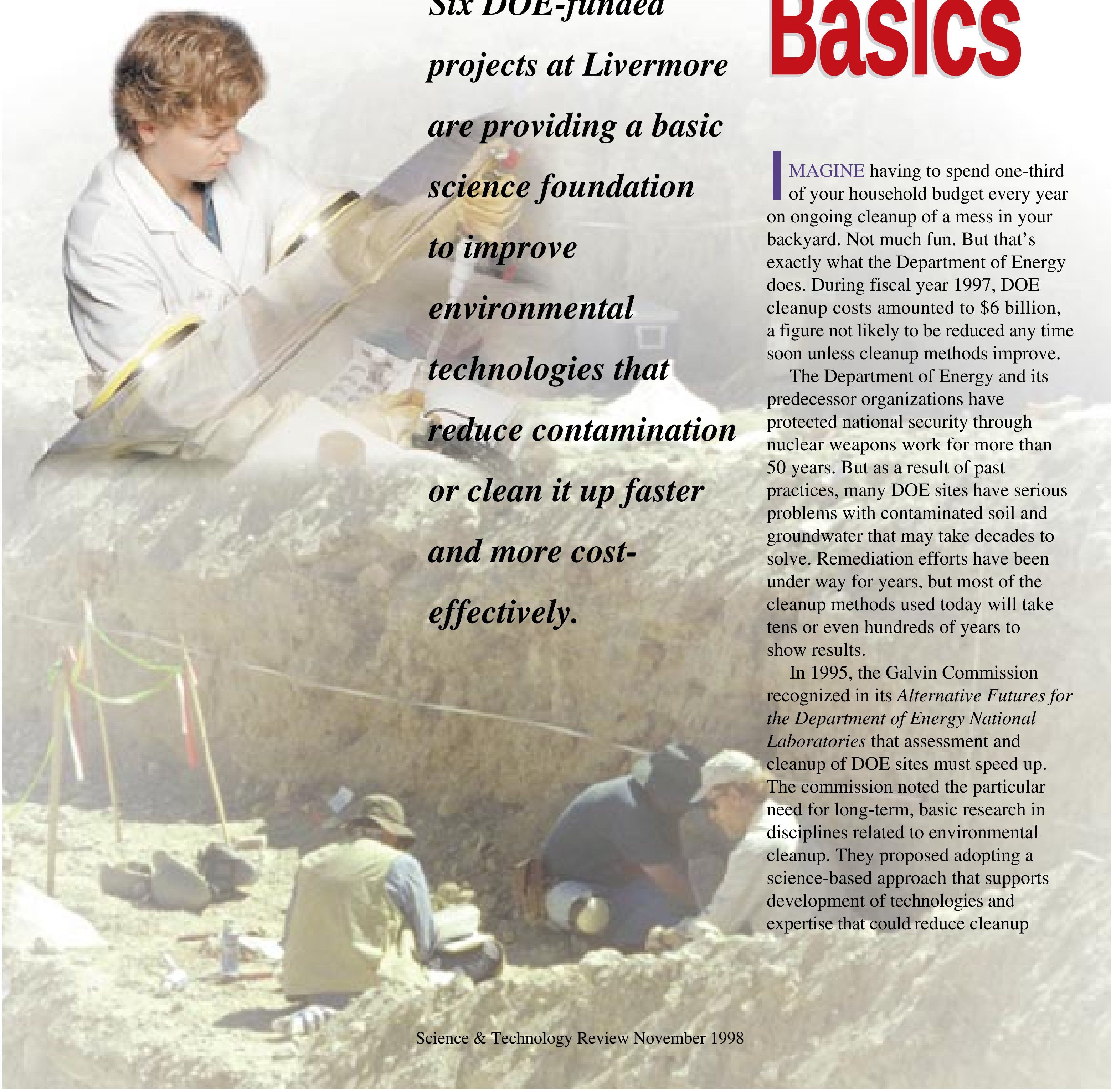
Getting Down to Environmental Cleanup Basics

Six DOE-funded projects at Livermore are providing a basic science foundation to improve environmental technologies that reduce contamination or clean it up faster and more cost-effectively.



IMAGINE having to spend one-third of your household budget every year on ongoing cleanup of a mess in your backyard. Not much fun. But that's exactly what the Department of Energy does. During fiscal year 1997, DOE cleanup costs amounted to $6 billion, a figure not likely to be reduced any time soon unless cleanup methods improve.

