



**MULTISCALE RESERVOIR
INVESTIGATIONS AND
APPLICATIONS TO TERRESTRIAL CO₂
SEQUESTRATION SYMPOSIUM**

HELD AT

LAWRENCE BERKELEY NATIONAL LABORATORY

ON

December 7-8, 2001

Forward

"Multiscale Reservoir Investigations and Applications to Terrestrial CO₂ Sequestration," is the ninth in a series of Geosciences Research Program Symposia dating from 1995. These symposia are topically focused meetings for principal investigators in the program and provide opportunities for our investigators to give presentations to one another and to discuss their Office of Basic Energy Sciences' supported research. Dr. Ernie Majer from Lawrence Berkeley National Laboratory has kindly agreed to serve as host of the meeting. I would like to thank Ernie and Joyce Pfeiffer of LBNL for their hard work in making this meeting possible. In addition to the recognition the symposium gives to all of the investigators, we traditionally also recognize one outstanding contribution from a DOE Laboratory Project and one from a University Project. The outstanding contributions are selected by our session chairpersons. We are fortunate to have as guest session co-chairs Prof. John Logan, Emeritus Professor from Texas A&M University, Dr. Robert Burruss of the U.S Geological Survey, Professor Bob Benson of Colorado School of Mines and Professor Tony Kavscek of Stanford University. They join our Principal Investigator co-chairs Dr. Grant Garven of Johns Hopkins University, Dr. Laura Pyrak-Nolte of Purdue University, Dr. Kevin Knauss of Lawrence Livermore National Laboratory, and Dr. Greg Newman of Sandia National Laboratory. For their efforts on behalf of the investigators I thank them all. We are looking forward to an outstanding series of presentations.

Nicholas B. Woodward, Manager
Geosciences Research Program
Office of Basic Energy Sciences
U.S. Department of Energy

Multiscale Reservoir Processes Symposium

Organized by Lawrence Berkeley National Laboratory

Friday December 7, 2001

7:30 Coffee/Introductions
8:00 Garven
8:25 Boles
8:50 Kennedy
9:15 Elmore
9:40 Preuss
10:05 BREAK
10:25 Meiburg
10:50 Graham
11:15 Wan
11:40 Meigs
12:05 LUNCH
1:00 Grove
1:25 Gledhill
1:50 Carroll
2:15 Eggleston
2:40 Schoonen
3:05 BREAK
3:25 Blencoe
3:50 Horita
4:15 Kirkpatrick
4:40 Klusman

ADDITIONAL ATTENDEES

Nick Woodward, DOE Host
Ernie Majer, LBNL Host
Robert Burruss, Guest Panelist
Robert Benson, Guest Panelist
Anthony Kavscek, Guest Panelist
John M. Logan, Guest Panelist
R. M. Turpening
Joyce Pfeiffer, LBNL Administration

Saturday December 8, 2001

8:00 Orr
8:25 Durham
8:50 Elsworth
9:15 Forster
9:40 Myer
10:05 BREAK
10:25 Wong
10:50 Olsson
11:15 Martel
11:40 Pyrak-Nolte
12:05 LUNCH
1:00 Nihei
1:25 Nur
1:50 Korneev
2:15 Segall
2:40 Datta-Gupta
3:05 BREAK
3:25 Lee
3:50 Roberts
4:15 Newmark
4:40 Newman
5:05 Alumbaugh

Friday December 7, 2001

A Numerical Model for Fault-Valve Behavior, Fluid Flow, and Earthquake Recurrence in Active Thrust Faults,

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The coupled behavior of pore fluids and crustal deformation is important in many hydrogeologic and reservoir processes. Active fault zones play a substantial role in controlling fluid migration in sedimentary basins and fluid pressures in turn provide a feedback on fault mechanics. For example, fault zones control fluid migration by changing their permeability during an earthquake cycle, usually acting as barriers during the interseismic period and as conduits immediately after an earthquake. An earthquake caused by buildup of shear stress can result in dilation effect within the fault zone, thereby changing the local pore pressure (Bosl & Nur, 2000). Fluid pressure itself affects the mechanical behavior of the fault by reducing the shear strength, which in turn can trigger more earthquakes as strength decreases.

The Coulomb failure function depends on normal stress, shear stress and fluid pressure. Once a fault fails, the earthquake is accompanied by both pressure and stress drops that will increase the fault strength. Further tectonic loading will reduce the fault strength until the next fault failure criteria are reached and the cycle repeats. Recurrence intervals between earthquakes may vary nonlinearly from one period to the next even when the tectonic loading remains constant, because the interval depends on rupture, permeability, the magnitude of the fluid discharge, and the rate of fault sealing due to mineralization. A major goal of this work is to test and quantify these coupled processes and to examine the feedbacks between fluid pressure, permeability, and geologic deformation in a petroleum reservoir environment.

We present a new two-dimensional, plane-strain, finite element model that simulates the hydromechanical coupling between fault-valve behavior and earthquake recurrence. This model is first applied to a regional cross section through the Wheeler Ridge-Pleito thrust fault system, California. The fault cuts Cretaceous, Tertiary and Pleistocene age formations (sandstones, mudstones, sands, gravels, etc.), which have been thrust along the western side of the San Joaquin Valley. The history and hydromechanic behavior of this fault system is geologically well constrained by geophysical imaging, petroleum exploration, structural analysis, and petrographic and geochemical studies of related fault mineralization. Preliminary modeling results reveal that the first failure occurs after 45,000 years, when loading the thrust from hydrostatic and lithostatic conditions. Further numerical modeling is planned to simulate a complete earthquake recurrence, quantify the rates of fluid discharge and internal deformation, explore the feedbacks of fault mineralization, and test hydromechanical effects on the storage and release of geofluids in crustal reservoirs.

Evolution of Methane Seepage along Faults in the Santa Barbara Coastal Area, California: geologic and modern evidence

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Hydrocarbons have been leaking to the surface through Tertiary sediments of the Santa Barbara basin for at least a half million years. Faults exposed onshore along the coast have calcite cement that indicate gas-fluid leakage. Some cements have textural evidence indicating multiple cement events that are contemporaneous with fault movement. Stable carbon isotopic values of the calcite are as light as $\delta^{13}\text{C} = -42$, indicating the carbon source is methane. Inclusions in calcite indicate the presence of meteoric and saline aqueous fluids and hydrocarbons. Homogenization temperatures are around 80-95°C. Thus, methane and hot fluids were leaking from 2-3 km depths in the basin and moving upward along faults on the basin flank. The leakage began at least 120,000 to greater than 500,000 years ago, based on U-Th dates from calcite (Jim Chen, Cal Tech).

Today, extensive seepage of methane occurs offshore in the coastal waters of the basin. Some of the most extensive methane seepage is from high angle faults along the crest of anticlines. Modern submarine seeps are sensitive to sea height (e.g. tides) and presumably long term differences in sea level could have significant effects on seepage rate if sufficient methane were available.

Modern seeps are “cold” and do not appear to be carrying significant amounts of basin fluids. Calcite cement has not been found at these modern seep localities. Thus, over a 10^5 year time scale, seepage has evolved from hot fluids and methane gas moving up basin flank faults tapping over pressured compartments to modern cold gas seepage from faults tapping hydrostatically pressured reservoir.

Development of Isotope Techniques for Reservoir and Aquifer Characterization B.
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Efficient and safe sequestration of large quantities of CO₂ will require reliable characterization of the storage potential of geologic formations, reservoirs and aquifers and a better understanding of the multiple processes that effect the fate and transport of CO₂ in the subsurface. Many oil and gas reservoirs are complexly partitioned by differing structural, petrologic and stratigraphic controls that will inhibit efficient CO₂ injection and limit reservoir potential. In groundwater aquifers, long term storage requires effective traps with minimal leakage to overlying strata. Hydrodynamic processes such as advection, dispersion, and mixing/dilution, as well as chemical processes such as diffusion into low permeability matrix rocks, phase partitioning, dissolution/precipitation of carbonate minerals, and water-rock interaction bear directly on the transport efficiency and fate of injected CO₂. To maximize CO₂ sequestration efficiency, it will be necessary to address these and similar issues related to reservoir and aquifer characterization.

The focus of this project is to develop noble gas isotope techniques for characterizing fluid sources, fluid flow paths, reservoir filling and compartmentalization, flow in homogenous versus fractured media, water-rock interaction, and relevant time scales. This project also seeks to merge isotope techniques with structural and imaging information provided by geophysical techniques.

Lost Hills Pilot Test: The field scale test of CO₂ injection into the Lost Hills, San Joaquin Basin, California, oil and gas field consisted of three parallel projects: seismic and electrical imaging, co-injection of chemical and isotopic tracers, and chemical and isotopic analyses of production fluids before, during and after CO₂ injection. The tracer and geochemical segment has been conducted in collaboration with Dave Cole, Oak Ridge National laboratory. We analyzed samples for noble gas abundance and isotopic compositions collected from observation wells, laid out in a rectangular grid surrounding several CO₂ injection wells, and from the source of the injected CO₂. Samples were collected prior to and at selected times during the injection tests. Preliminary analyses of these samples suggest significant atmospheric contamination that is either introduced during sampling or reflects a residual signal induced by prior production stimulation.

North Sea's Snorre and Stratfjord Oil Fields: Production fluid from the North Sea's Snorre and Statfjord oil fields show clear geographical correlation in their noble gas isotope and abundance characteristics. Mixing relationships coupled with the geographical compositional trends suggest that (1) both reservoirs were filled with oil from a common source, (2) with migration into each reservoir, the inherited noble gases from the hydrocarbon source area are diluted with noble gases from the existing *in situ* reservoir fluids, and (3) fluid flow was from a direction contrary to existing migration scenarios. The fluid in each reservoir had a different *in situ* noble gas composition, and the differences may be related to the regional tectonics—specifically the Viking Graben, a zone of active extension, may be the source of the ³He-enriched mantle-derived fluids found in the Snorre reservoir.

Development and Application of a Paleomagnetic/Geochemical Method for Constraining the Timing of Fluid Migration and Other Diagenetic Events

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Objectives: The goal of this project is to develop paleomagnetic methods for dating diagenetic events in sedimentary rocks. Specific objectives include testing the hypotheses that fluid flow (e.g. basinal fluids, hydrocarbons), clay diagenesis and organic matter maturation are viable mechanisms for the occurrence of pervasive chemical remanent magnetizations (CRMs) that are commonly observed in sedimentary systems.

Project Description: Investigations of diagenetic processes such as fluid migration, clay diagenesis and the maturation of organic matter with burial commonly lack temporal control. The ability to constrain the time of events such as oil migration would be of significant benefit for exploration. Also, temporal controls for the various stages of the cycling of organic matter in the Earth's crust is important for our understanding of the carbon cycle and the development of predictive models with respect to carbon sequestration.

The paleomagnetic dating method is based on a genetic connection between diagenetic processes and the precipitation of authigenic magnetite. Isolation of the magnetization carried by the magnetite and comparison of the corresponding pole position to the apparent polar wander path allows the timing of diagenetic events to be determined. The research involves paleomagnetic field and laboratory tests to constrain appropriate chemical and physical conditions for magnetite authigenesis.

Results: We are continuing to build on our previous work in which we have documented the occurrence of chemical remanent magnetizations (CRMs) resulting from the precipitation of authigenic, magnetic minerals via rock/fluid interactions, clay diagenesis, and the maturation of organic matter.

Studies of Cambrian-Ordovician serpentinite in a tectonic terrane along the Highland Boundary Fault (HBF) in Scotland indicate that the HBF was a conduit for warm fluids in the Carboniferous that caused dolomitization, silicification, and hematite authigenesis. Preliminary paleomagnetic and geochemical results from a number of lithologies along the Moine thrust in northern Scotland also date a pulse of hot fluids in the Carboniferous-Permian. These results provide direct evidence for post-orogenic fluid activity and release of heat along faults.

We are testing clay diagenesis and maturation of hydrocarbons for the origin of numerous, widespread, pervasive CRMs in sedimentary systems that have not been altered by externally-derived fluids. We have completed a study on Jurassic sedimentary rocks on the Isle of Skye, Scotland, which are consistent with a connection between fluid-enhanced clay diagenesis and magnetite authigenesis/remagnetization.

Results from Mesozoic rocks in western North America where the timing of the smectite-to-illite conversion can be reliably inferred are encouraging. We are comparing results from Mesozoic strata in the disturbed belt of Montana where the rocks contain ordered illite/smectite that formed by moderate heating as a result of thrust loading, with equivalent strata on the adjacent Sweetgrass Arch which contain unaltered smectite-rich

clay mineral assemblages. The results indicate that the magnetization in the rocks in the Sweetgrass Arch is weak and dominated by a modern viscous component. In contrast, the disturbed belt rocks have higher magnetic intensities and contain a pre-folding, reversed Tertiary magnetization that is interpreted to be a CRM residing in magnetite. A presence-absence test and the timing of acquisition for the CRM suggest that magnetite authigenesis is related to the smectite-to-illite conversion.

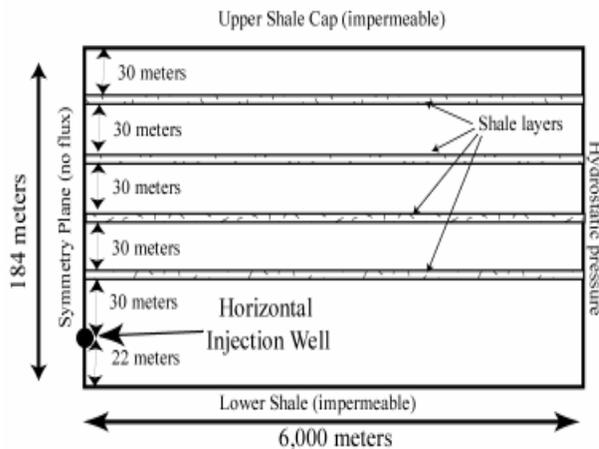
The results of laboratory simulation experiments indicate an increase in magnetic susceptibility when smectites are heated at moderate temperatures (65°C, 97°C). Rock magnetic studies indicate that the increase in susceptibility is at least partly due to authigenesis of magnetite that is capable of carrying a stable magnetization. The magnetite authigenesis is not apparently associated with significant conversion of smectite to illite but to an earlier stage of clay diagenesis. The source of iron may be on the surface of the clay particles. The results suggest that smectite diagenesis triggered by temperatures equivalent to low burial could cause magnetite authigenesis and acquisition of a CRM.

