

# Science & Technology

REVIEW

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Lawrence  
Livermore  
National  
Laboratory



**Faster Cleanup of  
Contaminated Soil  
and Groundwater**



# They All Like It Hot:

## Faster Cleanup of Contaminated Soil and Groundwater

**C**LEAN up a greasy kitchen spill with cold water and the going is slow. Use hot water instead and progress improves markedly. So it makes sense that cleanup of greasy underground contaminants such as gasoline might go faster if hot water or steam were somehow added to the process.

The Environmental Protection Agency named hundreds of sites to the Superfund list—sites that have been contaminated with petroleum products or petroleum products or solvents. Elsewhere across the country, thousands of properties not identified on federal cleanup lists are contaminated as well. Given that under current regulations, underground accumulations of solvent and hydrocarbon contaminants (the most serious cause of groundwater pollution) must be cleaned up, finding a rapid and effective method of removing them is imperative.

In the early 1990s, in collaboration with the School of Engineering at the University of California at Berkeley, Lawrence Livermore developed dynamic underground stripping. (For an explanation of this method, see *Energy & Technology Review*, July 1992, pp. 1–7). This method for treating underground contaminants with heat is much faster and more effective than

*The original estimate to clean the Visalia Superfund site was more than 100 years. Using technologies developed at Lawrence Livermore, cleanup is happening in one to two years and at a much lower cost than with pump-and-treat methods.*

traditional treatment methods. More recently, Livermore scientists developed hydrous pyrolysis/oxidation, a process that converts contaminants in the ground to such benign products as carbon dioxide, chloride ions, and water. By introducing both heat and oxygen, this process has effectively destroyed all petroleum and solvent contaminants subjected to laboratory tests.

During the summer of 1997, both processes were used for cleanup of a four-acre site in Visalia, California, owned by Southern California Edison (Figure 1). The utility company had used the site for 80 years to treat utility poles by dipping them into creosote, a pentachlorophenol compound, or both. By the 1970s, these highly toxic substances had seeped into the subsurface to depths of approximately 100 feet (30 meters). The Visalia pole yard bore the distinction of being named one of the original Superfund sites.

Southern California Edison and SteamTech Environmental Services of Bakersfield, California (the first commercial site licensee of the dynamic underground stripping technology), are cleaning up the Visalia site, with Livermore staff periodically on hand as operational consultants.

During the first six weeks of operation, between June and August 1997, the team removed or destroyed in place approximately 300,000 pounds (135 metric tons) of contaminant, a rate of about 46,000 pounds (22 metric tons) per week (Figures 2 and 3). For nearly 20 years, Southern California Edison had been removing contaminant from the subsurface using the standard cleanup method, known as pump-and-treat, most recently at a rate of just 10 pounds (0.03 metric ton) per week. In fact, the amount of hydrocarbons removed or destroyed in place in those six weeks was equivalent to 600 years of pump-and-treat, about 5,000 times the previous removal rate. Needless to say, the Visalia cleanup using dynamic underground stripping plus hydrous pyrolysis/oxidation is considered a wild success by everyone involved.

Geophysicist Robin Newmark and geochemist Roger Aines are Lawrence Livermore project leaders for the work at Visalia. Says Aines, "No one really knew what was underground at Visalia. Through the winter of 1998, Southern California Edison and SteamTech have removed over 540,000 pounds (245 metric tons), and the job still isn't finished. However, contaminant concentrations in recovered

groundwater continue to drop, so we know the end is in sight."

### **Finding a Better Way**

For years, scientists in Livermore's Earth and Environmental Sciences Directorate have been researching better methods to clean up soil and groundwater contamination, in part because both the Livermore site and Livermore's Site 300 are also Superfund sites as a result of U.S. Navy, Atomic Energy Commission, and DOE operations. Most contaminants at the Livermore sites are either petroleum distillates (e.g., gasoline, diesel fuel) or chlorinated hydrocarbons used as solvents. Existing methods to remove these compounds from soil and groundwater have halted their migration off the site, but cleanup will still take a decade or more to complete.

For about 20 years, the traditional method of cleaning up contaminated groundwater has been the pump-and-treat method. Water is pumped from the water table to the ground surface, treated to remove or destroy contaminants, and returned underground. Huge amounts of water must be flushed through the contaminated area for years or even decades to clean it, and even then the contamination may not be completely removed.