The Department of Energy and its predecessor organizations have protected national security through nuclear weapons work for more than 50 years. But as a result of past practices, many DOE sites have serious problems with contaminated soil and groundwater that may take decades to solve. Remediation efforts have been under way for years, but most of the cleanup methods used today will take tens or even hundreds of years to show results.

In 1995, the Galvin Commission recognized in its *Alternative Futures for the Department of Energy National Laboratories* that assessment and cleanup of DOE sites must speed up. The commission noted the particular need for long-term, basic research in disciplines related to environmental cleanup. They proposed adopting a science-based approach that supports development of technologies and expertise that could reduce cleanup costs, generate fewer environmental hazards at existing sites, and develop a scientific foundation for advances in environmental technologies.

The Department of Energy responded in 1996 by establishing an Environmental Management Science Program. It requested proposals from universities, national laboratories, and other research institutions for projects in basic science related to environmental management. That year, Lawrence Livermore received five grants for research and one more a year later. All are for three years of work and are under the direction of either Ken Jackson or Norm Burkhard, division leaders in the Earth and Environmental Sciences Directorate.

Five of the projects are geophysical and geochemical, with work ranging from a molecular view to a large-scale look at contaminant movement in the southeast corner of the Livermore site. The sixth is a chemistry project studying the vaporization of plutonium, uranium, and other radioactive elements when wastes containing them are burned. All six projects use experimental data to improve modeling codes and make them better predictive tools.

The payoff from these projects for DOE and other sites is expected to be long-term—basic research seldom pays off quickly. But over time, the benefits of this research will spread beyond the confines of Lawrence Livermore. And it is not just DOE sites that will benefit. Many other government and private sites are home to contaminated soil or groundwater or stored wastes that must be disposed of. The more environmental managers know about how contaminants behave, the smarter they can work to protect our environment.

The Water Table's Armor

One of the challenges for cleanup of contaminated soil and groundwater is learning more about how contaminants move in the area that lies between Earth's surface and the water table, a region known as the vadose zone. The vadose zone is critical because it is the only armor the water table has to protect it from contaminants on the surface. Yet the vadose zone is largely inaccessible to scientists except through core samples, monitor wells, other sampling methods, and a few underground imaging techniques.

The vadose zone is made up of soil, water, and air. It typically comprises more air and less water near the surface and is increasingly saturated closer to the water table. Depending on how deep the water table is, the vadose zone may be thin or nonexistent or up to hundreds of meters thick. Its soils may be sandy and gravelly and thus quite permeable, or they may contain dense clays that impede the downward movement of fluids.

Conventional wisdom says that a thick clay layer in the vadose zone should protect the water table from most contaminants near the surface. But even the most minute discontinuity in the soil layers—a chink in the armor, and there are many of them—provides an avenue for contaminants to migrate toward the water table.

What's Going on Down There?

Susan Carroll, Gregory Nimz, and Charles Carrigan are heading up projects to better understand the movement of contaminants in the vadose zone. Their projects cannot strengthen the armor, but they can fill some of the holes in our knowledge of this inaccessible region.

The Geochemistry of Strontium Movement. Carroll is seeking to determine the geochemical processes that govern the mobility of radioactive strontium in clays and iron hydroxides as a function of temperature, pH, and time. She notes, "Knowing more about strontium is important because strontium-90 is the fastest moving radionuclide except for tritium, and strontium has leached into soil and groundwater in places where nuclear weapons materials were manufactured, such as DOE's Hanford site in Washington."

Her objective is to obtain data needed to predict the behavior of strontium at temperatures and time scales typical for various thermal remediation processes. Her team is performing experiments on sorption/precipitation and desorption/dissolution that track changes in solution composition.

Batch sorption experiments were run at 25, 50, and 80°C, with pH ranging from 4 to 10. The experiments ran for 48 hours in various soil minerals using a nonradioactive strontium. As shown in Figure 1, temperature had no impact on sorption of strontium in goethite (an iron hydroxide) or in kaolinite. This figure also shows that sorption increased dramatically when the pH was greater than 7, with virtually no sorption when the pH was less than 7.