We are also continuing to investigate maturation and migration of hydrocarbons into reservoirs as a mechanism to cause remagnetization by investigating the Mississippian Deseret Limestone and Permian White Rim Sandstone in Utah. The hydrocarbons in the Deseret are interpreted to have been generated in the Early Cretaceous during the Sevier Orogeny and to have migrated into the White Rim Sandstone in the Tertiary. Preliminary results indicate that the hydrocarbon-impregnated White Rim contains a magnetization in magnetite that is probably related to the hydrocarbons. The Deseret contains at least one CRM that appears to be Mesozoic in age.

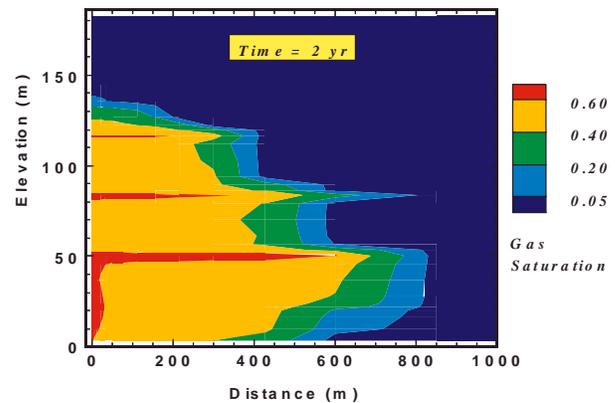
Recent Advances in Mathematical Modeling of Coupled Processes During CO₂ Disposal into Saline Aquifers

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Injection of CO₂ into saline aquifers will give rise to a process of immiscible displacement, which is accompanied by partial dissolution of CO₂ into the aqueous phase, chemical interactions between fluids and solid minerals, and geomechanical changes. We are developing and applying numerical simulation capabilities to gain an understanding of the fundamental processes involved, and thereby provide a sound basis for evaluating the technical feasibility of disposal of CO₂ into brine formations. Three interrelated codes are being developed that address, respectively, issues of fluid dynamics (TOUGH2/ECO2), reactive chemical transport (TOUGHREACT/ECO2), and geomechanics (TOUGH2-FLAC3D). These codes include a realistic description of the thermophysical properties of multiphase mixtures of CO₂, water and NaCl over a wide range of pressure and temperature conditions. Applications have been made to study dynamical processes that would be induced by CO₂ injection into brine formations over a range of space and time scales. Investigations to date have addressed CO₂ injection from a well or a group of wells, CO₂ leakage through a fault zone, displacement processes in media with spatially correlated heterogeneity, studies of viscous fingering, CO₂ sequestration by secondary carbonate precipitation, couplings between fluid flow and chemical reactions, stress effects on porosity and permeability of a caprock, and mechanical displacement of a leaky fault. As an example, the figure given below (left panel) shows a schematic 2-D vertical section model, with sand-shale sequences patterned after the Sleipner field in the Norwegian sector of the North Sea (Carl Steefel, personal communication). The right panel shows gas saturations after two years of CO₂ injection by means of a horizontal well completed in the lowest sand, at rates corresponding to the actual injection operations at Sleipner. The shales are seen to reduce effects of buoyant upflow of CO₂, and causing an improved volumetric sweep.



Schematic of 2-D vertical section model, consisting of a sand-shale sequence.



Simulated gas saturations after two years of CO₂ injection.

Miscible displacements in the quarter five-spot geometry

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A highly resolved numerical investigation is conducted into the dynamics of unstable three-dimensional miscible displacements in homogeneous and heterogeneous porous media. The overall geometry of the flow domain, in this case the quarter five-spot configuration frequently employed in enhanced oil recovery applications, generates a global potential flow field. This sets the background for complex interactions between the viscously and density-driven instability mechanisms and the heterogeneities of the porous environment. The dynamics of the displacement processes are analyzed in terms of the interaction mechanisms among the three vorticity components related to viscosity, density and permeability variations. When compared to earlier two-dimensional simulations, new effects are seen to arise in three dimensions, which produce both qualitatively and quantitatively different flow behavior. Depending on the aspect ratio, the initially vertical front has been seen to break up into several horizontal layers, which subsequently give rise to individual fingers. Even a moderate density difference leads to a considerable reduction in the breakthrough efficiency, as it redirects the fluid along one of the horizontal boundaries and thereby increases the local effective Peclet number, thus enhancing the fingering instability. For certain parameter combinations, a secondary instability is seen to emerge as a result of vertical density stratification.

Modeling of Mesoscale Phenomena During Sequestration of Carbon Dioxide in Porous Reservoirs

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Processes for the sequestration of carbon dioxide in porous reservoirs involve several components of multiphase flows. If hydraulic fracturing is used to develop local "sweet spots" (zones of high permeability), the flow and resulting distribution of the proppant can have a large impact on the subsequent sequestration process. Even without hydraulic fracturing, the creation of precipitates can drastically alter the characteristics of the porous formation itself. Furthermore, emulsions can form and fingering can take place at the supercritical CO₂/brine interface. The purpose of this research program is to combine experiments, computations, and theory to make fundamental advances in our ability to predict transport phenomena in concentrated, multiphase, disperse systems, particularly when flowing through geologic media. In order to be of use in designing effective CO₂ sequestration processes, significant enhancements to currently available continuum-level suspension flow models are required. Both experimentation and high performance computing at the mesoscopic level are used to obtain microstructural information that is necessary for the development and refinement of the continuum models.

The continuum models originally developed by Phillips et al. (1992) and Nott and Brady (1994) have been improved in the current research to account for normal stress contributions. This allows accurate predictions of suspended particle migration in curvilinear flows. The improved model also allows for non-neutrally buoyant particles and non-Newtonian suspending liquids. Results from the new models, which have been implemented into a general-purpose finite element computer code, show good agreement with experimental measurements based on nuclear magnetic resonance (NMR) imaging in idealized three-dimensional flows. However, model improvements needed include the development of more accurate hindered settling (drag) functions for particles interacting with other types of particles or in a porous medium, as well as a better understanding of the magnitude of the normal stresses developing from these same interactions. We are obtaining this information through particle level (mesoscopic) simulations and fundamental experiments.

Massively parallel computing has allowed particle level simulations, based on the boundary element method (BEM), with up to three thousand particles. Volume averaging of the stress tensor has been added to the codes to allow prediction of average macroscopically observed transport properties from particle scale simulations. These simulations lead to detailed information on individual particle and fluid motion that is unobtainable through experiments. For example, highly accurate transient calculations of collections of particles in nonlinear shear fields have demonstrated that particles in inhomogeneous shear fields migrate in the direction of the lower shear rate. This is to our knowledge the first explanation of this phenomenon from first principle physics.

These very fundamental studies are elucidating the fundamental physics that govern the particle transport phenomena in multiphase systems.

This work is complemented by experimental work to provide insights and benchmarks. A study of apparent particle slip in confined geometries has been performed. Due to the finite size of the particles, suspensions of particles form a boundary layer near containing walls. The walls impose an ordering of the particles that extends several particle diameters into the bulk suspension. In constrained geometries such as the small channels in porous media, this boundary layer can extend over the entire channel. NMR imaging is used to determine the mesoscale structure and falling and rolling balls are used to investigate the mechanical properties at locations ranging from the centerline to the walls of the containing cylinder. It was found that there exists markedly non-Newtonian wall effects in concentrated suspensions in which the volume fraction of particles is greater than 0.2. At these higher concentrations, wall effects are much larger and extend further into the suspension than in Newtonian fluids.

Partitioning of Clay Colloids at Air Water Interfaces

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Colloid sorption onto air-water interfaces has been previously documented in a variety of environments, but better quantification and understanding is still needed. Affinities of clay colloids for the air-water interface were measured using a bubble-column method and reported as partition coefficients (K). Four types of dilute clay suspensions were measured in NaCl solutions under varying pH and ionic strength conditions: kaolinite KGa-1, illite IMt-2, montmorillonite SWy-2, and bentonite. The K values of three types of polystyrene latex particles with different surface-charge properties were also measured for comparison. Kaolinite exhibited extremely high affinity to the air-water interface at pH values below 7. Illite has lower affinity to air-water interfaces than kaolinite, but has similar pH-dependence. Na-montmorillonite and bentonite clay were found excluded from the air-water interface at any given pH and ionic strength. Positively and negatively charged latex particles exhibited sorption and exclusion, respectively, at the air-water interface. These results show the importance of electrostatic interactions between the air-water interface and colloids, especially the influence of pH-dependent edge charges, and influence of particle shape.

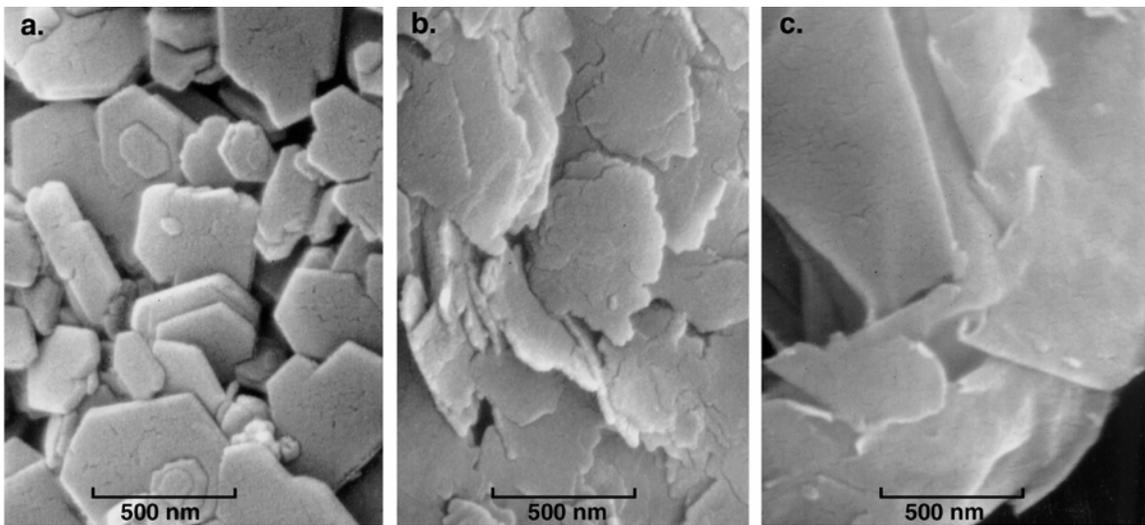


Figure 1. Scanning electron micrographs of clays, (a) kaolinite, (b) illite, and (c) Na-montmorillonite.

Transport Visualization for Studying Mass Transfer and Solute Transport in Permeable Media

Lucy Meigs, Sandia National Laboratory; Roy Haggerty, Oregon State University, and Charles Harvey, Massachusetts Institute of Technology

Understanding and predicting mass transfer coupled with solute transport in natural permeable media is important in several energy-related problems - CO₂ sequestration, nuclear waste disposal, hydrocarbon extraction, and groundwater remediation. Mass transfer is the set of processes that control movement of a chemical between mobile (advection-dominated) domains and immobile (diffusion- or sorption-dominated) domains within a permeable medium. Key consequences of mass transfer on solute transport include (1) increased sequestration time within geologic formations; (2) reduction in average solute transport velocity by up to several orders of magnitude; (3) long “tails” in concentration histories during removal of a solute from a permeable medium; (4) poor predictions of solute behavior over long time scales; (5) increased solute mixing and access to rock surface for reactions. Like hydraulic conductivity and dispersivity, effective mass transfer parameters are scale-dependent.

The objectives of our research are to determine the conditions under which mass transfer is a dominant process, and to develop models for predicting the effects of mass transfer over diverse time and length scales. Our approach is to conduct numerical simulations and laboratory experiments in heterogeneous media using conventional column techniques and novel transport visualization techniques. We are conducting numerical and laboratory experiments to 1) map transport regimes (conditions under which different equations adequately describe transport), 2) investigate the application of models developed at one time and space scale to larger scales, and 3) investigate reactive transport with mass transfer.

Numerical simulations and initial experimental work demonstrate that the upscaled solute transport behavior of a conservative solute is determined, not only by the standard spatial statistics of hydraulic conductivity, but also by the connectedness of the hydraulic conductivity field. Results demonstrate that hydraulic conductivity fields with the same standard spatial statistics may, or may not, produce mass-transfer behavior in a conservative solute depending on the connectedness characteristics of the media. Furthermore, mass transfer may be driven by both diffusion and advection.

We have developed a method by which tracer experiments conducted at different velocities can be used to construct a residence time distribution for the immobile domain that describes mass transfer in heterogeneous media over a wide range of time scales. The scaling behavior of breakthrough curves can be predicted with this residence time distribution. For media with multiple rates of mass transfer, the use of the traditional single-rate model (i.e., exponential residence time distribution) gives poor predictions of transport when the scale of experiments and predictions differ.

We have also developed a method using colorimetric chemical reactions to visualize reactive transport in porous media. Using this method we have demonstrated that commonly used models that assume perfect mixing between two reactants at the

pores scale as they are transported through a porous media can over predict the product formed.

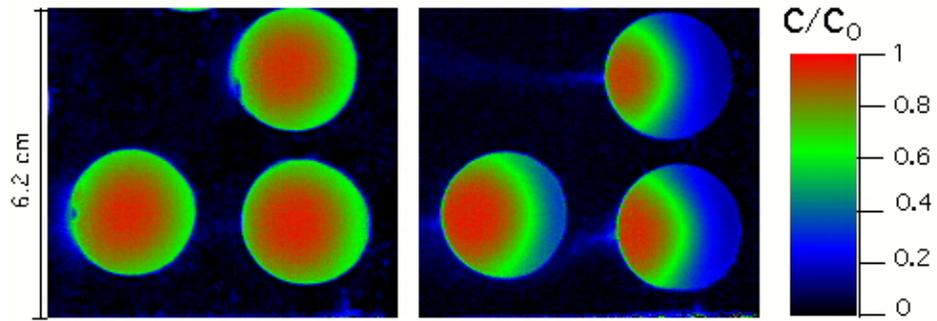


Figure: Comparison of solute concentration within low permeability regions for experiments conducted in two different transport regimes. The flow rate (1.32ml/min) and elapsed time (approx. 525 min.) are the same for both the diffusive mass transfer (left) and advective mass transfer (right) regime images.