Says Newmark, “Some of the solvents and other contaminants have very low solubility. So very small amounts can pollute millions of gallons

of water because contaminants leach out very slowly. When you try to clean them up with pump-and-treat, it’s like trying to rinse a soapy sponge. You have to run

vast amounts of water through the sponge before all the soap is finally out.”

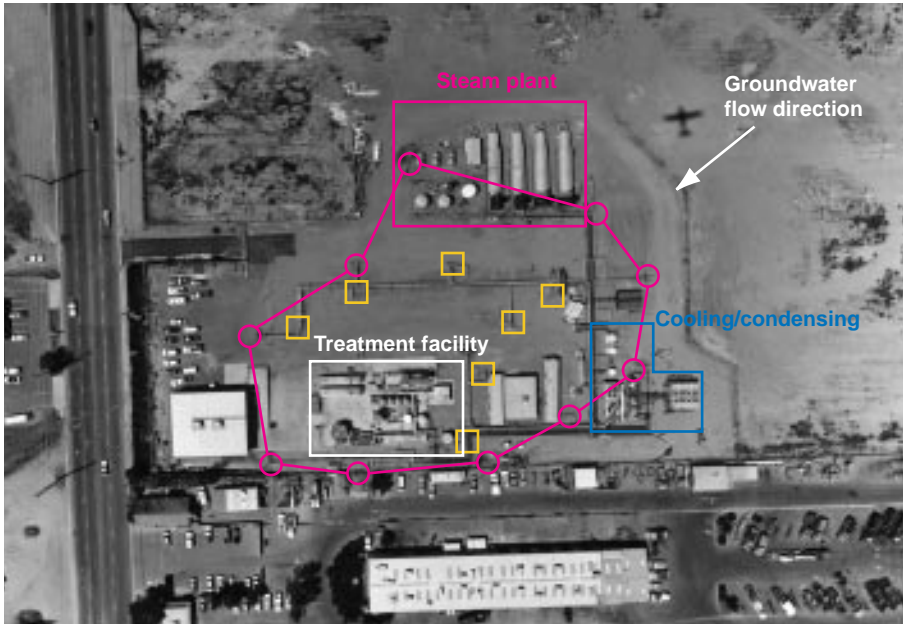
Pump-and-treat systems are relatively inexpensive to operate, but they represent a long-term cost. They offer compliance in a regulatory sense, but the results are not very satisfying because the site is unlikely to be completely cleaned up.

### Boiling Off Contaminants

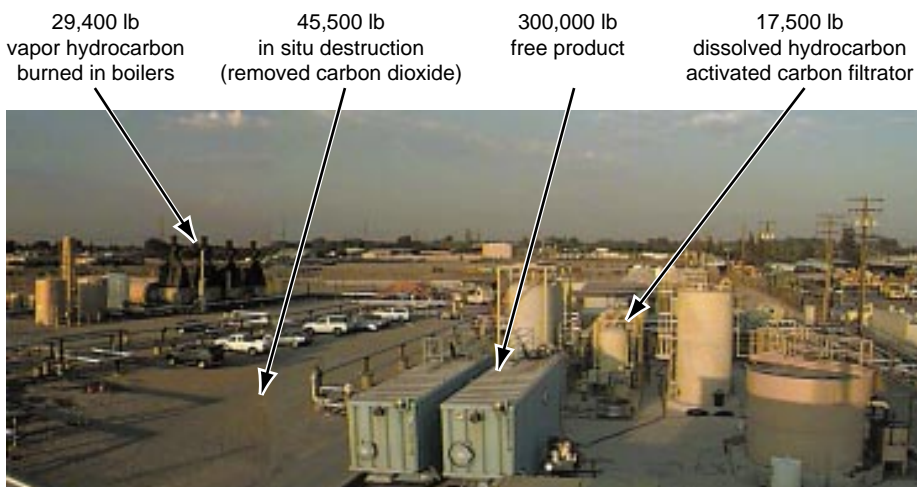
The dynamic underground stripping technology developed by Livermore and the University of California was first demonstrated in the cleanup of an underground gasoline spill at the Livermore site in 1993 (see *Energy & Technology Review*, May 1994, pp. 11–21). Dynamic underground stripping was so successful in this cleanup that contaminants were removed 50 times faster than with the pump-and-treat process. The cleanup, estimated to take 30 to 60 years with pump-and-treat, was completed in about one year. In 1996, the Environmental Protection Agency and other regulators declared that no further remedial action is required.

