feature article

Geoscience research for our energy future

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Understanding the complex interactions between pressurized fluids and porous rock is a key prerequisite to the safe sequestration of carbon dioxide and radioactive waste.

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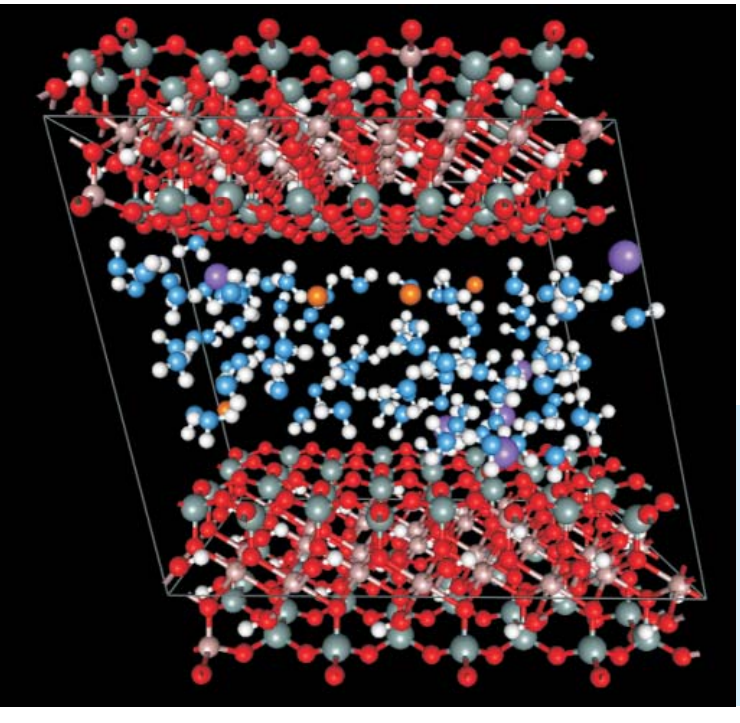
Worldwide energy consumption is projected to double by mid-century. For the next several decades, the world will continue to depend heavily on fossil fuels, even as renewable resources are increasingly used. To reduce the climate-changing influence of fossil fuels, a significant fraction of the carbon dioxide they produce needs to be captured and stored away from the atmosphere. (For a discussion of proposed geoengineering measures see page 26.)

Nuclear energy, by contrast, produces no significant CO_2, which makes it an appealing alternative to carbon-based fuels. But its radioactive waste materials have their own environmental and security implications. To sustain current levels of nuclear energy—and especially to increase production by a factor of 10 or more during the 21st century—it is necessary to store radioactive waste in underground repositories. Several countries, including the US, have programs under way to develop such repositories for nuclear waste as well as for CO_2.



Underground rock formations are attractive places because they can store large volumes of material and are relatively accessible.[1] However, rock formations were not designed by Nature as storage vaults. To understand, predict, and monitor the performance of rock formations used as storage sites, scientists and engineers are researching the fundamental properties of minerals, rocks, and fluids (both liquids and gases) and how they interact and evolve on time scales that range from seconds to thousands of years and on length scales from nanometers to kilometers.[2,3]

When foreign materials are buried underground, they alter the chemical and physical environment. In the case of CO_2, the relatively cool, low-density fluid is introduced under pressure and allowed to find its way into rock formations. Only natural barriers impede its movement. The injected CO_2 can dissolve in and change the acidity and density of the ambient fluids, and the increased pressure from the injection can induce flow in a wide region around the injection site.