Application of the Ion Microprobe to Stable Isotopic Analysis of Terrestrial Carbonates

Marty Grove, Mostafa Fayek, T. Mark Harrison, University of California at Los Angeles

The utility of using the fractionation of stable isotope ratios of hydrogen, oxygen, carbon and sulfur preserved in minerals as a geothermometer or tracer of fluid-rock interactions is well-established. While analysis of mg-size materials is routine, important geologic features such as zoned minerals and cemented intergranular regions require *in situ* measurements at the micron scale. An important breakthrough in this regard was the development of direct laser fluorination, which dramatically decreased sample size requirements for gas-phase mass spectrometric analysis permitting individual grains of $\sim 50 \mu\text{m}$ -size to be measured with $\pm 0.1\%$ precision in $\delta^{18}\text{O}$. Parallel progress has been made however, in developing precise and accurate (i.e., ‰ to sub-‰) methods for the analysis of O and C isotopes using the ion microprobe which is capable of performing *in situ* measurements with ca. $10 \mu\text{m}$ resolution and an internal and point to point reproducibility better than $\pm 1\%$.

Application of multicollection detection system permit such measurements to be obtained from $\sim 10 \mu\text{m}$ spots in less than 5 minutes. When applied to potential monitors climatic variability such as speleothems, $\delta^{18}\text{O}$ records with a resolution of 1 year or better may be rapidly obtained. This is well illustrated by ion microprobe results we have obtained from a Hulu Cave speleothem sample with optically visible annual bands that was previously determined to record a 2.5‰ decrease in $\delta^{18}\text{O}$ between 17.0 ka and 15.9 ka.

With these technical advances, the primary limitation upon accuracy has approached the level of standardization issues. As in most other forms of mass spectrometry, the ion microprobe must be calibrated with appropriate standards. Compositionally dependent fractionations in ion microprobe isotopic analysis are commonly referred to as “matrix effects”. To the extent that matrix effects are large, the accuracy of ion microprobe isotopic measurements will suffer if standards are not chemically similar to unknowns. This is an important consideration when analyzing Ca-Mg-Fe carbonates due to the extensive solid solution that exists in nature. We are developing an approach for calibrating instrumental mass fractionation produced by compositional variation in natural carbonates that is intended to reduce uncertainty related to this effect to below 0.5‰. To do so we have: (1) synthesized or otherwise obtained a broad suite of carbonates that span compositionally important regions of the $\text{CaCO}_3\text{-MgCO}_3\text{-FeCO}_3$ ternary; (2) characterized these materials in terms of both major element composition and oxygen and carbon isotopic compositions; and (3) systematically analyzed and oxygen and carbon isotopes in these carbonates using the ion microprobe to determine the instrumental mass fractionation produced by variations in major element composition. We have performed our measurements using analytical conditions we consider most promising for ion microprobe isotopic analysis of terrestrial carbonates. Hence the results will not be generally applicable when very different analytical conditions, most notably extreme energy filtering are employed.

Experimental and Analytic Studies to Model Reaction Kinetics and Mass Transport of Carbon Dioxide Sequestration in Depleted Carbonate Reservoirs

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Sequestration of carbon dioxide in depleted gas reservoirs appears to be a viable option, with a possible economic spin-off from the recovery of significant gas reserves. At the elevated temperatures and pressures encountered in reservoirs, carbon dioxide behaves as a supercritical fluid. Under these conditions, little is known regarding the kinetics of calcite dissolution by carbon dioxide, diffusion of carbon dioxide in natural gas, and displacement of natural gas by carbon dioxide. This project is conducting research to better understand these phenomena through experimental determination of the reaction kinetics for calcite dissolution in subsurface brines at temperatures and pressures typically found in reservoirs. The requisite data will be used to develop a model for mass transport and reaction kinetics for the injection and storage of carbon dioxide in carbonate or carbonate-bearing depleted gas reservoirs.

“Free-drift” experiments have been conducted that examine the influences composition, $p\text{CO}_2$ and temperature exert on the rate constant and reaction order of calcite dissolution in simulated brines. The dissolution is followed in an open-system by *in-situ* measurement of pH at fixed $p\text{CO}_2$ and allowed to proceed from extreme undersaturation ($\Omega < 0.1$) to near equilibrium ($\Omega > 0.95$). The experiments have focused on three brine compositions of different calcium to sodium ratios and total dissolved solid content. Preliminary results suggest that ionic strength may not impart a significant effect to the reaction but that the Ca:Na ratio does. Furthermore, despite an order of magnitude of change in $p\text{CO}_2$ there is not a prominent effect on the dissolution rates. Recent attempts have been made to switch to a closed-system “free-drift” apparatus that will allow for high temperature rate measurements the results of which will be presented and discussed.

Geologic Sequestration of CO₂: Experimental Determination of Ca-Silicate Dissolution Rates

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Determination of mineral dissolution and precipitation kinetics is fundamental to the successful disposal of greenhouse CO₂-rich gases in aquifers, because reservoir storage capacity is directly related to the conversion rates of CO₂ to carbonate minerals, and because secondary mineral precipitation will effect reservoir porosity and permeability. For example, acid water near the injection well will dissolve silicate and calcium minerals and increase porosity and permeability. As the acid plume is neutralized by mineral dissolution, carbonate and clay minerals will precipitate further away from the injection well. Unfortunately, there is a lack of experiments that measure the coupled dissolution and precipitation reactions of multi-mineral systems, and there are no experimental studies of the direct effects of high levels of dissolved carbon on silicate and carbonate reaction kinetics.

Our approach is to conduct single and multi-mineral dissolution and precipitation experiments in the Ca-Al-Si-CO₂ system as a function of pCO₂, pH and temperature. Our kinetic research will feed directly into reaction-transport codes that can evaluate aquifer storage of dissolved CO₂ and mineral carbonates, and resulting changes in porosity and permeability. We have experimentally measured the dissolution rate of labradorite (Ca_{0.6}Na_{0.4}Al_{1.6}Si_{2.4}O₈) in water saturated with supercritical CO₂ (pCO₂ = 1400 psi, CO₂ (aq) = 0.6 molal, pH 3.2) and in CO₂-free water of equivalent pH at 30, 60, 100 and 130°C using mixed flow-through reactors. Below we briefly describe the effects of CO₂, dissolved aluminum, and temperature on labradorite dissolution.

We observed no direct effect of dissolved CO₂ on labradorite dissolution. Labradorite dissolution rates measured at pH 3.2 with much lower dissolved CO₂ are the same as those reacted in waters saturated with supercritical CO₂ of the same pH.

In our experiments we took advantage of retrograde solubility of aluminum hydroxides, such as gibbsite, at acid pH to study the effect of dissolved aluminum on feldspar dissolution. Our results show that dissolved aluminum inhibits labradorite dissolution until a secondary phase (gibbsite) precipitates from solution. This suggests that feldspar dissolution will be higher in waters saturated with secondary phases than in undersaturated waters. This is important because a large portion of the affected aquifer will have a temperature and/or pH, which promotes precipitation of secondary phases.

We calculate the activation energy from the temperature dependence of labradorite dissolution rates normalized to the silicon release at a constant flow rate (0.9 ml min⁻¹), because higher release rates of Na, Ca, and Al relative to silica were observed at 30 and 60°C. It is important that the temperature dependence be in terms of a constant flow rate at this point in our study, because labradorite dissolution appears to be affected by aqueous aluminum, which changes as a function of flow rate. We calculate $E_a = 9.53$ (kcal mol⁻¹). This value is slightly lower than E_a ranging from 11.5 to 15.9 (kcal mol⁻¹) reported from other labradorite studies in acid solutions (pH 1-4, T 5-70°C)

The Dissolution Kinetics of Magnesite and Calcite as a Function of pH: Step Motion, Dissolution Flux, and the Importance of Well-Defined Hydrodynamics

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In constructing experiments designed to address the dissolution and growth kinetics of carbonates in the context of CO₂ sequestration in deep aquifers, it has become apparent that a more quantitative understanding of coupled surface chemical kinetics with mass transport is needed. We have monitored dissolution on the (104) surfaces of magnesite (MgCO₃) and calcite (CaCO₃) using *in-situ* atomic force microscopy (AFM) at elevated temperature and with well-defined and controllable fluid-cell hydrodynamics. Over the range $2.0 < pH_{\text{bulk}} < 5.0$ at 60 °C, the experimental data and the corresponding solution of the convective-diffusion equation for the hydrodynamic AFM system revealed that magnesite dissolution is slower by a factor of $10^2 - 10^4$ than the proton mass transport limit. Dissolution flux varied nonlinearly with the surface concentration of H⁺, $[H^+]_{y=0}$, and inclusion of the homogeneous chemical kinetics of H⁺ consumption to form carbonic acid was unnecessary. The non-linear behavior was best represented by a Langmuir isotherm for proton adsorption in which the adsorbed entity consists of a surface complex containing more than one proton. The apparent surface kinetic detachment coefficient, k'_n , for this surface complex was determined to be $5 \times 10^{-12} \text{ mol cm}^{-2} \text{ s}^{-1}$, but the determination of a particular coordination number, n , of this detachment complex was not possible. The velocity of dissolving + steps was constant, within error, over the entire experimental pH range while the dissolution flux varied by over an order of magnitude in this same range. AFM imaging revealed a dramatic increase in step density associated with a large increase in dissolution flux that was attributed to the protonation of terrace-adsorbed carbonate sites (*i.e.*, adions). We propose that the intrinsic protonation constant, K_{int} , differs for adions, kink, step and terrace sites based on the AFM observations of surface and step morphology as a function of pH.

Studies of calcite dissolution are generally in the mixed transport-kinetics controlled regime (even at high fluid velocities) where quantitative information can only be obtained by accounting for the transport components. Our measurements of calcite dissolution as a function of fluid flow rate show the importance of controlled hydrodynamics in this system. Furthermore, when more complicated systems are examined such as the dissolution of calcite in the presence of impurity ions such as Sr²⁺ and Mg²⁺, it becomes increasingly important to account for mass transport and the heterogeneous consumption/production of these species.

Interaction of Pyrite with Water: Combining Molecular and Macroscopic Observations

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Pyrite is a common mineral in sedimentary basins. Injection of fluids as part of CO₂ sequestration techniques or fluid injections as part of routine secondary hydrocarbon extraction procedures (e.g., steam injection and water flooding) can lead to oxidation of pyrite in the subsurface. Oxidation of pyrite has several consequences. Acidity produced in the oxidation process can dissolve cement well casing and corrode steel pipes[1]. Sulfate formed in the process may migrate into the reservoir and stimulate sulfate reducing bacteria, which can lead to souring (H₂S production). Large-scale acidification of formation waters could release dissolved carbon dioxide.

The primary objective of our interdisciplinary research program has been to develop a better understanding of the fundamental reaction steps in the oxidation of pyrite by dissolved oxygen. To achieve this goal we have integrated observations at the macroscopic scale with those at the molecular scale using a combination of geochemical and advanced surface science techniques. The most important outcome of this work is the finding that S-deficient sites on pyrite surfaces play a key role in initiating a complex sequence of surface reactions that lead to the oxidation of pyrite [2-7]. These defects appear to be able to induce the formation of hydrogen peroxide[8], which may be a key reactant in the subsequent oxidation of the S₂²⁻ moiety. We have also shown that it is possible to inhibit the oxidation reaction if the electron transfer chain can be interrupted[9].

Although the emphasis of our research has been on studying the interaction of pyrite and dissolved oxygen in static experiments we have recently also started to study the effect of tangential fluid flow on the surface properties of pyrite which would have direct implication in any CO₂ sequestration scheme. Streaming potential experiments have been used to investigate the development of charge on the pyrite surface as a function of fluid composition and initial state of the surface (clean vs oxidized). The main advantage of streaming potential measurements over electrophoresis, which we have used in earlier studies[10-12], is that larger grain sizes can be used (it may, in fact be possible to conduct measurements on a single crystal. With streaming potential determinations it is also possible to investigate charge development on natural sedimentary material. One of the surprising results of our work with pyrite is that fluid flow in itself may induce electron transfer reactions. It appears that the potential induced by fluid flow is dissipated in part by electron transfer reactions on the surface. This phenomenon is expected to be prevalent in sulfide minerals which have significant intrinsic conductivities. The implication of these preliminary results is that the injection of fluids into sedimentary formation may lead to pyrite oxidation, even if there are no oxidants in the fluid. We are currently conducting spectroscopic studies to corroborate these results.

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Experimental Investigations of the Thermophysical Properties and Phase Relations of CO₂-bearing Fluids at Elevated Temperatures and Pressures

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A custom designed vibrating-tube densimeter is being used to determine the densities, excess molar volumes, and liquid-vapor phase relations of binary and ternary CO₂-bearing fluids in the system CO₂-CH₄-N₂-H₂O at 35-400°C, 50-1000 bars. The volumetric and phase-equilibrium data produced are highly precise and accurate, and have important applications in: developing new equations of state for binary and multicomponent CO₂-CH₄-N₂-H₂O fluids; interpreting fluid-inclusion data; and modeling the rates and patterns of hydrothermal fluid flow in deep sedimentary basins, high-temperature geothermal fields, shallow contact metamorphic aureoles, and low-pressure regional metamorphic terrains.

Significantly, the results also have *immediate* applications in two major CO₂-sequestration technologies: mineral carbonation, and CO₂-enhanced coal bed methane (CBM) production. Since 1998, research on mineral carbonation has focused on conversion of serpentine [(Mg,Fe)₃Si₂O₅(OH)₄] to magnesite (MgCO₃) by the reaction $(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4 + 3\text{CO}_2 \rightarrow 3(\text{Mg,Fe})\text{CO}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}$. However, to achieve satisfactory carbonation rates at commercially feasible temperatures and pressures ($T \leq 300^\circ\text{C}$, $P \leq 200$ bars) under *oxidizing conditions*, it is necessary first to dehydroxylate the serpentine at 600-650°C. This heat-treating step is very energy intensive, and threatens the economic viability of the entire technology. Thus, experiments will soon be conducted at the Oak Ridge National Laboratory to investigate the possibility that *hydroxylated* serpentine can be carbonated rapidly at 300°C, $P \leq 200$ bars, under *reducing conditions*. In this new research activity, sample preparation, and interpretation of experimental results, will be guided by the densities and liquid-vapor phase relations of CO₂-H₂O fluids at 300°C, $P \leq 200$ bars, which have been measured precisely and accurately in the present BES-funded project.

This BES project has also produced density and excess molar volume data for CO₂-CH₄ mixtures at temperatures and pressures relevant to CO₂-enhanced CBM production. In that technology, CO₂ is forcefully injected into a deep, unmineable coal bed, where it displaces CH₄ from sorption sites on coal surfaces. Because the ambient temperatures and pressures of many deeply buried, CH₄-rich coal seams are close to the temperature and pressure at the critical point of CO₂ (~31°C, ~74 bars), the CO₂-CH₄ mixing that will occur in the coal bed during and immediately after CO₂ injection will be strongly nonideal, with large, positive excess molar volumes for CO₂-rich compositions. Thus, it is significant that the volumetric data for CO₂-CH₄ mixtures obtained in the present BES project indicate large errors in *calculated* densities and excess molar volumes for CO₂-CH₄ fluids at 50°C, 100 bars. This observation strongly suggests that existing thermodynamic models for CO₂-CH₄ gases are inadequate for *reliable* prediction of the volumetric properties of CO₂-CH₄ mixtures at *P-T* conditions near the critical point of CO₂ (25-50°C, 50-100 bars).