In this method, the area to be cleaned up is ringed with wells for injecting steam at temperatures above 100°C. Extraction wells in the central area are used to vacuum out vaporized contaminants. To ensure that thick layers of less permeable soils are heated sufficiently, electrode assemblies are sunk into the ground and the ground is heated, which forces trapped liquids to vaporize and move to the steam zone for removal by vacuum extraction. These combined processes achieve a hot, dry, contaminant-free zone of earth surrounded by cool, damp, untreated areas. Steam injection and heating cycles are repeated as long as underground imaging shows that cool (and therefore untreated) regions remain.

Although the initial capital outlay for dynamic underground stripping is higher



**Figure 1.** An aerial view of the Visalia site. Injection wells are shown in magenta, and extraction wells are shown in yellow.



**Figure 2.** During the first six weeks of operation in 1997, about 300,000 pounds (135 metric tons) of contaminated product was either brought to the surface or destroyed *in situ* at Visalia. Southern California Edison will treat the liquid “free product” on site and may use it as a lubricant in its operations.

than for pump-and-treat systems, the process saves money in the long run because it is completed much more quickly. Most of the equipment, such as boilers for generating steam, can be rented. Up-front costs include installing the heating wells, renting the equipment, and operating the system intensively for a short period of time. There are no long-term operation and maintenance costs.

That 1993 field trial of dynamic underground stripping cost about \$110 per cubic yard (\$140 per cubic meter), although Livermore scientists think that they could repeat the project for about \$65 per cubic yard (\$85 per cubic meter). Because contamination at the gasoline spill at the Livermore site migrated downward 40 meters, digging up the contaminated soil and disposing of it would have cost almost \$300 per cubic yard (\$400 per cubic meter). Soil removal and disposal costs are more typically in the range of \$100 to \$200 per yard (\$130 to \$260 per cubic meter); pump-and-treat method costs are as high as or higher than soil removal costs.

### Unexpected Help

The Livermore team discovered an unexpected benefit of dynamic underground stripping: it encourages bioremediation. Heating the soil at the gasoline spill site to temperatures above 100°C was expected to sterilize it, with the microorganisms that use petroleum products as food expected to return slowly as the soil cooled. But soil samples taken soon after completion of the cleanup revealed large numbers of microbes that thrive in high temperatures (known as thermophiles), apparently because predators and competition had been eliminated.

Bioremediation is an important final step in soil and groundwater cleanups because the microorganisms destroy

residual contaminants missed during the initial cleanup process.

### Oxygen Is Key to Approach

With dynamic underground stripping, the contaminants are vaporized and vacuumed out of the ground, leaving them still to be destroyed elsewhere. In fact, about half the cost of a typical cleanup is in treating the recovered groundwater and hauling away and disposing of the contaminated material that is brought to the surface.

“Livermore’s hydrous pyrolysis/oxidation technology takes the cleanup process one step further,” explains Aines, “by eliminating the treatment, handling, and disposal requirements and destroying the contamination in the ground.” The Visalia pole yard cleanup is the only application of this method to date, but indications are that large-scale cleanups with hydrous pyrolysis/oxidation could cost less than as little as \$25 per cubic yard (\$33 per cubic meter), an enormous savings over current methods. Best of all, the end product of a hydrous pyrolysis/oxidation cleanup with bioremediation as a final step is expected to be a truly clean site.

The hydrous pyrolysis/oxidation process builds on the team’s experience with heating large amounts of soil that was gained during earlier work with dynamic underground stripping. To provide the oxygen, steam and air are injected in parallel pipes, building a heated, oxygenated zone in the subsurface. When injection is halted, the steam condenses and contaminated groundwater returns to the heated zone. The groundwater then mixes with the condensed steam and oxygen, which destroys dissolved contaminants. This process avoids many of the mixing problems encountered in other *in situ* oxidation schemes. In such processes, an oxidizing reagent is typically injected into the subsurface, resulting in the displacement of the contaminant. Without a return process such as steam condensation, the contaminant and oxidant never mix or mix poorly at best.