In the case of nuclear waste, the radioactive materials are encased in containers and placed into particular geologic formations. Radioactive decay, however, heats the containers and their surroundings and potentially damages the containers as they age. The modifications to the local environment, which can continue for centuries or longer, are among the primary concerns in evaluating geological formations as repositories.[4]

In July 2007 the Department of Energy's Office of Basic Energy Sciences released a report of a workshop entitled "Basic Research Needs for Geosciences: Facilitating 21st Century Energy Systems." The workshop was part of a series designed to develop up-to-date fundamental research agendas

Figure 1. Snapshot of a molecular-dynamics simulation. Two clay mineral layers, whose constituent atoms are mainly represented in red and gray, are separated by an interlayer filled with water molecules (blue and white), sodium ions (purple), and methane molecules (orange). The interlayer is an example of a nanopore that can be used to study how the properties of water and its dissolved constituents are affected by confinement and the presence of mineral surfaces. (Adapted from ref. 12.)

for energy-related science. (To learn of another workshop in the series, see the article by Graham Fleming and Mark Ratner, PHYSICS TODAY, July 2008, page 28.) The emphasis of the geosciences workshop was on basic research needed to advance underground storage of CO_2 and nuclear waste. The former is a growing concern of DOE's Office of Fossil Energy. The latter has been a major concern of the Office of Civilian Radioactive Waste Management and is a critical component of future nuclear energy development. The scientific concerns are captured in the workshop report as a series of grand challenges, priority research directions, and crosscutting issues, some of which are described here. The workshop is available at http://www.sc.doe.gov/bes/reports/list.html.

Arguably, researchers know enough to begin sequestration activities. But the large scale of the proposed operations (for example, about 10 gigatons of CO_2 per year will need to be sequestered), the fact that the operations will be carried out over hundreds of years, and the likelihood that both efficiency and safety requirements will become more demanding with time imply a fundamental need for advances in geology, hydrology, geochemistry, and geophysics.

Molecular-scale simulation

Underground fluids can have a wide range of chemical compositions. Although the most common of those fluids are water and air, the water typically contains an assortment of dissolved constituents and in many cases is so salt-rich that it is referred to as brine. The brine can also be accompanied by organic gases and liquids such as petroleum. Improving our understanding of the chemical properties of aqueous and nonaqueous solutions, their mixtures, and their interactions with minerals is both a major objective and a challenge. The general term for the flow of fluids through rocks that interact chemically with them is reactive transport.

The time-honored way to study the chemistry of materials is by experimentation, with the results organized using macroscopic thermodynamic models. However, it is now possible to calculate some chemical properties of materials starting at the atomic level using first principles. Rapid advances are being made with that approach, but the added challenge for geological problems is to also simulate complex materials under a range of conditions.

Consider an example. Nuclear waste materials can escape to the environment when fluids—mostly water with dissolved constituents—corrode containment canisters and carry the toxic species away in flowing groundwater. The release of radioactive elements from solid waste is affected by several factors, including the chemical form the element takes when dissolved, its solubility, and its tendency to adsorb on mineral surfaces and colloidal particles carried in the fluid.

The release of uranium from solids into fluids is strongly affected by a change in valence. Spent nuclear fuel is 95% uranium oxide (UO_2), which contains U^{4+}, or U(IV). Experiments show that when U is released into solution, the most abundant uranium oxidation state is U(VI). The process that changes the insoluble U(IV) species into soluble U(VI) during the dissolution step remains obscure. To better understand what happens at the solid–fluid interface and to learn how to retard the release of U require computer simulations and experimental studies that can capture the nearly instantaneous (10^{-12} to 10^{-15} second) chemical interactions that control the process.

Determining the solubility of U ions sounds straightforward but is complicated by the formation of hydration shells—chemically bound water molecules—that surround the ions to produce multinuclear clusters, the size and composition of which change depending on conditions in the fluid. Examples include $AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ and $(UO_2)_2(\mu\text{-}OH)_2(OH_2)_6^{2+}$, which can be the dominant carriers of Al(III) and U(VI) under certain conditions.[5] Simulating the behavior of those and other species formed of actinide and transition-metal elements is challenging because of the presence of highly correlated and poorly screened *f* and *d* electrons, complex bond breaking and formation, changes in polarization and bond valence, and the large number of atoms in the cluster.