Carroll's research team is also looking at the molecular structure of strontium in its solid phase using x-ray absorption spectroscopy. Molecular spectroscopy experiments were performed over periods of 48 hours and two months to study how strontium bonds with various soil minerals and how those bonds change over time. For both time periods, it bonded only electrostatically with kaolinite and silica gel. With goethite, tight bonds were observed at 48 hours, but over time, the bonds disappeared.

Strontium's high mobility had been observed in the field, but these Livermore experiments were some of the first to confirm its mobility in the laboratory under a range of conditions. Strontium is so mobile because it does not sorb strongly to mineral surfaces; even its bond to goethite is short-lived and unstable.

"Our work is chemistry at its most basic," says Carroll. "We are working toward a geochemical model that will predict the right type of chemistry to mobilize or immobilize strontium. The model will also be able to predict the real hazard from the movement of strontium. Our data provide some very fundamental information about strontium's behavior, but they are only a small piece of the puzzle."

Radionuclide Movement in Undisturbed Soil. Gregory Nimz is also studying radionuclides in the vadose zone, specifically their migration in undisturbed soil. Says Nimz, "Detection of trace amounts of certain radionuclides—chlorine-36, strontium-90, zirconium-93, technetium-99, and iodine-129—was not possible prior to the development of accelerator mass spectrometry, a highly sensitive measuring technique. Without AMS, only a relatively high concentration of many radionuclides can be detected."

AMS is new enough that techniques did not exist when this project began for measuring strontium-90, zirconium-93, and technetium-99. Nimz's team developed them and also improved AMS methods for chlorine-36 and iodine-129. Livermore is home to one of the largest AMS facilities in the world and is at the forefront of AMS developmental work. (See *S&TR*, November 1997, pp. 4–11.)

Nimz's project is designed to fill two gaps in current knowledge about environmental management: how contaminant radionuclides move when they are far from the contaminant release point, and at what rate fluids move in unsaturated soils, a process known as moisture flux. The radionuclides he is studying were released into the atmosphere during aboveground nuclear testing in the 1950s and 1960s and have since settled into shallow soils, including permafrost, all over the world in a quite even distribution.

Nimz and his team are studying soil at the Nevada Test Site because it is handy, but they could have studied any desert location. They have trenched along a fault at the test site to get information about the shallow vadose zone (Figure 2). They trenched rather than bored to get as much information as possible about cracking and fracturing in the vadose zone—those chinks in its armor.

"Scientists now use the movement of chlorine as an indicator of moisture flux in low-moisture soil because it doesn't form compounds and stays in its ionic form in water," says Nimz. "But our field data indicate that nuclear test-related chlorine-36 is migrating faster than stable chlorine, casting doubt on the validity of using natural chlorine as an indicator of moisture flux."

The team is combining its new measurements of chlorine-36 and the other four radionuclides in the shallow vadose zone with NUFT, a Livermore flow-and-transport code, to develop a numerical model that simulates the movement of all five nuclides in the deep vadose zone. This model is designed to improve our understanding

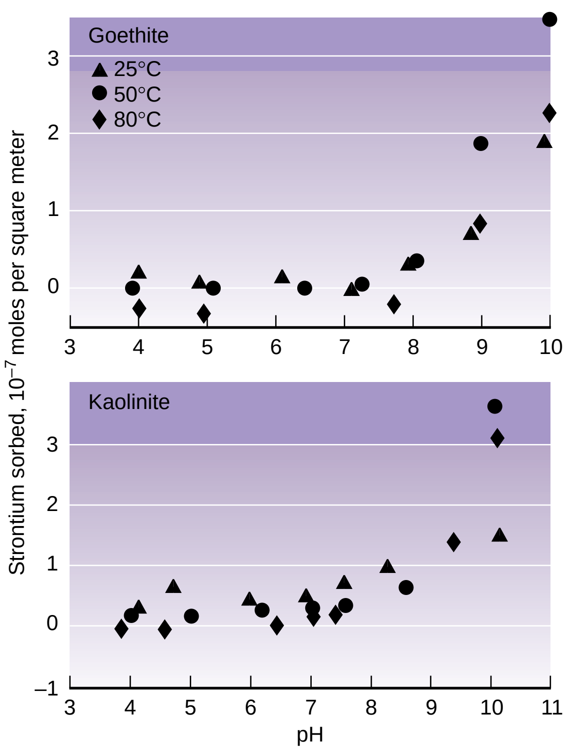


Figure 1. Experiments with strontium in two different types of clays showed that pH had a much greater effect on sorption than did temperature.

of the potential for radionuclide transport far from the contaminant release point and thus of the potential health risks in the far-field environment, where the public is most likely to come into contact with contaminants. The targeted radionuclides are not only common contaminants but also show migration behavior representative of radionuclides and heavy metals. The models developed in this research will thus furnish a foundation for a variety of contaminant migration assessments.