During the heating process in hydrous pyrolysis/oxidation, the dense, nonaqueous-phase liquids and dissolved contaminants are destroyed in place without surface treatment, thereby improving the rate and efficiency of remediation by rendering the hazardous materials benign by a completely *in situ*

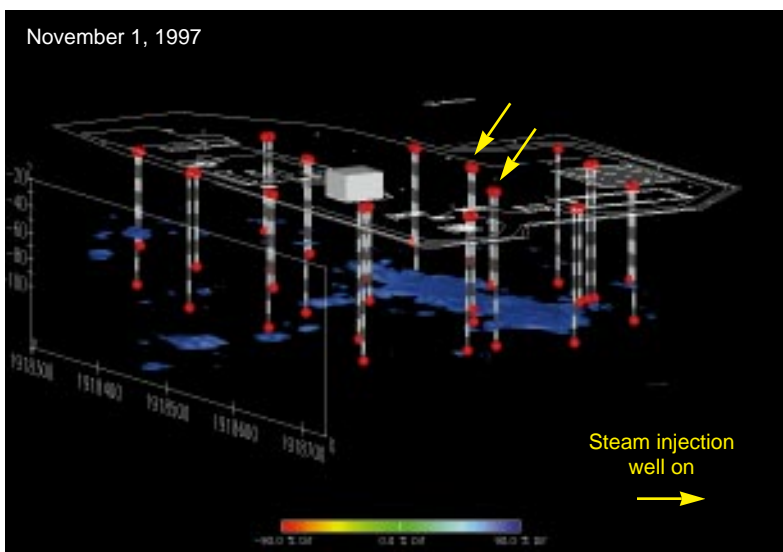


**Figure 3.** Contaminant floating on water in the dissolved-air-flotation tank (at lower right of Figure 2). Dissolved air forms bubbles that capture and lift free-product contaminant to the surface of the separator.

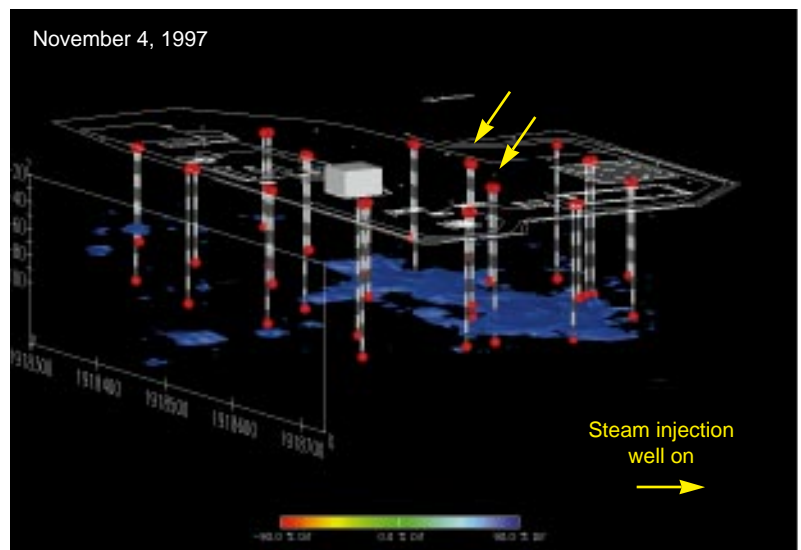
process. Hydrous pyrolysis/oxidation also takes advantage of the large increase in mobility that occurs when the subsurface is heated and makes contaminants more available for destruction. Many remediation processes are limited by the access of the reactants to the contaminant, making the lack of mobility the bane of remediation efforts in low-permeability materials such as clays.

Most early Livermore experiments on the hydrous pyrolysis/oxidation process, funded by DOE, were with trichloroethylene (TCE), a solvent that was widely used in degreasing and other industrial processes. TCE is the most common groundwater contaminant in the DOE complex as well as most industrial areas. Unlike gasoline, TCE and similar solvents are heavier than water, which means that they can sink below the water table, making cleanup extremely difficult if not impossible with conventional methods.

“The oxidation process occurs naturally, but without heat it is very slow,” explains Kevin Knauss, the Livermore geochemist who leads the effort in the laboratory, “so we needed to know how hot the soil had to be.” The team learned that with TCE, just a few degrees can make an enormous difference in how quickly the breakdown occurs. At 90°C, it takes a few weeks; at 100°C, it takes a few days; and at 120°C, it occurs in just a few hours. Laboratory results indicated that the contaminants at Visalia would react at similar rates.



**Figure 4.** Three-dimensional images from electrical resistance tomography data show how resistivity increases when steam injection is under way. After a short shutdown for hardware modifications, steam injection began on October 31, 1997. Even when a well is not in active use for steam injection, it is kept open with a very small amount of steam; hence, the small “puddles” near inactive injection wells. (Images are courtesy of SteamTech, Bakersfield, California.)