Although CO_2 and H_2O have fewer electrons than actinides and are thus simpler in some respects, the chemistry of CO_2-bearing fluids is complicated for other reasons. For example, CO_2 and H_2O are partially miscible, and pure CO_2 is a supercritical fluid at the temperatures and pressures normally encountered in CO_2 sequestration. Moreover, as noted previously, the water migrating in rocks is an impure, salty mixture. Simulating the changes in chemical properties of complex fluids near mineral surfaces and within confined

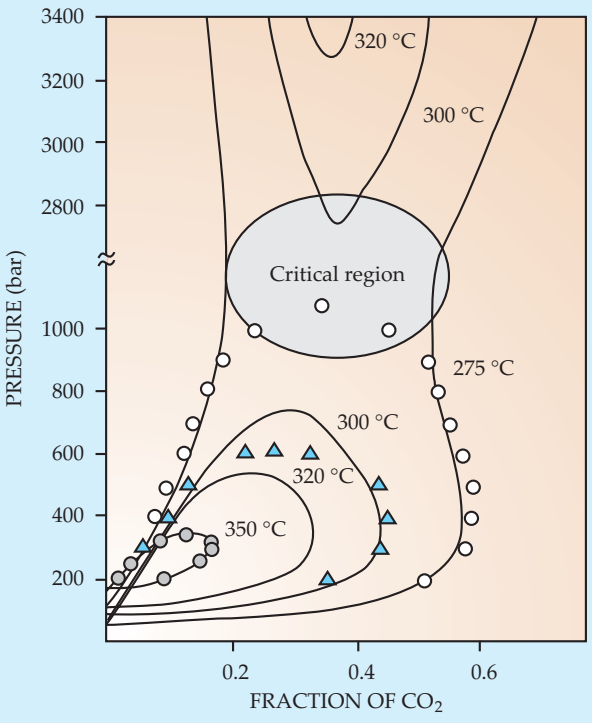


Figure 2. Predictions of an equation of state for mixtures of water and carbon dioxide at a range of temperature and pressure conditions deep underground. At a given temperature, those mixtures whose fraction of CO_2 lies between isotherm curves separate into H_2O-rich and CO_2-rich phases, with compositions given by the isotherms. The model (curves) fits the experimental data (symbols) well for 350 °C but is less accurate for 300 °C and 275 °C, especially in the critical region where thermodynamic properties are difficult to represent mathematically. To predict the physical behavior of CO_2 injected underground, where pressures fall between 100 and 1000 bars, researchers combine the type of information shown here with models for the density, viscosity, and wetting properties of the mixtures and the solubility of minerals and salts in them. (Courtesy of John H. Weare.)