Contaminant Migration to the Water Table. Charles Carrigan's project is on a somewhat larger scale. He says, "We've set up a vadose zone observatory in the southwest corner of the Livermore site where we are monitoring the migration of contaminants to the water table. We're also looking at the 'partitioning' of liquid contaminants into gas. Once gas has formed, it may move laterally, downward, or upward to vent to the surface."

Complex interactions between the atmosphere and groundwater take place in heterogeneous vadose zones where fractures or other discontinuities contribute to permeability. Liquid or dissolved contaminants may flow down by gravity and capillary action. Because of changes in atmospheric pressure, all or part of the liquid may also become vapor. Carrigan's team is thus looking at both liquid- and gas-phase transport in the vadose zone. The goal is to have a model to predict liquid- and gas-phase distributions and downward fluxes of contaminants in the vadose zone.

The Vadose Zone Observatory has a center well for introducing a slightly saline solution as a "contaminant." The infiltration well is surrounded by wells for taking electrical resistance tomography (ERT) measurements to show liquid transport and by other wells for measuring gas-phase pressure changes.

ERT measures changes in resistance between two underground electrodes. These changes indicate changes in saturation in the vadose region. (See *S&TR*, May 1998, pp. 8–10.) Prior to "contamination" of the area, ERT measurements, lithologic logs, soil samples, and other data were used to characterize the site. Then 6,300 gallons of slightly saline water spiked with noble gas tracers were introduced into the center well at an average rate of 0.4 gallons per minute for 10 days at a depth of 15 feet. Figure 3 shows the changes in resistivity over time. Two isotopes of neon, neon-22 in air and neon-21 dissolved in water, were also introduced at different times into the center infiltration well to permit measurement of gas-phase transport and the coupling of gas and liquid phases, respectively. (See *S&TR*, November 1997, pp. 12–17.)

"At our observatory, the vadose zone is 70 feet thick, and we've found it to be highly permeable to gas- and liquid-phase infiltration," Carrigan says. In the experiments, contaminant infiltration occurred much faster than indicated by geologists' logs of the monitoring wells and by laboratory soil analyses. In fact, past data from this area give little or no indication of the magnitude of the observed infiltration rate, perhaps because the high permeability pathways are so localized that they are not well represented in any of the borehole observations.

To date, numerical models based on the NUFT flow-and-transport computer program have been compared with the ERT and gas-sampling observations. Several different models have been used to determine ranges of values for properties, such as permeability, that affect the relatively rapid infiltration of the plume.

A Better View

Electromagnetic induction tomography (EMIT), a technique that uses magnetic fields to image the

Figure 2. The trench at the Nevada Test Site for studying radionuclide movement in undisturbed soil is perpendicular to an earthquake fault. Two-inch cores were drilled horizontally about 24 inches deep. Samples were taken from six cores and from profiles, 15 to 30 feet apart. Two profiles are far from the cracked area, and the others are in the fracture area.

subsurface, was developed for use by the oil and gas industry to determine where reserves are located. Livermore's Jim Berryman has a team working to develop the code necessary to bring this powerful imaging tool to environmental management.

Says Berryman, "While electrical resistance tomography maps changes in resistance using electric current injection, EMIT does the same using magnetic fields. With EMIT, no electrodes need to be inserted into the ground. We just put induction coil transmitters and receivers on the surface or in a borehole" (Figure 4).

ERT as usually applied is two dimensional, measuring the electrical field on a plane between two boreholes. EMIT, however, is inherently a three-dimensional process, which makes the code for imaging the subsurface through magnetic fields more complicated. EMIT has been used by the oil and gas industry for several years, but these applications use a low-frequency field. With low frequencies and their long wavelengths, one gets a fairly smooth look at the subsurface. Higher frequencies and shorter wavelengths result in better resolution, which the environmental remediation community needs to accurately determine the makeup of a heterogeneous subsurface.