Isotope Fractionation of Carbonate Systems Relevant to Subsurface CO₂ Sequestration

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The injection of fossil-fuel derived CO₂ into the subsurface (saline formations, depleted oil-fields, coal-beds, *etc.*) is gaining increasing support as a practical means for the sequestration of large amounts of CO₂. It is crucial to understand the interplay between inorganic and biological processes associated with CO₂ injected into the subsurface, so that both short- and long-term consequences of the CO₂ can be monitored and assessed with certainty. The stable isotopes of CO₂ can be utilized as a natural tracer for this purpose, because the CO₂ produced from fossil fuel combustion has a very distinctive isotopic signature compared to that of background atmospheric and subsurface CO₂. We have conducted a series of systematic laboratory experiments to investigate the both equilibrium and kinetic behavior of carbon and oxygen isotopes during key inorganic and biological processes (solution into brines, inorganic and microbial precipitation of carbonate minerals) that will lead to a fundamental understanding of how CO₂ interacts with the host environment during injection and migration.

First, the kinetics of oxygen isotope exchange between gaseous CO₂ and various salt solutions (NaCl, KCl, NH₄Cl, CaCl₂, MgCl₂, AlCl₃, *etc.*) were investigated in the temperature range from 15 to 50°C at high pCO₂. The rate of oxygen isotope exchange between gaseous CO₂ and brines is strongly affected by shaking rates. When the system is stagnant, gas-transfer at the interface between gaseous CO₂ and brines is rate-limiting of the isotopic exchange with a half-time in the order of tens of hours. With increasing shaking rate, chemical reactions within brines become rate-limiting, and the exchange rate increases rapidly. The rate of isotope exchange between gaseous CO₂ and brines depends strongly on the type and concentration of salts. The rate is more than 10 times slower in brines than in pure water.

Second, partitioning of carbon and oxygen was investigated during inorganic and biologically-induced precipitation of carbonates (calcite, siderite) from CO₂-rich brines at 10-80°C. Under reducing conditions in the subsurface, certain strains of anaerobic bacteria can reduce Fe(III) to Fe(II) during their metabolic processes. This induces the precipitation of siderite (FeCO₃) and other minerals (magnetite), facilitating the mineral sequestration of CO₂ injected into the subsurface. Our experimental results show that various Fe(III)-reducing bacteria can cause large (up to 10‰) positive or negative kinetic fractionations of the siderite, which persisted even after one-month incubation, *i.e.*, “locked-in” kinetic isotope fractionation.

Third, variations in the extent of oxygen isotope exchange have been measured in the system calcite-H₂O±CO₂±NaCl as a function of temperature (300-700°C), pressure (25-200 MPa), NaCl (0-5 molal), and X(CO₂) (up to 0.18). There is a pronounced increase in the rate of oxygen isotope exchange with increasing T, P and salinity associated with enhanced solubility and Ostwald ripening of calcite grains. The presence of CO₂ tends to dampen the growth rates, and hence the oxygen isotope exchange rates decrease with increasing X(CO₂). Results from these high P-T-X experiments can be extrapolated to lower temperature-pressure conditions appropriate for CO₂ sequestration, circumventing the intractable problem of experimentally sluggish isotopic exchange at low temperatures.

Molecular Modeling and NMR Spectroscopy of Aqueous Species Relevant to the Geological Sequestration of Carbon Dioxide

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We have undertaken an integrated molecular modeling and NMR spectroscopic approach to understanding the structure, dynamical behavior and physical properties of H₂O-CO₂-solute fluids and the structural and dynamical behavior of surface and internally exchanged anions in minerals. This presentation will focus principally on the results of molecular dynamics (MD) modeling for fluid phases. This work is motivated by the need for detailed understanding of the physical and chemical properties of such fluid phases and their structure and dynamical behavior in the context of evaluating the technical feasibility of possible methods of geologically sequestering CO₂. Atmospheric carbon may find long-term storage as a separate CO₂-rich fluid phase, dissolved as carbon-oxygen species in water (typically, saline), or in minerals (probably carbonates). The properties of CO₂ in the supercritical state probable for many methods of C-sequestration are very different from those in seawater and deep saline brines. How CO₂ interacts with brines and potential host rocks is still largely a matter of speculation. Present capabilities to quantitatively predict the time evolution of these systems is limited by, among other things, poor understanding of the factors affecting the mobility of species and reaction kinetics. Such data, especially in the case of heterogeneous reactions, involves complex averages over many individual processes on the atomic scale. Detailed understanding of these atomic-scale processes needs to be addressed.

Our modeling has focused principally on CO₂-H₂O-NaCl fluids and on aqueous carbonate solutions. Molecular modeling is an especially promising approach for understanding such fluids. Their structures are not readily studied experimentally using conventional X-ray or EXAFS methods, because the C and O atoms of the solute species are not distinguishable from O atoms of solvent H₂O. MD simulations of 0.5*m* Na₂CO₃ and 0.5*m* and 1.5*m* NaHCO₃ aqueous solutions under near-ambient conditions show that their structures and behavior are quite different. In Na₂CO₃ solutions, ionic clusters of Na⁺ and CO₃²⁻ are long-lived, and long simulation runs of up to 2 ns were needed to effectively probe the structure and dynamics of these clusters. Due to this ion cluster formation, the diffusion rates of both Na⁺ and CO₃²⁻ are ~3-6 times lower than in similar chloride solutions. In contrast, in NaHCO₃ solutions ion cluster is much less, and the diffusion rate of HCO₃⁻ is thus about the same as that of Cl⁻. Analysis of the solute hydration structure in terms of O-O and O-H radial distribution functions indicates that the negatively charged O atoms (Oc) of carbonate ions are hydrated by water molecules (Ow and Hw) in a manner similar to H₂O molecules themselves. Strong $g_{OH}(R)$ peaks at ~1.8 Å and $g_{OO}(R)$ maxima at ~4.5 Å indicate a high degree of hydrogen bonding around Oc. The hydration shells of carbonate and bicarbonate ions both contain approximately 10 water molecules, but the carbonate one is more structured due to the higher anion charge. Similar modeling of CO₂-H₂O-NaCl fluids over a geochemically relevant range of thermodynamic conditions provides comparable information. In dense CO₂-rich fluid phases, dissolved H₂O molecules exhibit a high degree of H-bonding and form relatively stable H-bonded clusters. In contrast, CO₂ molecules dissolved in water-rich fluids occur in clathrate-like cages formed by surrounding H-bonded water molecules. This structural arrangement results in an approximately tenfold decrease of the CO₂ diffusion rate in the H₂O-rich phase, compared to the CO₂-rich phase under similar thermodynamic conditions.

Search for Surface Leakage from a Large-Scale CO₂ Injection Project: Rangely, Colorado

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The success of CO₂ sequestration by deep injection is dependent on the seals and aquitards being able to confine the large amount of fluid injected under overpressured conditions. The Rangely, Colorado field has been undergoing large-scale CO₂ injection since 1986 for purposes of enhanced oil recovery (EOR). Cumulative gas injection has been 966 billion cubic feet (BCF), of which 398 BCF is new, the remainder being recycled gas from production wells. Currently, there are 238 injection wells and 348 production wells operating, producing 17,000 barrels of oil and natural gas liquids per day. This is a report on attempts to detect diffuse surface leakage of gases at the surface. A protocol for the detection of a deep source of gas in the presence of a large amount of surface and near-surface biological production of gas requires a thorough understanding of the noise being generated in the shallow parts of the system and processes influencing exchange with the atmosphere.

Measurements of CO₂, CH₄ and light alkanes in soil gas, and as fluxes into the atmosphere were made in the winter of 2000-01 and summer of 2001, and will continue in the winter of 2001-02. The measurements were made by field infrared spectroscopy and laboratory gas chromatography. The summer fluxes of CO₂ from the soil to the atmosphere had a median of 3 g CO₂ m⁻² day⁻¹ and CH₄ fluxes had a median of 0.4 mg m⁻² day⁻¹, with soil microbiological production/consumption dominating as indicated by stable isotopes. The preliminary winter measurements averaged 0.2 g CO₂ m⁻² day⁻¹ and 0.1 mg CH₄ m⁻² day⁻¹, respectively. Some evidence of a small magnitude deep source was indicated by stable isotopes, and supported by the presence of light alkanes in soil gas over the Rangely field, and their absence in a background area of similar surface geology, soils, and climate. Detection of a low intensity deep diffuse signal requires special care in selection of the parameters to be measured and measurement in the winter season when soil microbiological activity is low.

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Diffusion of CO₂ during Hydrate Formation

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Mechanisms of hydrate formation and dissolution will play key roles if direct disposal of CO₂ in the oceans is undertaken. When CO₂ is released at depths below about 350-400 m, hydrate forms at the interface of the CO₂ and water. Formation of a hydrate film reduces the rate of dissolution of the liquid CO₂ in the surrounding seawater. Better definition of the mechanisms and rates of hydrate formation and dissolution is needed to determine transport of released CO₂ and to allow design of release facilities that limit environmental impact of the CO₂, which reduces pH when it dissolves and can adversely affect benthic and midwater fauna in the ocean if dissolved concentrations are too high.

Hydrate film growth was measured in a controlled setting in a 3 mm ID capillary tube. In a typical experiment, an interface between CO₂ and water is positioned in the capillary, and the temperature and pressure are adjusted to conditions at which hydrate forms. The thickness of a plug of hydrate that forms between the liquid CO₂ and water is then measured as a function of time. New hydrate must form either at the interface between hydrate and water (as CO₂ diffuses through the hydrate to reach a location where sufficient water molecules are present to allow hydrate cage formation) or at the interface between hydrate and CO₂ (as water diffuses through the hydrate).

Significant difficulties were encountered in persuading hydrate to form initially in the capillary tube. Simply cooling the capillary tube contents at the experimental pressure did not produce hydrates in a reasonable length of time, nor did starting with ice in the capillary and warming to the experimental temperature. In the method finally adopted, the capillary tube was filled with water, and CO₂ at the experimental pressure and temperature was introduced into the tube, displacing the water. A very thin film of hydrate formed where water wetted the capillary walls, and a plug of hydrate then formed and grew at the water/CO₂ interface in the center of the capillary when the interface is positioned in the tube. Some nonuniformity in the growth front was observed.

In all the experiments film growth was observed only on the water side of the hydrate plug, an observation that is consistent with much faster transport of CO₂ molecules through hydrate cages than transport of water molecules through the hydrate lattice.

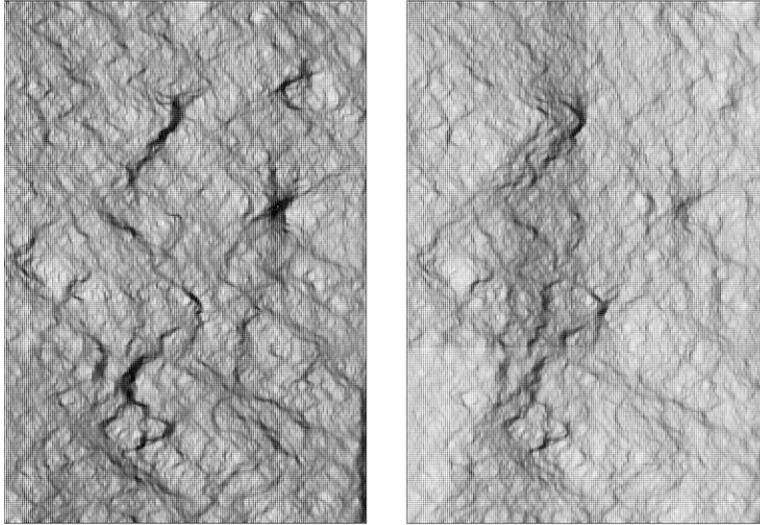
Diffusion coefficients for CO₂ through the hydrate were estimated from measured growth rates of the hydrate plugs. The concentration gradient across the hydrate plug was assumed to be set by the minimum cage occupancy for hydrate stability at the water/hydrate interface, and the maximum cage occupancy at the hydrate/CO₂ interface. Values obtained for most experiments were in the range 1 E-6 to 3 E-6 cm²/s, about an order of magnitude lower than the diffusion coefficient for CO₂ through liquid water (1 E-5 cm²/s) and three orders of magnitude larger than typical diffusion coefficients for CO₂ through solids (1 E-9 cm²/s).

Reactive Transport of CO₂-Rich Fluids and Precipitation and Dissolution in Rock Fractures

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Our laboratory experiments of reactive fluid flow in saturated fractures (with detailed topographic analysis of reacted fracture surfaces) demonstrate that the key length scales related to rock/fluid reactions are conveniently reached in the laboratory. In particular, in the system calcite + weakly acidic undersaturated aqueous fluid, stable growth of the dissolution front occurs at the scale of a few mm and below, while unstable growth (i.e., channels) occurs at scale of a few cm and above (see figure). These experiments, on discrete fractures in cylinders of calcite under a light external confining pressure at room temperature, also reveal effects that are obvious in hindsight, such as the fact that dissolution from fracture surfaces does not necessarily cause hydraulic conductivity to increase-- surfaces under confining pressure must remain in contact, so may close on one another if contacting points are dissolved. Further experiments are underway to examine similar effects in CO₂-rich fluids, in order to constrain issues related to geologic sequestration of CO₂, for example, the ability of subsurface conduits to remain open during CO₂ injection, and the ability of emplaced CO₂ reservoirs to remain sealed. The new round of experiments require elevated temperature (to 200°C) and pressure (to 50 MPa) in the fluid to simulate the higher CO₂ content of fluids related to geological sequestration, so while the experimental concept is unchanged, the experimental apparatus is radically different. The experiments are conducted in an externally heated pressure vessel, since a net confining pressure on the fracture requires external pressure to exceed the fluid pressure inside the fracture.