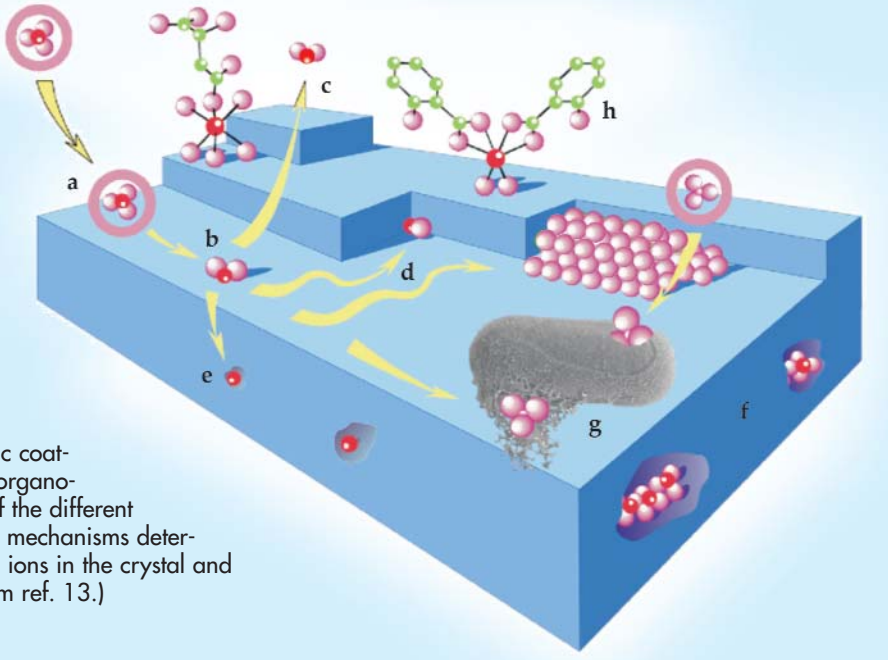


Figure 3. A variety of chemical transport processes (yellow arrows) and structures exist at a mineral surface in contact with a fluid. A trace-metal ion (red) is carried in the fluid as a complex with a hydration shell (pink circle). The processes depicted include **(a)** physical adsorption, **(b)** dehydration followed by chemical adsorption, **(c)** detachment, **(d)** surface diffusion and attachment at a step, **(e)** ionic substitution with an atom in the bulk, **(f)** trapping at crystal imperfections, **(g)** the binding of atoms to an organic coating (gray), and **(h)** adsorption of an organo-mineral complex. The relative rates of the different adsorption, desorption, and diffusion mechanisms determine the concentration of trace-metal ions in the crystal and the crystal growth rate. (Adapted from ref. 13.)

pore spaces, as pictured in figure 1, may be essential in determining how the fluids will react in storage environments.

To translate the advances in molecular-level dynamical simulation into applications at the macroscopic level, what's needed are accurate representations of bulk thermodynamic and transport properties in the computational model. The equation of state, for example, must capture the variation in free energy, including changes in phase and the species in solution, for a wide range of conditions (see figure 2). The research effort in this area has been considerable, but for many relevant problems, the molecular understanding is insufficient to develop macroscopic thermodynamic models. Theorists need to improve their formulations of equations of state for all kinds of systems, including compressible fluid mixtures, aqueous electrolyte solutions, mixtures of aqueous electrolyte solutions and nonaqueous liquids, solid solutions, adsorbed species, nanoparticles, and colloids.

Mineral surface dynamics

Over the past two decades, researchers have pieced together the molecular-level details on the structure and reactivity of idealized mineral–water interfaces and suspended phases of particles. However, the surfaces of geological materials are complex: Composition, roughness, and defect content can all vary, as can any organic and mineral coatings on the surface (see figure 3). The complexity makes it difficult to apply information gained from idealized laboratory systems to the field environment. The size dependence of surface properties may control the adsorption of aqueous species to, and hence the transport of, particulate materials. And the time dependence of surface properties is especially important given the need to describe processes that continue for thousands of years.

X rays can probe the water–mineral and water–particle interface in situ and in real time through spectroscopy, diffraction, and microscopy.[6] To strengthen the link between idealized and natural interfaces, researchers need to address the role of inhomogeneities. For example, the incorporation of trace impurities into minerals alters the rate at which crystals grow from solution. Changes in the interfacial composition during growth, due to ion-dehydration kinetics or the incorporation of vacancies, lead to lattice strain that can affect both the crystal's geometry and growth rate.

Furthermore, defects can strongly influence the thermodynamic stability of surfaces, and hence the kinetics of crystal growth and dissolution and the incorporation or release of minor constituents. The chemistry of the fluid phase is also altered near mineral surfaces and within the pores of rocks. New and improved molecular probes using next-generation light sources and neutron sources are needed to investigate the structure and dynamics of those complex interfaces. Neutron scattering is an especially effective technique for studying fluid properties.

Characterization, modeling, and monitoring

Rocks in Earth's crust are heterogeneous on many scales. The challenge is to characterize their complex structure and then capture in a mathematical model the scale-dependent processes that affect fluid flow and chemical reactions. The approach to date has been to develop separate models that treat distinct portions of the spectrum of scales and processes. The long-term goal is to develop models that can integrate across spatial and temporal scales, data types, and geological processes. Large and varied data streams can be assembled, but they cannot yet be incorporated into models in a comprehensive and adaptive way, and it is difficult to estimate uncertainties. It is increasingly evident that data collection must be integrated into and performed in concert with modeling to maximize the value of both approaches.