Experiments with dissolved oxygen showed that the oxygen in air is sufficient to degrade the contaminants. Because oxygen is corrosive, pumping pure oxygen into the ground could very quickly damage the piping system, but the less concentrated oxygen from the air is less corrosive and easy to introduce.

The demonstration of hydrous pyrolysis/oxidation at Visalia confirmed the effectiveness of this technology for dense, heavier-than-water groundwater pollutants such as creosote and pentachlorophenol. The method has also been tested successfully in the laboratory on contaminants resistant to cleanup in the past—for example, carbon tetrachloride, a chemical used as a refrigerant and a dry-cleaning solvent, and polychlorinated biphenyls (PCBs), a chemical used in electrical transformers and capacitors.

Project co-leader Aines notes, “This new technology could also be used to mop up methyl tert butyl ether (MTBE), a gasoline additive that has begun showing up in California groundwater.”

The method can also be used to clean up groundwater and soils to almost any depth.

### Controlling the Process

Several geophysical techniques were used at Visalia to monitor the underground movement of steam and the progress of heating. One technique is electrical resistance tomography, a technology developed at Livermore, applied during the 1993 gasoline cleanup, and now available commercially. Electrical resistance tomography is an imaging method like a CAT scan that provides near-real-time images of the underground processes between pairs of monitoring wells (Figure 4). Soil electrical

properties vary with temperature, soil type, and fluid saturation. For example, higher electrical resistivity is found in more permeable sand and gravel soils. Conversely, less permeable clay soils show lower resistivity (higher conductivity). Baseline measurements with electrical resistance tomography are used to characterize a site and to predict steam pathways.

During treatment at Visalia, daily resistivity measurements supplied a picture of the progress of the steam front and the heated zones. Monitoring the progress of the heating fronts ensured that all soil was treated. Temperature measurements made in monitoring wells revealed details of the complex heating phenomena in the individual soil layers.

To evaluate the progress of the chemical destruction of contaminants *in situ*, the team also developed field methods for sampling and analyzing hot water for contaminants, oxygen, intermediate products, and products of reaction. Because hydrous pyrolysis/oxidation is an “aqueous-phase” reaction, capturing and

evaluating the fluid in that phase is essential. At elevated temperatures, many of the key constituents are sufficiently volatile that traditional sampling techniques are not suitable. The Livermore team developed high-temperature systems that can deliver a pressurized, isolated fluid stream to the surface, where in-line analysis can be performed.

Building on Livermore’s experience in using noble-gas tracers to track water movement (see *S&TR*, November 1997, pp. 12–17), Bryant Hudson designed tracer experiments to help verify hydrous pyrolysis/oxidation in the field. Noble-gas tracers—including helium, neon, krypton, and xenon—were added to injected water and steam to track the movement of the steam (and subsequent condensation to liquid water) and the movement of other gases initially present in the steam (Figure 5). Naturally occurring dissolved gases (nitrogen and argon) provided measurements of atmospheric and native groundwater interaction. Once a “packet” of water had been tagged with gas tracers, it could later be identified



**Figure 5.** Livermore physicist Bryant Hudson (right), who has developed several methods for monitoring groundwater with noble-gas tracers, adjusts the gas flow with mechanical technician Allen Elsholz. Tanks of noble gases are nearby, and boilers are in the background.

by the types and amounts of tracers in it. The tracers thus assisted with many tasks, including:

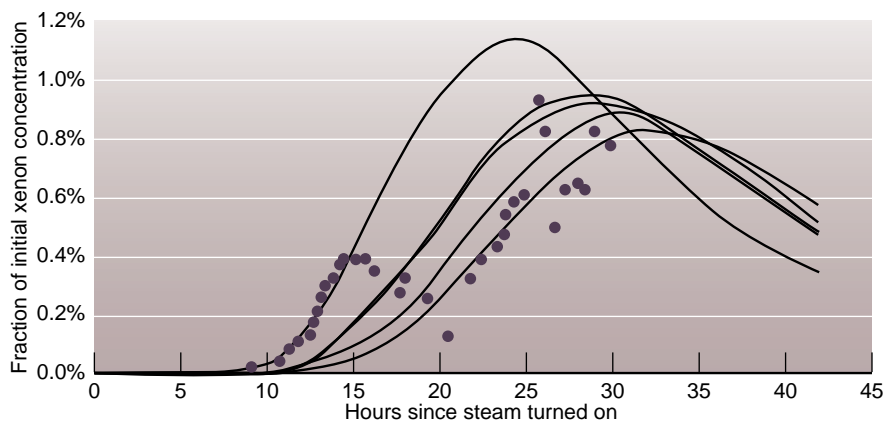
- Following the injected steam–water–oxygen pattern from each injection well.
- Determining how much mixing occurred.
- Determining oxygen consumption, carbon dioxide production, and transport.