Future experiments will focus on the role of scale in the dissolution process. Our experiments to date were conducted in 5 x 7.5 cm fractures and the fluid flowing through the fracture reached calcium concentrations that were about 30% of the saturated concentrations; thus the fracture was dissolving over its entire length. Experiments in larger fractures will allow the flowing fluid to reach saturation resulting in a fracture-scale dissolution front. Surface measurements will allow us to observe how this dissolution front propagates through the fracture. We expect that at low flow rates (i.e., diffusion controlled mass transport) the dissolution will occur along a diffuse front whereas higher flow rates will result in advection dominated transport and instabilities along the dissolution front resulting in the growth of distinct channels as we have seen in our smaller fractures. Such results are expected based on the results of published computational investigations, but they have not been systematically tested through experimentation.

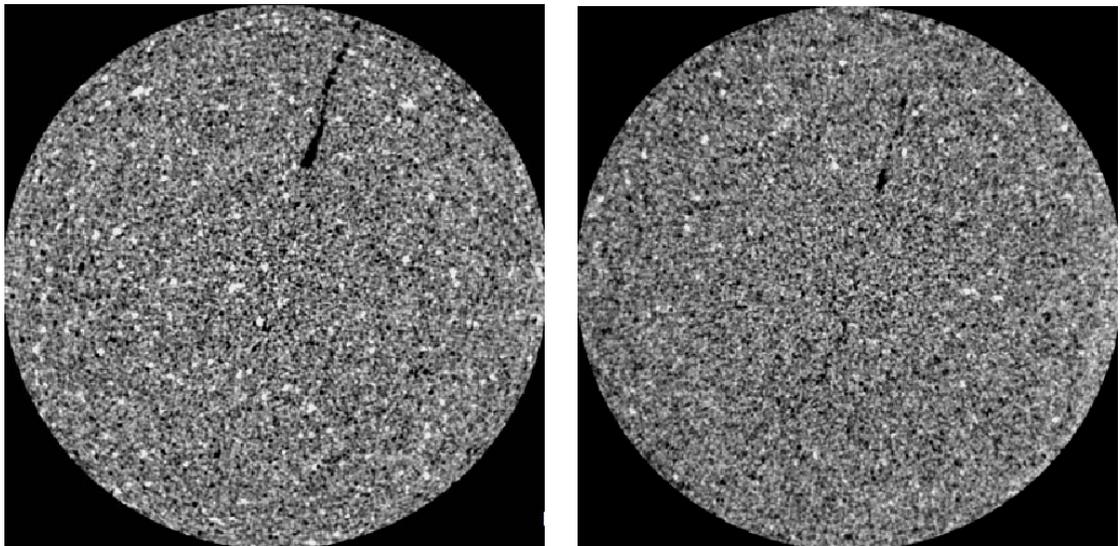


Comparison (in plan view) of fluid flux in a 20 mm x 40 mm fracture in calcite before (left) and after dissolution (right). Flux is indicated by the direction and length of small arrows at each pixel (4/ μm), not individual resolvable in this illustration. Dissolution has decreased tortuosity of flow at fine scale, but at larger scale has caused a top-to-bottom flow channel to appear.

X-ray CT Imaging of Changes in Permeability due to Dissolution and Precipitation in Fractured Berea Sandstone

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We report the results of permeability tests conducted on an artificial fracture in Berea sandstone at confining pressures of 6 MPa and at a temperature of 120°C using water as the permeant. The tests comprise through-flow in a core containing a single axial/diametral fracture, and are completed in an X-ray transparent pressure cell. Confining stress is applied to the core periphery through a flexible neoprene jacket. In-sample water pressures are a small fraction of the confining stress, that, correspondingly approximates the effective stress. Axial pressure-drop is continuously monitored across the sample during the test, and is used as a proxy for permeability change with time. Sample scans, both dry and wet, and at various stages during the saturated flow-through cycle are used to link inferred changes in permeability with observed changes in fracture and matrix porosity. Scanner resolution is of the order of 10 microns, as illustrated in the two successive scans of a fracture through the 5 cm diameter core in the figure. The figures illustrate the one o'clock to seven o'clock trending fracture both before fluid circulation (left) and at the end of the test (right), where a reduction in fracture porosity is tentatively apparent. Water chemistry is sampled during the test to define dissolution and precipitation processes, and to constrain mass balances.



Models are developed to define and quantify key processes of pressure solution, free-face dissolution, and shear-dilation, and the influence of temperature, stress level, and chemistry on the rate of dissolution, its distribution in space and time, and its influence on the mechanical and transport properties of the fracture. Two approaches are used. The

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first involves the transformation of pressure solution data for clean quartz sands to represent behavior of a fracture in sandstone. Long-term closure is evaluated from a known fracture roughness profile and an evaluated equilibrium stress, defined from the prescribed surface activity of the asperity interface. The progress of fracture closure to this final equilibrium state is conditioned by rates of viscoelastic compression of the fracture asperities, in turn defined by pressure solution or precipitation rates. The second approach involves the representation of pressure solution at the asperity contact as diffusion along a grain-boundary interface. The rate of fracture closure is conditioned by rate of mass transfer of quartz to the periphery of the asperity contact, and the availability of this mass flux for either precipitation on available free faces, or for mass advection out of the system.

Feasibility of CO₂ Sequestration in Faulted and Fractured Sandstone Reservoirs

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Structural features and associated permeability heterogeneity can negatively impact CO₂ well injectivity and reservoir integrity in aeolian sandstone aquifers proposed for CO₂ sequestration. For example, low permeability (k) faulted rock in sandstone can limit injection rates and create a system of reservoir compartments that complicate assessments of CO₂ sequestration feasibility. Furthermore, permeable fault-related fractures in sandstone can focus CO₂ flow to leakage points where permeable faults breach reservoir sealing units and enable injected CO₂ to leak towards the ground surface. We are working in aeolian Navajo Sandstone, at the wellbore (1 m) to interwell (100s of m) scales, to assess how faults and fault-related fractures might impact CO₂ flux to and from CO₂ sequestration reservoirs. The Navajo Sandstone of Central Utah provides excellent outcrop exposure, extensive previous/ongoing assessments of fluid flow properties and several natural CO₂ reservoirs that serve as analogs for CO₂ sequestration targets. We integrate outcrop and drillhole-derived data from the 4-km long Big Hole normal fault to quantify structure-related k heterogeneity within small volumes (10s to 100s of m on a side) of faulted sandstone. The maximum fault offset is ~29 m. Thus, where faults similar to the Big Hole are found at sequestration depths in Navajo Sandstone, only the central segment of the fault would be resolved in geophysical surveys. Yet, the fault is clearly visible as a low k zone in drillcore and borehole geophysical logs, even where fault offset is less than 3 m. We will use numerical simulations of CO₂ injection and migration in fresh-to-saline sandstone aquifers to assess how unseen faults might compromise CO₂ sequestration. The first model volume is 200 m by 100 m in plan and 80 m deep, located in outcrop near the tip of the Big Hole fault, and contains four well-defined aeolian facies. The permeability (k) structure of each facies is defined using detailed probe permeameter measurements from 300 meters of drillcore. Average k values for each unit are 250, 700, 850 and 1300 md. The detailed facies-based k model has been vertically faulted with normal displacement varying from 3 to 10 m. Synthetic versions of the discrete structural features mapped in detail on outcrop, such as permeable open fractures and low permeability deformation bands, are modeled using FracMan®. Deformation bands with $k \sim 1$ md are the principal structural features. Thus, equivalent fault zone k depends mostly on the size, orientation, intersection and spacing of deformation bands. Computed k across the fault zone is typically about 60 md, or 0.1 to 0.01 times the permeability of the host sandstone. *In situ* cross-well injection tests show how sparse fractures provide enhanced, localized connectivity within the low- k fault. Superimposing the k heterogeneity of both facies and structural features yields an aggregate, fault-related distribution of anisotropic k tensors. Geochemical modeling results combined with CO₂ fluxes and CO₂ saturations computed from two-phase flow simulations will provide a basis for estimating how localized permeability loss, or enhancement, might compromise well injectivity and reservoir integrity near fault zones. Planned surveys of soil CO₂ fluxes above the Farnham Dome CO₂ reservoir will aid in assessing whether faults associated with this analog sequestration reservoir in Navajo Sandstone might cause localized CO₂ leakage.

Deformation and Fracture of Poorly Consolidated Media

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The objective of this study is to understand the effect of the micromechanical properties, such as intergranular bond strength and porosity, on macroscopic properties, including load-displacement response, ultimate strength, acoustic wave velocities, and failure mode, of weakly cemented granular rock. We developed a technique to fabricate synthetic sandstone containing weak and brittle intergranular bonds. A series of laboratory experiments were conducted on samples with a range of micromechanical properties. The primary micromechanical parameter studied during the experiments was the strength of intergranular cohesion. Porosity of the samples was also varied but its range was limited to relatively high values (32-42%). The experiments included SEM and optical microscope observations, load-displacement tests (uniaxial and confined biaxial tests), fracture toughness tests and acoustic wave propagation. In order to investigate the effect of weakly cemented sandstone on the failure of boreholes, we also conducted a series of unconfined compression tests using thin rectangular brick samples containing a single simulated borehole. The results of the experiments revealed strongly friction-controlled deformation and failure behavior of weakly cemented sandstone that augmented the effect of intergranular cementation. We also observed that a borehole drilled within the weak sandstone can exhibit a thin, fracture-like breakout. The conditions for the formation of this breakout mode included high porosity, smooth grain texture and weak intergranular bond strength. Another important factor was the presence of external, mechanical, and hydrodynamic forces, which could remove the failed material from the breakout.

Compaction Band Formation as a Failure Mode in the Brittle-Ductile Transition in Porous Sandstone

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Since dilatancy is generally observed as a precursor to brittle faulting and the development of shear localization, attention has focused on how localized failure develops in a dilatant rock. However, recent geologic observations and reassessment of bifurcation theory have indicated that strain localization may be pervasive in a compactant porous rock. The localized bands can be in shear or in compaction, and occur as diffuse or discrete bands oriented at relatively high angles (up to 90°) to the maximum compression direction. Microstructural characterization of the spatial distribution of damage in failed samples have confirmed that localized failure modes involving such compaction bands and high-angle conjugate shears can develop in Bentheim, Berea, Boise, Darley Dale and Rothbach sandstones with porosities ranging from 13% to 35%. These failure modes are generally associated with stress states in the transitional regime from brittle faulting to cataclastic ductile flow. The laboratory results suggest that these complex localized features can be pervasive in sandstone formations, not just limited to aeolian sandstone in which they were first documented. They may significantly impact the stress field, strain partitioning and fluid transport in sedimentary formations and accretionary prisms.

Two different patterns of strain localization can be distinguished: diffuse conjugate shears at relatively high angles, and discrete compaction bands subperpendicular to the maximum compression direction. Whereas the development of diffuse bands is characterized by the continuous accumulation of acoustic emissions (AE), discrete bands are associated with episodic surges in AE that are characterized by an overall strain hardening trend punctuated by episodic stress drops. The number of discrete bands correlates with the number of AE surges and stress drops. While bifurcation theory provides an useful framework for analyzing the inception of compaction localization, our data rule out a constitutive model that does not account for the activation of multiple damage mechanisms in the transitional regime.

Effects of Fluid Flow on Inelastic Deformation and Failure in Dilating and Compacting Rock

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One of the proposed strategies for mitigation of carbon dioxide emissions is the sequestration of CO₂ in depleted oil or gas reservoirs. For the implementation of this strategy, it is critically important to understand how production of the original contents of the reservoir has changed the stress and deformation states and the properties of the rocks making up the reservoir. Inelastic deformation resulting from tectonic stress or stresses created during production of oil or gas, or reinflation with CO₂, may produce deformation bands that interfere with fluid migration and make the reservoir unattractive as a potential producer of oil and gas or repository of CO₂.

We instrument cylinders of Castlegate with 14 acoustic transducers and subject them to triaxial loading at 20 to 80 MPa initial confining pressure and deform them along constant mean stress or constant shear stress paths. Acoustic emissions (AE) are monitored continuously throughout the experiments, and then locations of the events are determined. During triaxial loading, near peak stress, one or two narrow tabular zone(s) of AE events, perpendicular to the maximum compression direction, invariably appear near one or both ends of the cylinder. (Fig. 1). These zones in panels 1-9 moved toward the center of the specimen with increasing applied axial strain, and were forced to coalesce by continued shortening of the specimen. Microscopy shows that the rock behind the AE zones is highly compacted by extensive grain breakage. We interpret these moving zones of AE events to be the boundaries between compacted and uncompacted material. Therefore, compaction of the specimens occurs nonuniformly by the initiation and slow propagation of compaction fronts into the uncompacted material.

Fluid flow measurements have been made axially across the specimens during compaction experiments. The apparent permeability dropped dramatically upon formation of the bands, and then continued to decrease steadily with propagation of the bands (Fig. 2). Total change in apparent permeability as the AE zones traverse the specimen is about 2 orders of magnitude. Complicating the analysis of this type of experiment is the addition to the applied flow rate of water being squeezed from the compacting regions.

The appearance of tabular zones of compaction that lie perpendicular to the maximum compressive stress, and which grow in the direction of maximum compression, may create unrecognized problems during withdrawal or reinjection of fluids such as CO₂ into porous rock reservoirs.

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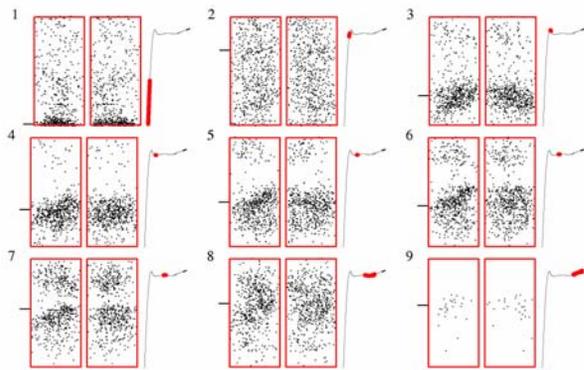


Fig.1 Dots are AE. Curve on right is stress-strain. Red increment is window corresponding

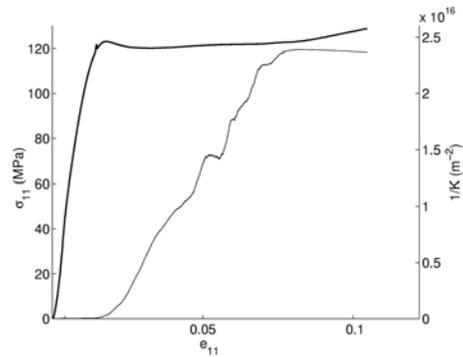


Fig. 2. Axial stress-strain with inverse permeability.