Fluid flow, reactive transport, and the deformation of rocks are nonlinearly coupled processes, each with different spatial and temporal scales. The challenge is to describe the processes at a level of detail limited enough to make the problem tractable without losing the underlying physics and chemistry. One way to identify the appropriate level is to work with models that capture the statistical character of the heterogeneity. Models can be constructed using representa-

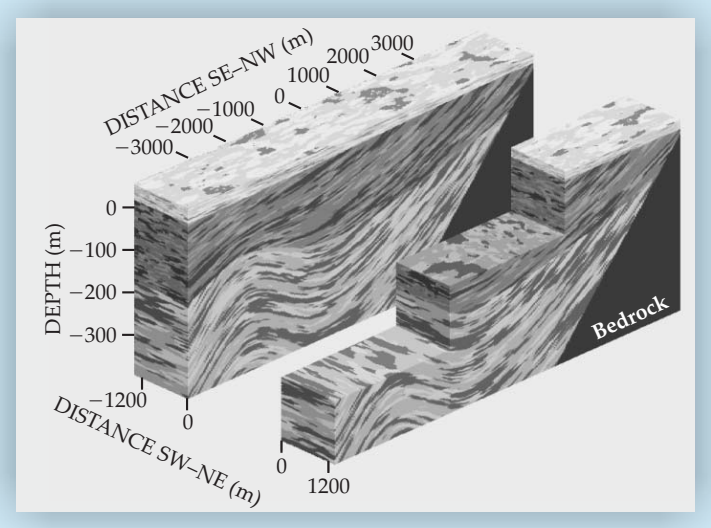


Figure 4. A simulation of a sedimentary basin beneath Orange County, California, showing the three-dimensional structure of the rocks there. The light, dark, and medium shades of gray shown from top to bottom indicate three distinct geological formations. In each formation the shading specifies sediment grain size, with darker shades signifying more permeable domains that have larger grains. The simulation combines observational data with a stochastic hydrodynamic model of sediment deposited by streams. The resulting geology helps researchers understand how groundwater may flow through the region and chemically interact with the sediment. A depth of zero corresponds to sea level. (Adapted from ref. 7.)

tions of known geological processes and available site-specific data.

Figure 4 shows, for example, a simulation of a sedimentary basin below Orange County, California, based on stratigraphic and surficial soils data and a model of sediment deposition.[7] The model uses the hydrodynamics of sediment transport, subsidence, and erosion to predict the spatial variability in grain size of the resulting deposits. That, in turn, gives a representation of the variability in the porosity, permeability, and flow-path interconnectivity. Fractures must also be accounted for, but evidence indicates that their distribution can be related to certain sedimentary structures and textures.

Dynamic imaging

Remote sensing techniques, including three-dimensional seismic reflection, gravity, and magnetic methods, offer an efficient way to characterize large-scale subsurface structures.[8] Used in concert with inverse modeling, those methods can provide an image of properties such as density, seismic-wave velocity and reflectivity, and electrical conductivity. Optimally, one would like to translate the directly measured properties into porosity, permeability, fluid content, fluid composition, mineralogy, and fracture density. But the resolution of the remote methods is typically quite coarse, which complicates image interpretation.

Nevertheless, geophysical methods have been used in recent years to provide estimates of such sediment properties as water content and permeability. The work is still at an early stage; so far, only relatively small regions can be imaged, and the data-inversion methods are fairly crude. A promising approach is to monitor perturbations as they are introduced. For example, a comparison of images taken