- Correlating the intermediate hydrous pyrolysis/oxidation destruction products with temperature and oxygen.
- Identifying the overall isotopic content of the extracted carbon with regard to carbon-14 ( $^{14}\text{C}$ ) and carbon-13 ( $^{13}\text{C}$ ).

Using soil-gas and water samples, evidence of the progress of hydrous

pyrolysis/oxidation (Figure 6) came from a number of sources, including the disappearance of dissolved oxygen (consumed through the hydrous pyrolysis/oxidation reactions), the appearance of oxidized intermediate products, and the production of carbon dioxide (the final product of this process). Important information on the isotopic content of the carbon in the carbon dioxide was obtained from Livermore's Center for Accelerator Mass Spectrometry. The ratios of  $^{14}\text{C}/^{12}\text{C}$  and of  $^{13}\text{C}/^{12}\text{C}$  in carbon dioxide from the subsurface were more similar to those of the petroleum-based contaminants than to those of groundwater in the area, indicating that the contamination was being destroyed and converted to carbon dioxide.

**Figure 6.** Gene Kumamoto and Robin Newmark take measurements in Livermore's mini-laboratory, which houses a mass spectrometer, gas chromatograph, and other equipment.



**Figure 7.** Modeled results using the NUFT code indicate when xenon gas would appear at monitoring wells after having been injected into the subsurface.

### Modeling to Predict/Evaluate

The team used NUFT, a widely used three-dimensional groundwater modeling code developed several years ago at Livermore, to model such important process parameters as mixing of steam, air, and groundwater. In general, simulations with models such as NUFT provide a diagnostic means for anticipating the results of a decontamination scheme in complicated soil environments and, later, for evaluating field results.

In the case of a cleanup such as the one at Visalia, where much of the decontamination occurs *in situ* and is therefore not directly observable, the noble-gas tracers provide data critical for validating initial modeling results.

"Modeling proved invaluable at Visalia and remarkably accurate as well, compared with results from monitoring wells," explains Newmark. "Livermore models predicted steam and tracer movement to within an hour or two in most instances." (See Figure 7.)



Modeling also effectively predicted the time of thermal breakthrough, which occurs when sufficient heat has built up in the subsurface for vaporization of contaminants to begin, and steam collapse, which is the opposite phenomenon.

The team found that the ratio of tracer gas to natural air mixed into water was much greater than predicted by the model's initial assumption of no mixing of the atmosphere and steam zone. These data demonstrate that mixing is important and the process is more efficient than envisioned.

### From Liability to Asset

In short order, just months after laboratory experiments were completed, the new hydrous pyrolysis/oxidation method succeeded at the Visalia site. The project team had brought together Livermore's expertise in underground imaging, noble-gas-tracer monitoring, supercomputer modeling, and accelerator mass spectrometry to create and verify the field results of a technology to transform the groundwater and soil cleanup process. Far faster than other techniques, the technology provides a relatively inexpensive way to clean up difficult contaminants that plague dozens of sites across the country. For their efforts, the team was recognized with the Laboratory Director's Performance Award in December 1997.

The project team was mindful of the need to make the techniques simple for others to operate and maintain. Integrated Water Technologies of Santa Barbara, California, recently became the first nationwide licensee of Livermore's new cleanup technologies. The company plans to begin using the methods to clean up several Superfund sites this year.

Work at Visalia is not yet complete. The best estimates today are that cleanup will be completed in a year, with another four years of monitoring the site. Southern California Edison had expected to meet Environmental Protection Agency requirements in about 120 years with traditional pump-and-treat technology combined with enhanced bioremediation. Instead, a piece of real estate that had been a major liability will soon become a valuable asset.

**Key Words:** dynamic underground stripping, electrical resistance tomography, groundwater contamination, hydrous pyrolysis/oxidation, modeling, noble-gas tracers, NUFT code, remediation, soil contamination.