"Unfortunately," says Berryman, "the code used by the oil and gas industry cannot be used easily for these higher frequencies, so we chose to start from scratch."

Despite complications with the algorithms used to interpret the magnetic field data, the code is almost fully functional, a promising new tool in Livermore's kit for underground imaging. The EMIT imaging technique may soon be field tested at a Superfund site in Visalia, California, where compounds used to treat utility poles have contaminated the soil. Livermore is already assisting with cleanup of this site, working with SteamTech Environmental Services of Bakersfield, California, and the site owner, Southern California Edison. To date, Livermore has been using ERT for underground imaging on this project. (See *S&TR*, May 1998, pp. 4–11.)

Another Way to Look at It

Another improvement in subsurface imaging is in the works in the laboratories of Pat Berge and her team. Their new algorithm will allow "joint inversion" of several data sources—seismic (sound-wave) data, electrical properties, or magnetic data—to derive direct estimates of porosity and saturation.

Says Berge, "The current state of the art is to look at each set of data individually. Our goal is to combine multiple data sets and invert them together. It's like a crime: every witness tells a slightly different story, and some may even lie. We are like the detective, assembling all the information to come up with the truth. If all of the data

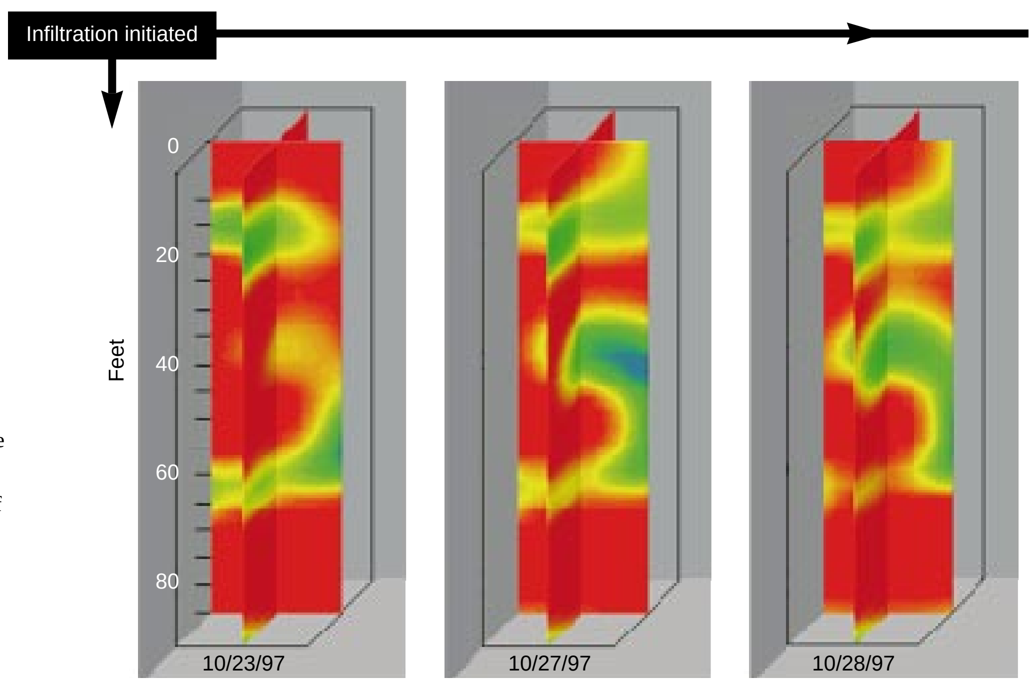


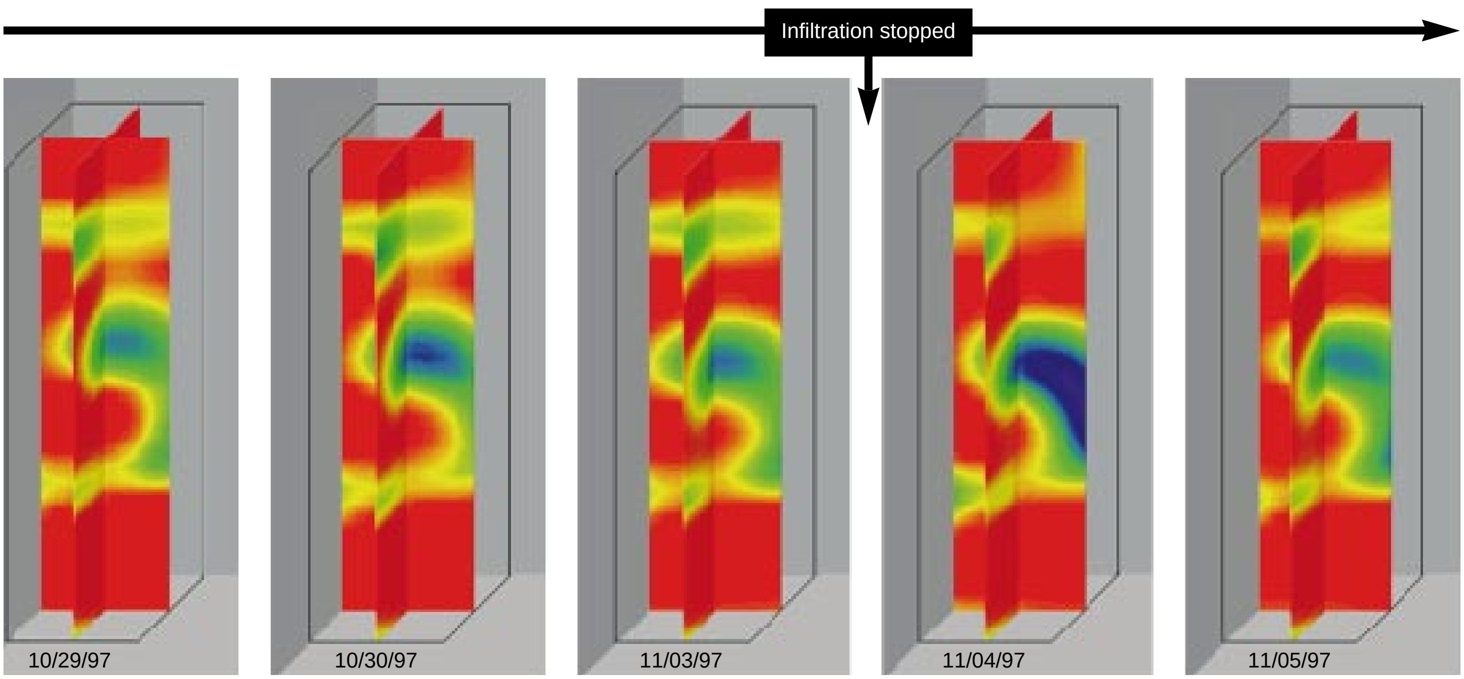
Figure 3. Several days following the start of the infiltration experiment, resistivity changes are apparent at the 40-foot level in the vadose zone. Oscillations in colors also occur (red = no resistivity change, blue = most negative resistivity change, or greater saturation). These changes in saturation result from the periodic upward flow of air in the vadose zone along permeable channels in a manner similar to the periodic flow of air through a narrow-necked, water-filled bottle turned upside down.