Scaling Issues Regarding the Formation of Fault Zones and Fluid Flow

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Faults commonly exploit pre-existing fabrics and structures as they develop. Indeed, this might be characteristic of how faults grow. At a microscopic scale, the grain scale structure (i.e., fabric) of the rock dictates how shear fractures form. For example, in high porosity rocks, such as certain sandstones, the rock contracts prior to the formation of shear fractures. In contrast, in low porosity rocks, such as most crystalline rocks, the rock dilates prior to the formation of shear fractures. At a macroscopic scale, faults exploit pre-existing joints, dikes, bedding surfaces, and geologic contacts. The type, orientation, and distribution of such pre-existing features are entirely independent of the fault that might subsequently develop from them. For example, segmented faults that develop from joints might have segment lengths of several tens of meters, whereas faults that develop from dikes might have segment lengths of kilometers. The processes by which faults grow by linkage depend in part on the distribution of these structures. For example, depending on the geometric relationship of echelon faults, they could link by two entirely different processes: fracturing and crystal plastic deformation. Fluids generally would flow more readily between fault segments linked by fractures than by plastically deformed rock. The geometric distribution of flaws also effects how faults grow in another way. If two faults of equal height but different length develop from an otherwise identical distribution of pre-existing flaws, the flaw-to-fault spacing will be greater for the short fault than for the long fault. The mechanical interaction of the fault with the flaws will be greater in the latter case than in the former, and the nature of the interaction can dictate how faults grow and how they terminate. For all these reasons, faulting processes must depend at least in part on the distribution and scale of pre-existing rock fabric and rock structure. Although simple scaling rules might capture gross behavioral and structural characteristics of faults, such rules by themselves can not capture the rich variety of structure and processes that occur along natural faults and that effect fluid flow.

Seismic Monitoring of Time-Dependent Multi-Scale Heterogeneity in Fractured Rock

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A strategy for reducing carbon dioxide (CO₂) emissions into the atmosphere from power plants burning fossil fuel is to capture CO₂ and sequester it in subsurface reservoirs. Candidate sites for geological sequestration differ in lithology and structure, but fractures are common to all. An issue that arises for long-term subsurface sequestration of CO₂ is whether seismic methods be used to monitor the injection process once underway or after completion to determine leaks. We performed a laboratory investigation to determine the ability of seismic methods to detect the presence of gas in a fracture.

Preliminary experiments were performed to examine the effect of reactive fluid flow on wave propagation across a single fracture. The goal of the preliminary experiments was to determine if laboratory seismic methods were sensitive to changes in a fracture induced by geochemical alteration. Results from a seismic tomographic imaging experiment showed that dramatic changes in the acoustic wave arrival time, amplitude and spectral content occurred when the reactive flow began. Signal attenuation increased as the flow rate through the sample increased. The preliminary results indicated that geochemical alterations of the fracture as well as the fluid content in the fracture (i.e., gas to liquid ratios) can be detected. However, from the reconstructed tomograms, the effect of gas saturation could not be separated from geochemical alteration.

Three separate experiments were designed to investigate the effect of partial gas saturation on seismic waves propagated across and reflected from a fracture. The first set of experiments involved measuring the acoustic properties at a fixed location over a period of time while a gas was invaded into a fracture in limestone. When the fracture was saturated with water, the fracture specific stiffness was observed to be frequency independent. However, when the fracture was invaded with gas, the fracture specific stiffness was found to depend on frequency, in which the fracture appeared to be stiffer at higher frequencies (1 MHz) than at low frequencies (200 kHz) by almost an order of magnitude. The frequency-dependent fracture specific stiffness is hypothesized to be a consequence of the spatial heterogeneity in fracture geometry highlighted by the impedance contrast caused by the air. When the fracture is fully saturated with water, the local heterogeneity in the fracture stiffness is masked by the low impedance contrast of the fluid.

To further explore this phenomenon, a second set of experiments was performed on synthetic fractures in acrylic. For these experiments, acoustic measurements were made over a two-dimensional region to determine the effect of the spatial distribution and saturation of gas on fracture specific stiffness. The acrylic enabled directed visualization of the distribution of the gas-water phases in the fracture. The acoustic map clearly delineated regions of gas versus regions with water. A third set of experiments has been designed to exam the scaling nature of the acoustic measurements for a partially gas-saturated fracture. A several acoustic lens have been designed to examine the scaling behavior (over two orders of magnitude) of compressional wave amplitude as a function of gas saturation and the size of the sampling region. These experiments should provide an understanding of the ability to delineate changes in fluid saturation on different scales.

Decomposition of Scattering and Intrinsic Attenuation in Rock with Heterogeneous Multiphase Fluids

Kurt Nihei, Lawrence Berkeley National Laboratory

Heterogeneity in rock is ubiquitous appearing at scales ranging from pores and grains at the sub-millimeter scale to depositional units such as channels, slumps, and fractures at the meter scale to faults and other tectonic features at the kilometer scale. These multi-scale heterogeneities are especially important in the analysis of fluid transport in reservoirs and the migration of contaminants in the subsurface since they often control the spatial distributions of the fluids and, hence, the strategies for fluid mobilization and recovery. Geophysical methods such as seismic imaging are now routinely used to locate and monitor fluids in the subsurface. While some success has been reported for quantitative estimation of rock properties such as pore pressure, saturation, and permeability from seismic velocities using empirical correlations, the use of seismic amplitudes for these estimates has been limited. A possible reason is the correlations are often strongly frequency-dependent, presumably a result of the combined effects of scattering and intrinsic attenuation.

The basic premise of the proposed research is that an essential step in the use of seismic attenuation for monitoring fluids in rock is an understanding of the relative contributions of scattering and intrinsic attenuation to the observed amplitude changes. Presently, we are focusing our research efforts along three fronts: laboratory studies of fluid+gas systems in sands, viscoacoustic and viscoelastic seismic imaging, and seismic imaging of anisotropic scatterers (e.g., fractures). Results from these studies and their implications for monitoring the movement of fluid and gas in the subsurface will be presented.

Fluids in the crust: Megascale and Microscale

Amos Nur
Stanford Rock Physics Laboratory

Identifying fluids in the crust and monitoring their migration is one of major tasks facing the geophysicist. The actual situation in the subsurface is hidden from us by many sedimentary layers. Fortunately, its imprints are often visible and measurable. One readily available observable is surface subsidence. Surface subsidence often accompanies pore pressure changes and pore fluid migration in aquifers and petroleum reservoirs. It can be precisely measured and monitored by satellite remote sensing. The challenge remains to relate it to the changes in the subsurface. Quantitative rock physics analysis allows one to make this link and, by so doing, quantitatively monitor pore fluid migration via satellite interferometry. We show two examples of such monitoring, one from a geothermal aquifer and the other from a California's Central Valley oil field.

Identifying and monitoring fluid migration paths in the subsurface often allows us to make conclusions about permeability. This basic rock property defines the patterns of fluid flow at the field scale. At the same time, it is determined by the pore-scale topology. We present a new, numerical experimentation, approach to quantifying relative permeability in porous rocks and predicting its changes due to compaction and diagenesis. Modern measurement techniques and emerging super-computing power determine the direction of geophysical research in the years to come.

Seismic Monitoring of a Gas Storage Reservoir with Low-Frequency Analysis.

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Conventional processing of time-lapse monitoring data did not reveal detectable changes. Application of low frequency analysis found changes which include the effects of stronger reflections and travel time delays at low frequencies. These effects match similar effects seen in laboratory data. The existing theoretical explanation suggests very low Q values for porous, fluid-saturated layers primarily as a result of internal friction between grains. This explanation needs further investigation. Low-frequency amplitude and phase reflection properties can be used for detecting and monitoring liquid saturated areas in thin porous layers.

Experiment

The Northern Indiana Public Service Company (NIPSCO) operates naturally fractured reservoirs for seasonal storage of natural gas. The gas is injected during summer and withdrawn during winter. As part of DOE sponsored research in fractured gas production, Lawrence Berkeley National Laboratory (LBNL) conducted a VSP (Vertical Seismic Profile) experiment to aid delineation of NIPSCO's reservoir, and to study the seismic effects of variable gas pressures. The reservoir is in NIPSCO's Royal Center field in Northern Indiana. The annual displacement of water by gas within the natural fractures of the reservoir make this field a good candidate for time-lapse monitoring.

The Trenton formation is a Paleozoic Ordovician dolomite which is part of the mostly shale and carbonate stratigraphy of the Royal Center field. It is believed by the field operators that the top section of the Trenton dolomite is unfractured and forms a cap for the reservoir. Thickness of the fractured reservoir is 30 ft approximately. There were two phases of time-lapse VSP acquisition at the field site with essentially identical acquisition geometry (source/receiver locations) under distinctly different reservoir conditions. During the initial survey in December 1996 the reservoir gas pressure was near its maximum of about 400 psi; during the second survey in May 1997 the reservoir gas pressure was reduced to about 250 psi. Since the natural water pressure within the Trenton formation is about 310 psi, the reservoir was mostly gas saturated in the first survey and mostly water saturated in the second survey.

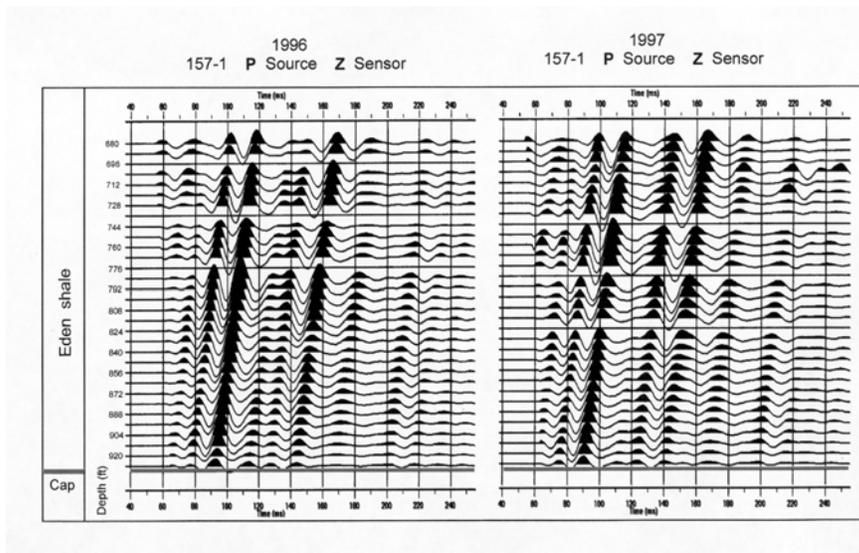


Fig.1 Upgoing wave fields for 1996 and 1997

Conventional processing of NIPSCO monitoring data did not reveal detectable changes in VSP data. The application of low frequency analysis (Fig.1) found changes which include the effects of stronger reflections and travel time delays from the water saturated layer at low frequencies. Laboratory data obtained for a model of artificial sandstone reveal similar phase and amplitude changes. These results match theoretical frictional wave propagation model.

Volume and Mass Changes within Volcanic Reservoirs

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Long Valley caldera, located on the eastern front of the Sierra Nevada range in California, formed by collapse of the roof of the magma chamber during the catastrophic eruption of the Bishop Tuff 0.73 million years ago. Since mid 1980, the caldera has experienced ground uplift and numerous earthquake swarms, and emission of CO₂, prompting the U.S. Geological Survey to issue a "Notice of Potential Volcanic Hazard" for a few months in 1982 and to start an intensive monitoring effort in the area. We have conducted field experiments to determine whether the unrest is caused by hydrothermal fluids, volatile constituents, and/or magma. Our results strongly support the conclusion that magmatic intrusion is the underlying cause of the observed caldera uplift.

Combined geodesy and gravity measurements allow us to infer the density of intrusive bodies, and thus better constrain deformation sources. The U.S. Geological Survey occupied the Long Valley gravity network six times from 1980 to 1985. We reoccupied this network twice, in the summer of 1998 (33 stations), and the summer of 1999 (37 stations). Before gravity data can be used to estimate the density of the intrusion, they must be corrected for the effect of vertical deformation (the free-air effect) and changes in the water table.

To determine uplift we also surveyed 44 leveling monuments in Long Valley caldera in July 1999, using dual frequency GPS receivers. We have been able to tie GPS and leveling to a common reference frame in the Long Valley area, and compute the vertical deformation by differencing GPS-based and leveled orthometric heights. We find that the resurgent dome stands 74 +/- 7 cm higher today than in 1975. To constrain the inflation source, we invert two-color EDM and uplift data from the 1985-99 unrest period using spherical or ellipsoidal sources. We find that the ellipsoidal source satisfies both the vertical and horizontal deformation data, whereas the spherical point source cannot. According to our analysis of the 1985-1999 data, the main source of deformation is a prolate ellipsoid located beneath the resurgent dome at a depth of 5.9 km (95% bounds of 4.9 to 7.5 km). This body is vertically elongated, has an aspect ratio of 0.475 (95% bounds are 0.25 to 0.65) and a volume change of 0.086 km³ (95% bounds are 0.06 to 0.13 km³).

Estimates of the depth, volume change, mass change and density of the intrusion in volcanic areas are often computed matching gravity and uplift data to an isotropic point source in a homogeneous half-space. We investigate three factors that should help in obtaining a more realistic picture of the intrusive body: (1) coupling between elastic and gravitational effects; (2) a layered Earth model, with depth dependent elastic properties and densities and (3) non-spherical source geometries. Our results show that coupling between elastic and gravitational effects (self-gravitation) is second-order over the distance and time scales normally associated with volcano deformation. We find no significant differences in any of the source parameters due to self-gravitation effects. For an elastic model appropriate to Long Valley caldera, we find only minor differences between modeling the intrusion using a point source in a homogeneous or layered

medium. Choosing the right source model to invert geodetic and gravity data, however, is critical in the geological interpretation of the data. If the source does not possess spherical symmetry, the standard approach of using a point source to invert uplift and gravity data will lead to biased estimates of the source parameters (e.g., a deeper location and a larger density).

We use geostatistical techniques to interpolate uplift and water table changes at the gravity stations. From the gravity and deformation data (EDM, GPS, and leveling), we estimate the density of the fluid filling the ellipsoidal deformation source to be approximately 1700 kg/m^3 . A bootstrap method was employed to estimate 95% confidence which range from 1180 to 2330 kg/m^3 for the density. Our results do not support hydrothermal fluid intrusion as the primary cause of unrest, and confirm the intrusion of silicic magma beneath Long Valley caldera. Failure to account for the ellipsoidal nature of the source biases the estimated source depth by 2.9 km (a 33% increase), the volume change by 0.019 km^3 (a 14% increase) and the density by about 1200 kg/m^3 (a 40% increase).

