will be developed.

Accomplishments:

- Mathematical models were developed and capacity factors derived for brine formations to assess the relative contributions to sequestration capacity from CO_2 (1) in gas phase, (2) dissolved in aqueous phase, and (3) in solid minerals.
- Location and identifying information were compiled for 10 large industrial CO_2 sources in a nine-county area of the upper Texas Gulf Coast.

Summary:

The objectives of this task are to: (1) improve the methodology and information available for assessing the capacity of oil, gas, brine, and unminable coal formations and (2) provide realistic and quantitative data for construction of computer simulations that will provide more reliable sequestration capacity estimates.

Progress this Quarter: The GEO-SEQ project plans to use realistic data sets generated by the Texas Bureau of Economic Geology (TBEG) to perform simulations of sequestration capacity in brine formations. Location and identifying information were compiled on 100 likely large, industrial CO_2 sources in a nine-county area of the upper Texas Gulf Coast and added to the GIS database so that emitters and sinks can be readily compared. This is an area centering on Houston where abundant power plants, abundant industrial sources, and abundant high-quality reservoirs intersect. Therefore it is proposed as a good target where early pilot activities could be performed and readily scaled up to reduce large-volume emissions. Compilation of abundant geologic data for the Frio and Oakville reservoirs in the Texas Gulf Coast was begun and the first large box of reports organized for transmission to partners. Information on Texas regulations for underground injection control has been received from the Texas Natural Resources Conservation Commission (TNRCC).

As a first step in performing capacity-assessment simulations, mathematical models were developed for brine formations to assess the relative contributions to total sequestration capacity from CO_2 (1) in the gas phase, (2) dissolved in the aqueous phase, and (3) in solid minerals. Capacity factors for the three different storage modes were defined as the equivalent gas saturations that would be required to store the same amount of CO_2. These capacity factors were partially evaluated through analytical estimates and numerical simulations. For thermodynamic conditions expected in typical brine formations suitable for CO_2 disposal, the gas-phase capacity factor was estimated to be in the range of from 20 to 30%; that is, approximately 20–30% of pore volume may be available to a CO_2-rich gas-phase during the disposal operation. Aqueous phase capacity factor was found to depend weakly on temperature and pressure, but varying with salinity (from 2% for saturated NaCl brines to 7% for dilute waters). Sequestration by solid minerals varies considerably with rock type and is expected to be a slow process, with little impact on flow processes during the operational life of a CO_2 disposal scheme. Over long time periods (hundreds to thousands of years), the amount of CO_2 that may be sequestered by precipitation of secondary carbonates may be comparable to CO_2 dissolution in pore waters.

Work Next Quarter: A joint meeting between TBEG geologists, supplying reservoir scale data on the Frio and Oakville, and the LBNL modeling team will be held to develop location- specific data sets from models and follow-up preparation of needed data sets. We will continue to work with industrial and utility emitters and reservoir operators to identify prospects for pilot projects.