about the vadose zone are combined properly, environmental managers will have a more accurate picture of the subsurface for site characterization and remediation monitoring."

Before the joint inversion algorithm can be completed, however, a good deal of basic science research must be done on unconsolidated sediments (particularly for sediments containing clays) at the low pressures found in the near surface. To fill the need for sediment data, Berge and her colleagues are conducting numerous laboratory experiments to study a range of unconsolidated sand–clay mixtures (Figure 5).

Fully saturated samples are used for conductivity measurements. Dry and fully saturated samples are used for velocity measurements because partial saturation introduces a significant degree of complexity to the problem. Various clays are investigated as well as various mixing techniques because the microgeometry of the mix—the arrangement of sand grains, clay, and

Figure 4. From the location of a magnetic field transmitter in a borehole at Lost Hills, California, radial magnetic field receivers can be seen on the surface at 5, 10, 15, and 20 meters along a survey line.



Difference, percent

fluid-filled pores—affects both elastic and electrical properties.

All of this information is key to developing relationships between geophysical properties and the hydrogeologic parameters that are most useful for environmental applications. Laboratory measurements suggest that microstructure controls the geophysical properties. Thus, studies of the microstructure assumptions used in empirical or theoretical methods may determine which methods are most successful in relating geophysical properties to porosity and saturation.