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### About the Scientists



ROBIN L. NEWMARK, leader of the Applied Geology and Geophysics Group in the Earth and Environmental Sciences Directorate, has been at Livermore since 1985. Her early work focused primarily on borehole geophysics applications. Since 1990, she has been involved in the development of thermal remediation methods and subsurface detection and imaging techniques essential for monitoring and process control of *in situ* environmental remediation. She earned a B.S. in earth and planetary sciences from Massachusetts Institute of Technology in 1978, an M.S. marine geophysics from the University of California, Santa Cruz in 1980, and a Ph.D. in marine geophysics from Columbia University in 1985. Author of many papers, reports, and patents, Newmark is associate editor of *Geophysics*, the journal of the Society of Exploration Geophysicists.



ROGER D. AINES came to the Laboratory in 1984 and is currently leader of the Geochemistry Group in the Earth and Environmental Sciences Directorate. Since 1990, he has been working on the development of thermal remediation methods. Earlier, he gained experience centered on geochemical research and modeling for the Yucca Mountain nuclear waste repository project. Roger received a B.A. in chemistry from Carleton College in 1978 and a Ph.D. in geochemistry in 1984 from California Institute of Technology. He is an author of many papers, patents, and reports related to disposal of nuclear waste and thermal remediation of contaminated groundwater.



## Changing the Gameplan

**T**HE Department of Energy's cleanup problems are often represented as intractable. Their budget, now the largest single component in DOE's budget, is seen as inadequate, unlikely to decrease, and detrimental to other DOE functions. Although unique problems with poorly contained and characterized radioactive wastes dominate DOE's problems, the issue of spills and plumes of conventional materials such as solvents, fuels, and mixtures of organics and radioactive materials is significant, too. Estimates have shown that DOE has a \$10-billion legacy to clean up. The total cost of cleaning Department of Defense and industrial sites across the country is larger still. When Director Tarter established the Earth and Environmental Sciences Directorate in 1994, he challenged us to change the game in environmental cleanup. The story of the Visalia pole yard in this issue of *S&TR* demonstrates the first success in response to that challenge.

Plumes of contaminants in groundwater pose several problems: hazards to public safety and health when the water is used, cleanup cost burdens to property owners, and, because of the associated liabilities, transfer of property ownership. While transferring property is not a burden to most DOE sites (which are likely to remain in government possession indefinitely), it is an obstacle to DOD site closure and reuse of valuable lands (like California's Mare Island or Alameda Naval Air Station). Remediation steps to date commonly rely on pump-and-treat. That method works well for near-term regulatory compliance (the site owner is doing something in good faith) to control the spread of plumes, but it rarely removes all the contaminants. Toxic compounds in spills have had decades to sink and bind to fine silts and clays. They are unlikely to be removed by simply slowly flushing water through them.

By applying steam to the subsurface environment, difficult materials such as heavy oils are mobilized and can be extracted at greatly accelerated rates. By adding oxygen (through air injection), contaminant materials are further destroyed by direct oxidation. (Remember the elementary chemistry lesson that shows how water at 100°C is a very reactive substance.) As an added benefit, heating the subsurface promotes the growth of thermophilic bacteria that move into a region and actively bioremediate remaining traces of contaminants.

The technical success of Visalia resulted from finding a corporate sponsor, Southern California Edison, that was willing to invest the funds up front for a significant deployment of a new technology at the scale (\$20 million) required for a substantive engineering and economic test. DOE sites tend to be constricted by budgets annually competing for money to complete the tasks, producing a context in which "experiments of scale" are perceived as activities that divert funds from ongoing remediation or delay tasks required under Records of Decision. A corporation understands the value of accelerating cleanup and moving the liability off its books, which DOD now finds attractive as well.

Lawrence Livermore's role in this project was to develop and demonstrate relevant cleanup and diagnostic techniques on its own site and then transfer the technologies to a corporate partner who owns a Superfund site and a subcontractor with steam-injection experience. We functioned as a supporting science and technology team, bringing our experience in supercomputer modeling of subsurface flow and reactive transport, isotopic tracer and electrical tomographic diagnostics, and isotopic analyses to validate results. These tools are not available in the commercial sector, and the processes are not readily done by the academic community, proving that there is a role for a national laboratory in solving this problem. Some of these tools, now in the hands of the industrial participants, are available for use at other sites.