Multiscale Data Integration and Seismic Monitoring for CO₂ Sequestration in Hydrocarbon Reservoirs

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The goal this project is to assess the feasibility of time-lapse seismic monitoring of CO₂ sequestration using coupled fluid flow, geochemical and seismic modeling. Concurrently we want to develop a formalism for the assimilation of static and dynamic data sources in the reservoir and quantification of uncertainty in the performance predictions. We have utilized numerical modeling of both carbon dioxide sequestration and seismic wave propagation in a representative model of a sequestration site to quantify the changes in seismic reflections that might be observed in realistic applications. Changes in rock velocities caused by variations in pore fluids were computed using the Gassmann's equation, and empirical equations based on laboratory data were used to model the dependence of velocities on pressure. Synthetic seismograms were generated using the ray-Born method and the changes in seismic amplitudes were computed before and after CO₂ injection. Both liquid and supercritical fluid phase CO₂ injection have been considered. The results indicate significant amplitude change for the SCF CO₂ injection because of the larger contrast between the density and compressional wave velocity of SCF CO₂ and the corresponding properties of water. These preliminary results seem to strongly indicate the feasibility of using seismic monitoring of CO₂ sequestration into hydrocarbon reservoirs. We have also identified the water-rock reactions relevant for trapping supercritical CO₂ for incorporating into a fluid flow simulator. These include precipitation-dissolution and other geochemical processes such as hydrolysis and complexation reactions in solution and absorption and partitioning reactions in two-phase systems that may significantly affect CO₂ sequestration. Finally, as part of our effort to construct reservoir models by integrating multiscale data sources, we have developed a hierarchical approach to spatial modeling based on Markov Random Fields (MRF) and multi-resolution algorithms in image analysis. Our proposed method is computationally efficient and well suited to reconstruct fine scale spatial fields from coarser, multi-scale samples (e.g., based on seismic and production data) and sparse fine scale conditioning data (e.g., well data). It is easy to implement and can account for the complex, non-linear interactions between different scales as well as precision of the data at various scales in a consistent fashion. Several examples are included to illustrate the procedure.

Joint Inversion for Subsurface Imaging

Ki Ha Lee and Hung-Wen Tseng, LBNL

Objectives: To develop a joint inversion methodology using geophysical data to predict subsurface hydrologic properties. Specifically, the data are from in-hole, surface-to-borehole and borehole-to-borehole electromagnetic and seismic surveys, and the in-hole gravity survey, to extrapolate borehole log or core data to the interwell volume. The underlying concept of using the geophysical data to predict the hydrologic properties is borrowed directly from the well-established field of well logging. Here borehole geophysical measurements of sonic velocity, electrical resistivity and density are used jointly to estimate porosity and saturation (usually oil/water saturation). Cross-plots of different physical properties are often reliable site-specific indicators of lithology and, in conjunction with pumping tests, site-specific correlations can be established between the physical properties and permeability. It is the objective of this proposal to extend these concepts to the mapping of hydrological properties in the interwell volume using both in-hole and large-scale cross-hole and hole-to-surface geophysics.

Project description: Accurate mapping of geophysical and hydrological parameters are increasingly more important in the broader study of groundwater supply, development of long-term injection strategy for CO₂ sequestration, characterization and monitoring of petroleum reservoirs and environmental remediation processes, and in almost all aspects of subsurface engineering in general. Geophysical methods can map the distribution of seismic velocity and electrical conductivity beneath the surface and between holes. These physical properties are dependent on density, porosity, fluid saturation, clay content, and in some circumstances, permeability. While general quantitative relationships are elusive, on a site-specific basis this geophysical data can provide spatial information that is ideal for the interpolation of well log data and for constraining or conditioning the inversion of data from pumping tests. The relationship between seismic properties, conductivity, and the hydrologic parameters are now so well known that we propose to develop a means to jointly invert the geophysical and well data to a distribution of properties that satisfies all the field data.

Results: To assess the feasibility of deriving hydrological properties directly, we have developed a joint inversion technique using EM and seismic travel-time data. Inversion parameters are the rock porosity and the fluid electrical conductivity instead of the usual bulk electrical conductivity and seismic velocity. The substitution is based on simple empirical relationships such as Arch's law and the Wyllie time average equation. To begin we chose a simplest earth model in which the formation is fully saturated and the P-wave velocities in the rock matrix and pore fluid are fixed, so the travelttime is only a function of porosity. For this simple model the bulk electrical conductivity is a function of fluid conductivity and porosity. The inversion is based on a least-square criteria that minimize the misfit. A smoothness constraint is implemented to reduce non-uniqueness. To simulate EM responses we chose a model that is axially symmetric about the

transmitter borehole. Numerical simulation is carried out with the algorithm based on the Born approximation technique and developed by Alumbaugh and Morrison (1995). The bulk electrical conductivity used for the EM simulation is estimated using a simplified Archie's law. A straight ray path is assumed for the seismic method, and travel-time data are calculated based on the simplified Wyllie equation.

A model (Figure 1) containing three horizontal slabs with various conductivity and porosity is used to verify the proposed approach. All three heterogeneities are reasonably well resolved in terms of the two hydrological properties: porosity and fluid conductivity, respectively. The optimum result of the joint inversion has been obtained by alternating the selection of inversion parameters, in which only one parameter is allowed to change while the other parameter is held fixed at each iteration.

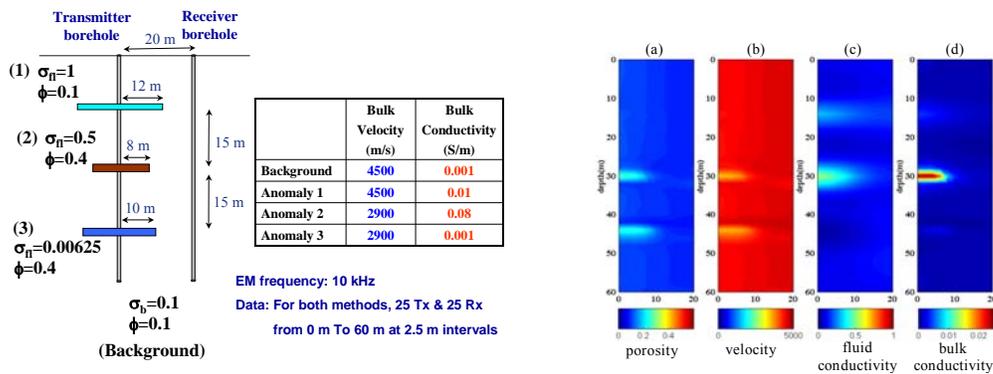


Figure 1. A synthetic model used for joint inversion study is shown on the left. Shown on the right is the inversion result for: (a) formation porosity; (b) calculated velocity; (c) fluid conductivity; and (d) calculated bulk conductivity.

The Electrical Properties of Rocks Containing Liquid Water, CO₂ and Steam

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The electrical properties of fluid saturated rocks are sensitive to many factors including microstructural properties, the nature and amount of pore saturant, temperature, and pressure. The composition and phase of the pore saturant (i.e., liquid versus steam or gas) are important factors that can dominate electrical properties. Most dry rocks are excellent insulators, but saturation with conducting fluids can decrease their resistivity by many orders of magnitude. Field EM methods are used to track the movement of water and CO₂ injected into geologic formations and interpretation depends on reliable laboratory measurements. An objective of this work is to understand the relationships among electrical properties, microstructure, and fluid distribution. As water in pores flashes to more resistive steam or as resistive fluids are forced into a sample electrical pathways are cut-off or diminished and the resistivity of the sample increases. Conceptually, if these changes are sufficiently large, such regions could be sensed remotely using surface- and borehole-based electrical surveys and could provide the means to evaluate changing geothermal reservoirs, track steam fronts during enhanced oil recovery (EOR), CO₂ sequestration, or environmental remediation.

Laboratory measurements designed to enhance interpretation of field in situ electrical measurements were performed on sandstones and rocks from areas where geophysical tests were in progress, including a geothermal field (The Geysers), Lost Hills, CA (EOR site), and Fran Ridge, NV. Experiments were performed on selected samples from 23 to 250°C and 100 kPa to 10 MPa. Pore and confining pressures were measured and controlled separately. The complex impedance was measured between 0.001 Hz and 1 MHz utilizing platinum electrodes and a four-electrode two-terminal pair technique. A four-electrode cell was developed that could be used up to ~180°C and high pressure. Initial results indicate that both techniques are effective at monitoring changes in resistivity. For measurements utilizing CO₂ a new pore-pressure system was developed and tested. Liquid, gas and supercritical CO₂ has been used as injectate.

Measurements of electrical resistivity of fractured materials containing liquid water and steam were performed and the results applied to the task of detecting fractures based on field electrical measurements. Fractures manifest themselves as regions of rapidly changing saturation, and hence, high electrical resistivity contrast. The electrical results were verified using other geophysical techniques.

Initial experiments have been performed on rocks as CO₂ was injected into the samples. As expected, the resistivity of a sample rapidly decreases as liquid water is displaced. Intermediate to long term changes (one to six days) in resistivity appear to be controlled by a number of factors including amount of water displaced, specific mineralogy, and the nature of surface conduction mechanisms. For example, two sandstones with similar microstructural properties have different long-term (days) resistivity changes. When saturated with CO₂ the Berea SS has a long-term drift toward lower resistivity while the St. Peter SS quickly reaches a steady value that is nearly constant. This difference in response is possibly due to the presence of clay or the effect of carbonic acid on surface minerals. Run products will be examined to detect changes in mineralogy and grain surface properties and additional experiments are planned to learn more about the long-term changes in resistivity of rocks containing water and CO₂.

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Geophysical Monitoring of Carbon Dioxide Sequestration using Electrical Resistance Tomography (ERT): numerical and physical model sensitivity studies

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Successful geologic sequestration of CO₂ will require monitoring to confirm the performance of the reservoir system, assess leaks and flow paths, and understand the geophysical and geochemical interactions between the CO₂ and the geologic minerals and fluids. To minimize cost and impacts to the integrity of the disposal reservoir, remote methods are preferred. Electrical methods are well suited for monitoring processes involving fluids, as electrical properties are sensitive to the presence and nature of the fluids contained in the medium. Electrical resistance tomography (ERT) is a relatively new modality for imaging that is being used with increasing frequency in shallow subsurface imaging applications including site characterization and monitoring subsurface migration of fluids. ERT surveys are commonly conducted utilizing vertical arrays of point electrodes in a crosswell configuration. Recent developments enable field surveys to be conducted using steel well casings as electrodes. If ERT imaging can be performed using existing well casings as long electrodes, this reduces the need for additional drilling. The purpose of this work is to accurately determine spatial resolution and target sensitivity for ERT under controlled conditions similar to those found in field applications.

We have been conducting sensitivity studies using numerical simulations and physical models to evaluate the effectiveness of 3D ERT as a potential monitoring approach for CO₂ sequestration. Using a model patterned after an oil field undergoing CO₂ flood, we ran forward and inverse simulations of ERT surveys to test the sensitivity of the method to detect the changes resulting from CO₂ migration. Factors evaluated include resistivity contrast, anomaly location (proximity to electrodes), anomaly size and shape, noise level and measurement configuration. The initial numerical model approximates the complexity of a layered reservoir, and is consistent with previously published results. Carbon dioxide migration is introduced into a thin layer by changing the resistivity in the targeted layer, producing an anomalous region. The geometry of the anomalous region ranges from a planar, horizontal mass with vertical protrusions simulating CO₂ leakage to a thin horizontal finger. Measurement geometries include both arrays of point electrodes in each well (simulating high resolution surveys) or assuming the well casings themselves are used as long electrodes. Results of simulations run assuming both point electrode arrays, and long electrodes show good detection for many contrasts and configurations for even the narrow simulated CO₂ fingers.

Physical scale models are used to control experimental conditions while providing data with realistic data errors, which is not possible with computer simulation data (even when synthetic but unrealistic errors are included in the analysis). The strategy is to compare the known physical models with the reconstructed images, and from this comparison, evaluate the strengths and weakness of ERT under different conditions. Initial measurements in the long electrode configuration using metallic and plastic targets

revealed other factors effecting image fidelity. We discovered that the measurement schedule used for data acquisition is important; the sensitivity of the results change spatially when asymmetric measurement schedules are used. Highly conductive (metallic) targets have the poorest match; this may be due to surface effects rather than contrast alone. Targets of lower electrical contrast show better spatial reconstruction. This result is consistent with the properties of the reconstruction algorithm, which searches for the numerical model of smoothly varying electrical conductivity.

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Three Dimensional Transient Electromagnetic Inversion Project

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This project seeks to develop a three-dimensional imaging capability for transient electromagnetic fields in a manner similarly developed for seismic wavefields for high resolution imaging of the subsurface. Specific applications considered include the characterization of DOE hazardous waste sites and nuclear waste repositories and monitoring of sequestered CO₂ in gas depleted reservoirs.

Although the development of practical multidimensional TEM inversion methods are just beginning, seismic imaging techniques have advanced the idea of back propagating or migrating the wavefield into the earth in order to image the subsurface. By applying a similar concept for electromagnetic fields, an imaging algorithm will be developed, which employs a conjugate gradient search for an optimal solution. This algorithm will be governed by the diffusive Maxwell's equations and is efficiently implemented by back propagating the data residuals into the model. To achieve realistic model complexity, the algorithm will use finite difference methods for computing predicted data and cost functional gradients. Parallel computing platforms will also be utilized for reasonable computation times. Finally the algorithm will be tested on TEM data acquired over hazardous waste sites and nuclear waste repositories. It will also be used in an experiment design to determine its resolving power for monitoring the sequestration of CO₂ in gas depleted reservoirs.

Implementation of the 3D finite difference modeling codes on single and parallel processor machines are near completion. These codes solve the diffusive Maxwell equations in the presence of the air-earth interface using explicit time stepping scheme. They have been checked for a range of earth models. A borehole version of the code, which neglects that air-earth interface condition, is also available. This later code is now being employed in an experiment design study to access the applicability of TEM method for monitoring sequestered CO₂. A non-linear conjugate gradient solution, using the finite difference code, is also under development and will employ back propagation to efficiently compute functional gradients.

The Physics of Down-Hole TEM Monitoring of CO₂ Sequestration Processes

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A numerical study has been initiated to investigate the use of the ‘time domain electromagnetic’ (TEM) method as a down-hole imaging tool for monitoring CO₂ sequestration processes within subsurface reservoirs. Initial work in this area has applied forward modeling and linear inverse theory to analyze the physics behind the method. Numerical modeling has been accomplished via the finite difference time domain (FDTD) scheme developed under this project (Newman, 2001), while the geoelectric models employed are identical to those developed by researchers at Lawrence Livermore and Lawrence Berkeley National Laboratories to assess the applicability of other geophysical imaging techniques for monitoring CO₂ injection. The models consist of interbedded conductive and resistive layers, with the injected CO₂ represented by 3D resistive bodies within the conductive zones.