The necessary algorithms for the joint inversion are under development. Berge and her colleagues are assessing geostatistical methods, empirical techniques commonly used in borehole geophysics interpretation, and rock physics theories that describe how elastic wave velocities and electrical conductivities depend on porosity and saturation in porous materials with different microgeometries. The team is finding that methods developed in the oil industry generally cannot be applied to environmental applications because oil industry methods are optimized for consolidated rock at depths of one or more kilometers. Environmental site characterization focuses on depths of a few meters to a few hundred meters of mostly unconsolidated sediments.

Berge is quick to admit that a commercially usable joint inversion code will not be complete in the three years allotted for this project. "At that point, our results will still be a basic research tool. It would take perhaps 10 years to put together a code that can be used commercially."

Figure 5. Pat Berge works with team member Eric Carlberg in studying conductivity and wave velocity in a range of unconsolidated sand–clay mixtures. Her team's research seeks to discover relationships between geophysical properties and hydrogeology in the vadose zone. This basic science research is preparatory to developing a new joint inversion algorithm that environmental managers will use to directly estimate porosity and saturation in the vadose zone as part of site characterization and remediation monitoring.

Emission-Free Treatment

The DOE today is responsible for the disposal of a variety of wastes left from weapons production, operation of nuclear power plants, and other sources. Some can only be stored, but some organic-based mixed and radioactive wastes can be treated thermally to reduce or destroy them. Martyn Adamson and his team at Livermore are studying the vaporization of wastes containing uranium, plutonium, and other actinide elements under the high-temperature conditions of thermal treatment.

Notes Adamson, "The DOE lists emission-free destruction of organic low-level and mixed low-level wastes as a primary science need. They need to be able to dispose of these materials, but at the same time, the public is concerned about fugitive radioactive emissions during thermal treatment." His team's work on what happens to radioactive materials under high temperatures will contribute to the design of safe and effective treatment systems.

A number of mixed-waste thermal treatment processes are being considered, including conventional incineration, plasma arc technologies, pyrolysis, thermal desorption, gasification, molten salt oxidation, and hydrothermal oxidation, as well as vitrification of plutonium residues and ceramification of surplus plutonium oxides. Some of these processes are being studied or developed at Livermore and some elsewhere. Key to the success of all of them is assurance that radioactive elements will not escape into the atmosphere in significant amounts.

The team's work is a combination of experimental studies and thermodynamic modeling. Using conditions comparable to those found in various treatment processes, the team is making transpiration measurements, conducting thermal gradient transport experiments, and determining key thermodynamic parameters for gaseous actinide species. Figure 6 shows the setup for one type of experiment involving pressure measurements for actinide oxides.

Livermore is performing work on plutonium and neptunium (and possibly americium, if time permits), while Professor D. R. Olander and a small team at the University of California at Berkeley are doing work on uranium.

In parallel with the experimental effort, a complete thermodynamic database for expected gaseous actinide species is being developed from literature data, proposed measurements, and data predictions using bond energy correlation and statistical thermodynamic estimation methods.

Out of this work will come an understanding of the thermodynamics of actinide vaporization and partitioning/ speciation behavior under conditions that exist during thermal treatment, which should help in predicting the behavior of radioactive and volatile metals during treatment.

A Quick Payoff?

These projects represent a blend of new measurement technologies and new processes, pieces of a large environmental management puzzle. Some of those pieces will likely be field tested in the not-too-distant future. Equipment and field operations for environmental cleanup are changing rapidly, as environmental managers learn more about how the vadose zone and the contaminants in it operate.

The cleanup of the Visalia pole yard is an example of rapid payoff from basic research. Two processes, dynamic underground stripping and hydrous pyrolysis oxidation, are being used to clean up the site. Dynamic underground stripping was born in the laboratories of Lawrence Livermore and the University of California at Berkeley in the early 1990s. Livermore scientists developed hydrous pyrolysis oxidation more recently. During the first six weeks of cleanup at Visalia in the summer of 1997, contaminants were removed from soil and groundwater at a rate of 46,000 pounds per week. The site's owner, Southern California Edison, had been using traditional pump-and-treat cleanup methods for 20 years, most recently removing about 10 pounds per week (earlier rates were higher). Thus, with the new cleanup techniques, 85 years of pump-and-treat at 1997 rates were accomplished in just six weeks. (See *S&TR*, May 1998, pp. 4–11.)