We now are exploring with DOE and other agencies the next possible sites for testing these techniques. At each site, we will encounter a new combination of subsurface variables and a new cocktail of contaminants. The remediation process will have to be validated anew on each site—we have no silver bullets for subsurface contamination.

As we work at these sites, more technology, understanding, and tricks of the trade will move into industrial hands. The rewards for us will be helping to remove pressing health hazards cost effectively throughout the nation and gaining future support to move on to the next set of "intractable" problems.

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■ Jay C. Davis, Associate Director for Earth and Environmental Sciences

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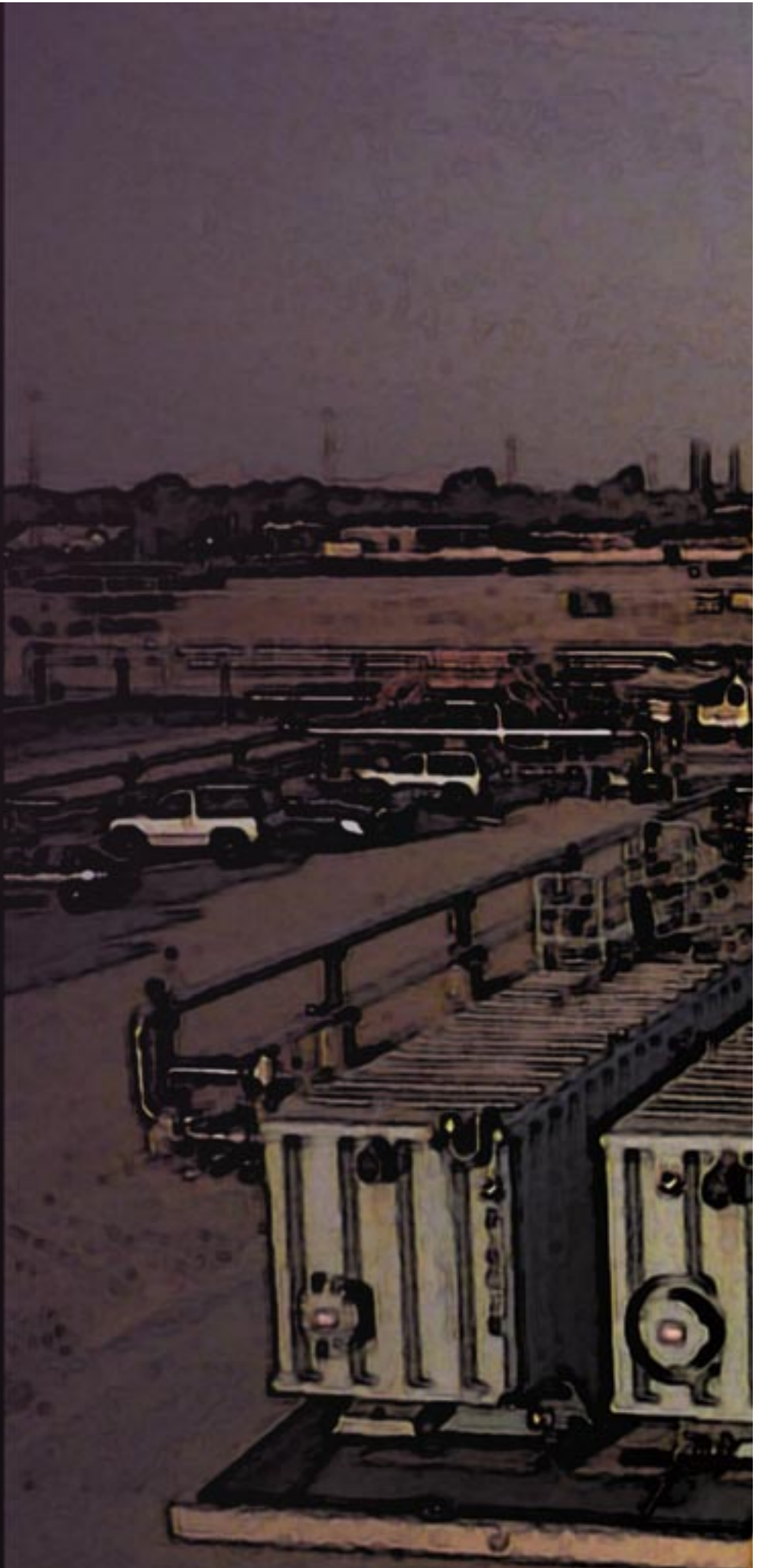
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