The first step in the assessment process has been to simulate magnetic field measurements at receiver locations both in the source borehole, as well as in a second borehole some distance away. The single well TEM responses show dramatic differences at early (micro seconds after excitation) to mid (tens of micro seconds after excitation) times depending on whether the source-receiver system lies within a conductive or resistive section. At late times (hundreds of micro-seconds after excitation) the single well results converge, i.e., the fields become independent of the measurement location within the reservoir. The cross-well TEM measurements at different locations are nearly time invariant at early times, diverge at mid-times depending on the source/receiver positions relative to conductors/resistors, and then converge again at later times. The injection of CO₂ causes dramatic changes in the early-to-mid time responses if the source and receiver are both within, or near, the injection zone, and less dramatic changes in the mid-times if either one or both are located away from the injection zone.

In order to better understand the underlying physics, the FDTD scheme has also been employed to calculate the electric fields, and hence the current densities, within the simulated reservoirs. Time-slices of current density indicate large differences at early times for current systems generated by sources located in resistor versus conductors. With increasing time, however, the currents become focused in conductive layers. The current system continues to evolve such that at late times the distribution is independent of the source location with the current confined to conductive layers. In addition, the current maximum tends to rapidly diffuse through resistive CO₂ injection zones. This rapid movement of the current through these zones results in the differences in the magnetic field measurements pre- and post-CO₂ flood.

The calculated electric fields have also been employed in sensitivity calculations using the convolution method given in Hordt (1998). The goal of these calculations is to estimate how the spatial sensitivity of various source-receiver configurations develop over time, at what time they maximize, and again, how they are affected by injected CO₂. For the single-well configuration the TEM sensitivity is maximized near the borehole at the early times right after excitation, decreases in magnitude with increasing time as the current diffuses outward, and decreases/diffuses more slowly when the tool is located in a conductive medium compared to a resistor. For the cross-well configuration the TEM method is more sensitive to perturbations in resistive zones at early times, and transitions to being more sensitive to conductors in the mid- to

late times. In addition, the sensitivity magnitude is small in the early times and is focused in the region between the wells, increases to a maximum value that peaks at the time where the measured responses begin to deviate from the early time 'invariant' value, and then decreases in amplitude at late times while spreading out.

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Additional Research Projects:

Nucleation and Growth Kinetics of Clays and Carbonates on Mineral Substrates

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Sequestration of $\text{CO}_2(\text{g})$ in subsurface rocks may result in increased acidity of pore waters, which in turn would accelerate dissolution of clastic sedimentary minerals such as quartz, feldspars, and micas. Subsequent precipitation of secondary minerals such as clays and carbonates may alter a reservoir's capacity to retain the $\text{CO}_2(\text{g})$. Observations from sedimentary basins have shown that clays and carbonate minerals form heterogeneously on mineral substrates, implying nucleation at saturation conditions below that needed for homogeneous nucleation in solution. This implies that the substrate minerals play a role in reducing the free energy barrier to nucleation. For example, calcite is known to precipitate on the basal surfaces and in interlayer spaces of mica crystals. Clays such as illite, kaolinite, or chlorite can nucleate or grow on mica, quartz, or feldspar in a manner suggesting topotaxial or epitaxial relationships. Our research is to determine fundamental mechanisms and rates at which clays and carbonate minerals can form on disparate mineral surfaces by using controlled kinetics experiments and characterizing the nucleation and growth process at the micrometer to molecular scales using techniques such as atomic force microscopy and X-ray reflectivity.

Our focus has been to investigate nucleation and growth on micas and quartz. In order to determine how Ca adsorbs on the basal surface of mica, one of the first steps in growth of calcite on this surface, we studied the muscovite surface in water and in calcium-chloride solutions using in-situ synchrotron X-ray reflectivity (in collaboration with P. Fenter and N. C. Sturchio at BESSRC-CAT, Advanced Photon Source, Argonne National Laboratory). Results show that water takes on an ordered three-layer structure extending approximately 1 nm outward from the surface. In the presence of 0.01 and 0.5 m CaCl_2 solutions, under atmospheric PCO_2 conditions, modeling of electron density profiles obtained from specular reflectivity suggest the presence of monovalent CaCl^+ rather than divalent Ca^{2+} at the surface. This has important implications for the nucleation mechanism of calcite at the mica surface under acidic to neutral pH conditions or at PCO_2 values above atmospheric, where monovalent CaHCO_3^+ occurs in significant concentrations. CaHCO_3^+ may adsorb similarly to CaCl^+ resulting in a density of Ca at the surface twice as high as expected for adsorption of Ca^{2+} (assuming that the density corresponds to the negative permanent charge on the mica surface). This sorbed species would require deprotonation in order to form part of the molecular structure of calcite. In-situ reflectivity data obtained on the sorption of K^+ and Ba^{2+} can be related to the nucleation and growth of clay minerals on the same muscovite surface. We have also carried out a baseline investigation of the structure of the quartz-water interface, using growth surfaces on natural quartz crystals. In contrast to the mica-water interface, water does not form an extensive layered structure. Investigations are underway to precipitate calcite on mica using atomic force microscopy under controlled flow-through conditions as well as in-situ X-ray reflectivity. We have also conducted preliminary laboratory and synchrotron experiments on the sorption of Zn and nucleation of a dioctahedral clay on the quartz surface.

Microscale Flow Modeling in Porous Media

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Natural as well as many engineering materials exhibit complex pore structures that exert fundamental control on physical and mechanical properties such as permeability, electrical conductivity, elastic moduli, compressibility, seismic velocity, thermal conductivity, poroelastic parameters, and strength. In this work, we investigate the effect of pore geometry on permeability using a combined experimental and numerical modeling approach. The combined experimental and numerical approach also allows us to investigate directly our ability to predict the macroscopic physical properties of porous geomaterials via microscale modeling. Synthetic sandstones were prepared by sintering glass bead packs to varying final densities and porosities. The permeability of seven 1x2 inch samples with porosities ranging from 5 to 35 percent was measured in the laboratory using the steady-state technique at bench conditions (~200 psi) as well as at elevated confining pressures. The data exhibit the classic power law relationship between permeability and porosity (with evolving exponent) observed in natural sandstones such as Fontainebleau. High-resolution (3.4 micron) three-dimensional image data were obtained for four ~1 mm sized samples via synchrotron computed microtomography experiments performed at the GSE-CARS CAT sector 13 BM beamline at the Advanced Photon Source. The three-dimensional image data were analyzed quantitatively to characterize the three-dimensional pore structure (Figure 1), and subsequently used in massively parallel lattice Boltzmann fluid flow simulations. The permeabilities predicted by the simulations are in excellent agreement with the experimental measurements that indicate over four orders of magnitude permeability variation over the range of porosity explored (Figure 2). Synchrotron computed microtomography experiments were also performed on pristine and experimentally deformed samples of a natural sandstone, Castlegate, that serves as an analogue for weakly consolidated reservoir rocks. Three-dimensional image data were acquired for multiple volumes and at two different resolutions (1.7 and 3.4 micron) within single samples, and then used in massively parallel lattice Boltzmann fluid flow simulations. The characteristic length scale for the natural sandstone is larger than that for the synthetic sandstones, and consequently, reliable predictions of permeability are not obtained using sub-sets of the data of the same physical dimension as the synthetic sandstone data. Reasonable agreement is found only for larger volume sizes. Besides allowing direct investigation into aspects such as representative volume and the effect of image resolution, the three-dimensional image data for the Castlegate sandstone also complement quantitative higher-resolution scanning electron microscopy studies that were undertaken to elucidate the micromechanical processes associated with compactive deformation.

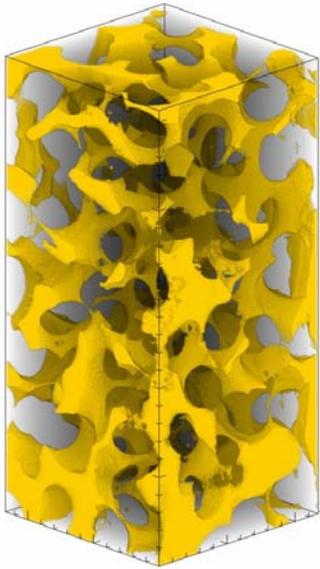


Figure 1. Three-dimensional rendering of the pore space for synthetic sandstone with porosity of 17%.

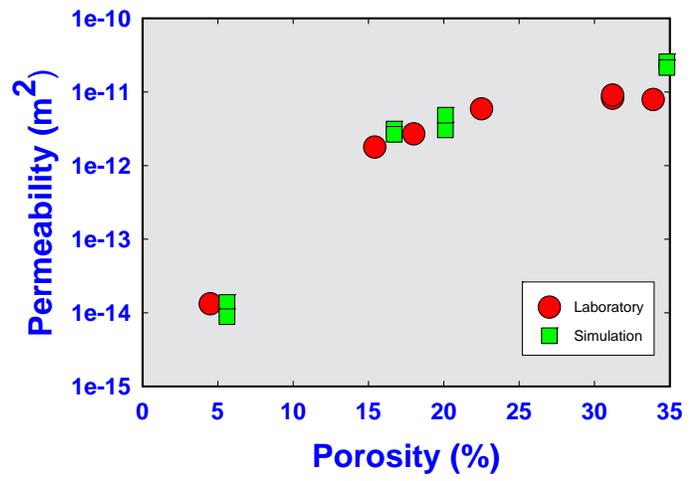


Figure 2. Comparison of permeability predicted from lattice Boltzmann simulations performed on three-dimensional synchrotron microtomographic image data versus laboratory measurements for four samples of synthetic sandstone.

Testing Deep Saline Aquifers for Long-term CO₂ Leakage Using In-Situ Noble Gases

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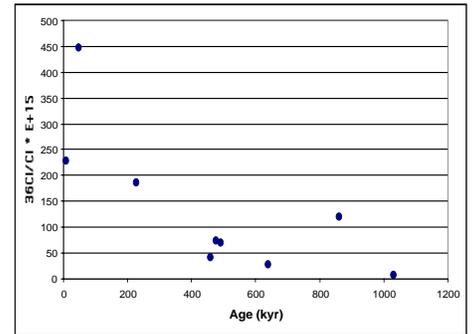
The objective of this project is to develop techniques based on noble gas isotopes for the purpose of testing deep saline aquifers for long-term leakage of gases. Such aquifers have been suggested as repositories for industry-derived CO₂ effectively sequestering this “greenhouse” gas rather than releasing it to the atmosphere. Some noble gas nuclides, notably ⁴He, ²¹Ne, ⁴⁰Ar, and ^{134,136}Xe, are produced in-situ in aquifers continuously over geologic time, and accumulate in measurable excess abundances. If CO₂ is capable of leaking as a gas either continuously or episodically, these noble gas nuclides would likely also be affected, and their full accumulation would not be observed.

The in-situ production of most of the noble gas nuclides we are investigating is due either directly or indirectly to uranium and thorium in the aquifer, through spontaneous fission and radioactive decay. As a guide to the integrated history of U and Th “exposure” for the saline waters under investigation, we are using ³⁶Cl and ¹²⁹I. Our primary assumption is that most of the ³⁶Cl and ¹²⁹I originated in the aquifer rock, and that the magnitude of the ³⁶Cl/Cl ratios will reflect the neutron flux resulting from U-Th decay, and the ¹²⁹I/I ratios will reflect the magnitude of spontaneous fission of U.

We have been able to investigate this assumption through the combined analysis of ³⁶Cl and ¹²⁹I in a variety of aquifer lithologies. Carbonate aquifers provide a very low U-Th environment, providing an endmember case. We analyzed a suite of Gulf Coast carbonate brines for ³⁶Cl/Cl which had previously been analyzed for ¹²⁹I/I (Moran et al., 1995). The suite produced ³⁶Cl/Cl = 5.2E-15 ± 2.1E-15. Assuming the aquifer Th/U ratio to be ~2, common for carbonates, the ³⁶Cl/Cl ratio implies [U] ≈ 1.35 and [Th] ≈ 2.70. This U concentration would produce a calculated ¹²⁹I/I ratio of 30E-14, assuming a spontaneous fission half-life of ~7E+15a and a fission yield of 0.04%, both within the range of published values. This calculated ¹²⁹I/I ratio compares well with the measured values of 27E-14 ± 6E-14, suggesting that the ³⁶Cl/Cl and ¹²⁹I/I ratios are accurately reflecting aquifer [U] and [Th].

Another endmember test was provided by saline waters from a young andesitic volcanic complex associated with geothermal activity. The mean age of the complex is several million years, old enough for ³⁶Cl to exhibit andesitic in-situ values, but sufficiently young that ¹²⁹I would still exhibit depleted mantle values. Average ³⁶Cl/Cl ≈ 6.5E-15, implying [U] ≈ 1, too high for depleted mantle. Average ¹²⁹I/I ≈ 5.7E-13, suitable for mantle [U]/[I] ≈ 2, at any [U]. This demonstrates a situation in which both ³⁶Cl and ¹²⁹I reflect isotopic equilibrium with aquifer rock, but only ³⁶Cl is able to reflect aquifer [U].

Other tests demonstrate the importance of considering interactions between deep saline waters and shallower meteoric waters. This is an important screening criterion for CO₂ sequestration, since such interaction must be avoided. A deep saline arkosic sandstone and mafic igneous aquifer complex in central Nevada produced uniform ³⁶Cl/Cl ratios of 50E-15 ± 5E-15. This implies [U] ≈ 7, far too high based on published [U] for similar outcrop rocks in the region. Analysis of shallower regional waters suggests the measured ³⁶Cl/Cl represents mixing of meteoric and saline waters. Similarly, a non-carbonate saline aquifer system in central Iowa produced a range of ³⁶Cl/Cl ≈ 5E-15 to 450E-15. In an attempt to understand these values from the perspective of recharge age, ⁴He was measured and helium ages were calculated (see Figure). The correlation again implies meteoric mixing. For those samples with very old ages and low ³⁶Cl/Cl, ¹²⁹I/I values are being obtained.



To expand our database and obtain samples for integrated ³⁶Cl-¹²⁹I-noble gas isotopic measurement, we are now active participants in projects in the saline Frio Formation in eastern Texas and Enhanced Oil Recovery field brines in western Texas (in collaboration with Chevron/Texaco).