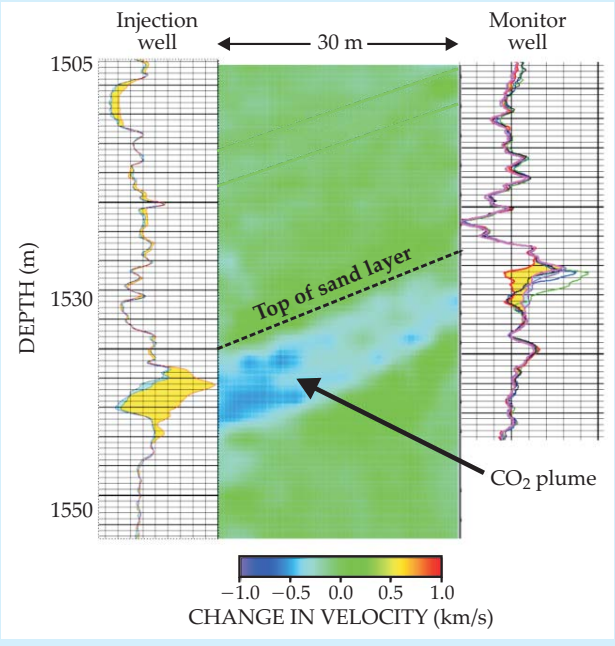


Figure 5. Some 1600 tons of carbon dioxide were injected into a well to a depth of about 1540 m in an experiment performed in southeast Texas. The CO_2 then flowed laterally and upward through a porous layer of sandstone into a second well. The plume of CO_2 is evident in this seismic tomography image (center) as a decrease of about 0.5 km/s in the seismic P-wave velocity. Inelastic neutron scattering, which measured the amount of CO_2 (or, more accurately, the ratio of C to O atoms) in the fluid adjacent to the injection well (left) and monitor well (right), confirmed the plume's path. The scattering experiments were run several times during the injection; the change due to the presence of CO_2 is shown in yellow. Note the small scale of this experiment; for industrial-scale sequestration, the injected CO_2 can penetrate 10 km or more into the surrounding rock formations. (Adapted from ref. 9.)

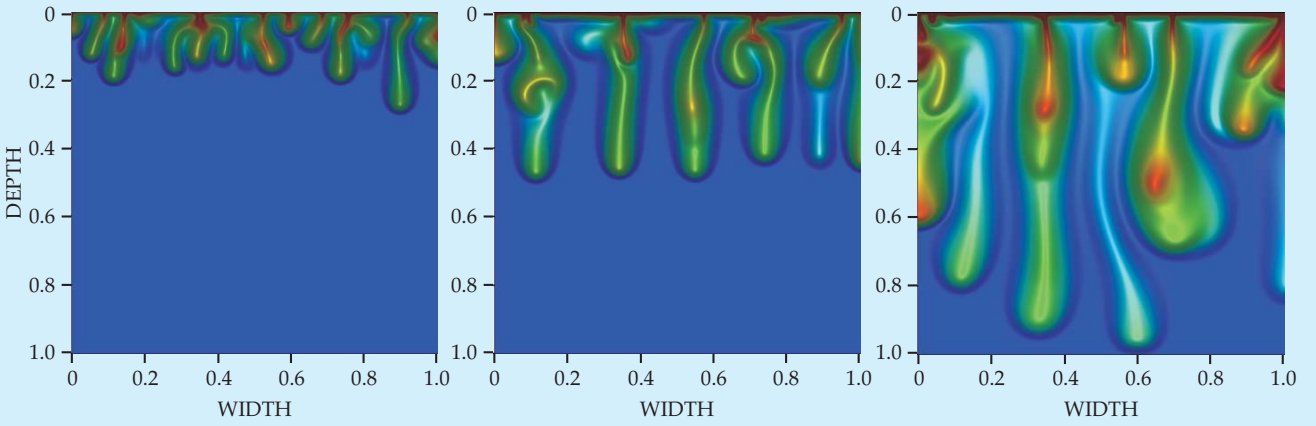


Figure 6. A low-density carbon dioxide fluid mixes with a salt-rich fluid in a porous medium analogous to sandstone in this computer simulation. The CO_2 gas accumulates along the top boundary, assumed to be impermeable to upward flow. The low-density CO_2 slowly dissolves into the underlying brine and forms a dense layer of CO_2-saturated brine (red). The resulting gravitational instability gives rise to downward convection as fingers or plumes. A large number of plumes develop initially, but they later coalesce into a smaller number of larger plumes. The lateral and vertical distance scales are nondimensional, as is the elapsed time between frames. When scaled using the properties of sandstone and brine, the calculations indicate that the length of time required for plumes to develop can range from weeks to thousands of years, depending on permeability, and the width of a plume can range from less than a meter to greater than 100 meters. (Adapted from ref. 14.)

before and during CO_2 injections underground can ameliorate the effects of heterogeneity because only differences between images are important (see figure 5).[9] However, that kind of time-lapse method still suffers from the uncertainties of relating geophysical signals to actual changes in the rocks and fluids. To improve the approach, researchers need a much better understanding of the interaction of physical fields, such as elastic waves or electromagnetic disturbances, with fluid-filled porous rocks.