The Visalia cleanup is considered a big success by everyone involved. Not only have the processes proved to be

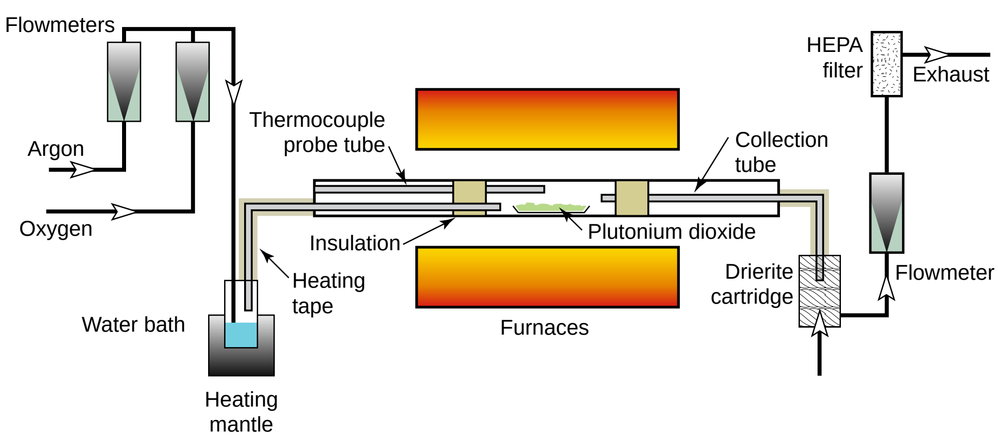


Figure 6. Schematic of the apparatus used for transpiration studies of plutonium dioxide vaporization in the presence of oxygen and steam.

remarkably effective, but the time between development and field use has been relatively short.

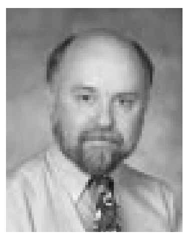
Right now, we can't know how or when these basic science projects will benefit environmental management, but it is fair to say that many of them will. Those with payoffs similar to the one at Visalia would make everyone at Livermore very happy indeed.

—*Katie Walter*

Key Words: accelerator mass spectrometry (AMS), electromagnetic induction tomography (EMIT), electrical resistance tomography (ERT), environmental geophysics, environmental management, joint inversion, mixed waste, modeling, moisture flux, Nevada Test Site, NUFT flow transport code, rock physics, rock properties, site characterization, thermal treatment, underground imaging, vadose zone.

For further information, contact Kenneth Jackson (925) 422-6053 (jackson8@llnl.gov) or Norman Burkhard (925) 422-6483 (burkhard1@llnl.gov). See also the Department of Energy's Environmental Management Science Project web site at **http://www.em.doe.gov/science/**.

About the Scientists



KENNETH JACKSON joined the Laboratory in 1983 after graduating with a double major in geology and chemistry from the University of New Mexico, Albuquerque, in 1976 and completing graduate work in geology at the University of California at Berkeley (M.A., 1979; Ph.D., 1983). Beginning in 1986, he has filled a series of leadership positions for environmental geochemistry projects. Today, he is leader of the Geosciences and Environmental Technologies Division in the Earth and Environmental Sciences Directorate. His responsibilities include three of the environmental management basic science projects reported on in this article: electromagnetic induction tomography adaptation, joint inversion algorithm development, and organic-based mixed and radioactive waste treatment. Jackson's areas of research interest are aqueous solution chemistry, geochemistry modeling, organic geochemistry, and environmental geochemistry.

NORMAN BURKHARD is leader of the Earth and Environmental Sciences Directorate's Geophysics and Global Security Division. Among other duties, he is responsible for directing Livermore's three projects investigating contaminant movement in the vadose zone. He joined the Laboratory in 1977 after receiving his Ph.D. in physics from the University of California at Los Angeles. He also holds an M.S. in physics from UCLA (1973) and a B.A. in physics from Pennsylvania State University. Burkhard has extensive experience in supporting the Defense and Nuclear Technologies Directorate's work at the Nevada Test Site to address underground containment issues for subcritical experiments.