There is also promise of obtaining more information by sampling boreholes or using other direct in situ methods. Accurate measures of state variables—pressure, temperature, concentration, and phase saturations—and of flow, transport, fluid age, and reaction rates would dramatically improve predictive models. Yet more detail could come from smart tracers—either chemical devices, whose presence or state can be probed with electric or magnetic fields, or miniature sensors that can be distributed underground.[10]

The age of subsurface fluids is an important clue for understanding how fluids flow through and react with rock formations. The age is also ambiguous because a sample taken from a well could be a mixture of fluids that have come from different sources at different times. If the distribution of ages as well as the bulk age could be measured, it would be a real breakthrough in our ability to characterize fluid-flow pathways and reaction rates. But the ability to date fluids is quite limited, particularly samples between 50 and 3000 years old, the age range in which such information would be most useful. Methods are also needed for measuring pressure, temperature, and other variables continuously in space and time rather than as local averages at discrete points or within conventional well bores.

Long time scales

The perturbations caused by storing materials underground can occur over tens of years, a standard time scale for engineering design. However, the subsequent performance of those perturbed systems must be predictable for hundreds of years in the case of CO_2 sequestration and for up to 1 million years in the case of nuclear-waste isolation. Both time scales are long compared with the relaxation time of normal chemical and hydrological processes. Geological models do exist for Earth processes on long time scales, but they are for the most part heuristic.

As noted previously, modeling geological systems is complicated by the large range of spatial and temporal scales over which processes occur. For example, when CO_2 is injected underground, the short-term effect is to raise fluid pressure and create a pressure gradient within the reservoir, an effect that induces flow. The increased pressure can also deform rock and change its permeability. But on longer time scales, the pressure gradients relax; gravity moves the CO_2 upward until it reaches a low-permeability flow barrier, and the CO_2 spreads out under that barrier.

Dissolution of CO_2 into an aqueous fluid produces mixed fluids with new properties and can initiate chemical reactions that dissolve or precipitate minerals. The effects of buoyancy also complicate the flow of mixed fluids. The instabilities inherent in buoyant flow are well known, but when fluids occupy a porous medium, new behaviors emerge at the pore scale from variations in the permeability and capillary pressure (see figure 6).

A key part of the geological simulation challenge is to formulate mathematical descriptions of fluid flow that are self-consistent across many length and time scales. Because fluid flow and reactive-transport processes have characteristic length and time scales, while geologic heterogeneity occurs at all length scales, it is necessary to identify and map the scales at which connections between process and heterogeneity are important. Such maps can inform efforts to describe reactive transport with models that span different scales and allow for an organized description of emergent behavior.

One common way to treat multiscale processes is to as-

sume that every scale behaves as a continuum. That approach breaks down when chemical, thermal, and velocity gradients within the smallest-scale computational domains are large enough to change the predicted behavior. Hybrid approaches that account for those subgrid-scale processes are then needed. The problem is that the links between models that treat the different scales are not well established. To develop confidence in hybrid models requires coordinated laboratory and field experiments designed specifically to improve the models and validate the mathematical framework behind them.[11] With recent advances in pore-scale (roughly 100 μm) rock imaging, pore networks can be mapped in three dimensions at submicron resolution. Microfluidic experiments are also useful for investigating the effects of pore-scale interfacial phenomena.

Next steps

A deep understanding of the fundamental physical and chemical processes that control migration of chemical constituents underground is essential for safe and effective sequestration of CO_2 and radioactive waste. Building that understanding will require a new generation of experiments and computational models. The latest generation of synchrotron light sources, neutron-scattering and microscopy facilities, nanoscience centers, and high-performance computing centers are likely to prove invaluable to the success of those studies. But they will also require innovative new laboratory and field techniques and, perhaps most importantly, a continuing supply of broadly trained geoscientists.

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