EXAMPLES OF DEPARTMENT OF ENERGY SUCCESSES FOR REMEDIATION OF CONTAMINATED GROUNDWATER: PERMEABLE REACTIVE BARRIER AND DYNAMIC UNDERGROUND STRIPPING ASTD PROJECTS

Caroline Purdy, Kurt Gerdes
U.S. Department of Energy
Washington, DC

Jihad Aljayoushi
U.S. Department of Energy
Idaho Falls, ID

Dawn Kaback, Thomas Ivory
Concurrent Technologies Corporation
Denver, CO

ABSTRACT

Since 1998, the Department of Energy's (DOE) Office of Environmental Management has funded the Accelerated Site Technology Deployment (ASTD) Program to expedite deployment of alternative technologies that can save time and money for the environmental cleanup at DOE sites across the nation. The ASTD program has accelerated more than one hundred deployments of new technologies under 76 projects that focus on a broad spectrum of EM problems.

More than 25 environmental restoration projects have been initiated to solve the following types of problems:

- characterization of the subsurface using chemical, radiological, geophysical, and statistical methods;
- treatment of groundwater contaminated with DNAPLs, metals, or radionuclides; and
- other projects such as landfill covers, purge water management systems, and treatment of explosives-contaminated soils.

One of the major goals of the ASTD Program is to deploy a new technology or process at multiple DOE sites. ASTD projects are encouraged to identify subsequent deployments at other sites. Some of the projects that have successfully deployed technologies at multiple sites focusing on cleanup of contaminated groundwater include:

- Permeable Reactive Barriers (Monticello, Rocky Flats, and Kansas City), treating uranium and organics in groundwater.
- Dynamic Underground Stripping (Portsmouth, and Savannah River), thermally treating DNAPL source zones;

Each year more and more new technologies and approaches are being used at DOE sites due to the ASTD program. DOE sites are sharing their successes and communicating lessons learned so that the new technologies can replace the baseline or standard approaches at DOE sites, thus expediting cleanup and saving money.

INTRODUCTION

Since 1989, Department of Energy's (DOE's) Office of Environmental Management (EM) has been responsible for environmental restoration and waste management throughout the nuclear weapons complex. Many DOE, commercial, and industrial sites associated with weapons production have groundwater and soils contaminated to such a degree that the concentrations of organic and inorganic constituents must be reduced to acceptable levels. U.S. DOE sites alone have more than 1.7 trillion gallons of groundwater that require some degree of remediation. While many technologies are available to address different groundwater and soil contaminants, not all technologies are suitable to meet site-specific and contaminant-specific requirements.

The "Accelerating Cleanup: Paths to Closure" document, published in 1998, describes the EM program efforts to accelerate the clean up of DOE sites. As part of this goal, EM requested the Office of Science and Technology (OST) to investigate better methods and approaches to bring technical solutions to clean up problems. In many cases, new technologies could not only accomplish the cleanup more effectively with less cost and under schedule, but often there was no solution to a cleanup problem unless a new technology or process was developed. Even though the OST program had been developing and demonstrating new technologies for years, the introduction of these technologies into the cleanup projects was slow. Thus the Accelerated Site Technology Deployment (ASTD) Program, originally known as the Technology Deployment Initiative (TDI), was initiated in fiscal year (FY) 1998 to provide a means and incentives to promote multi-site deployment of new technologies and processes than can accelerate cleanup.

ASTD is a leveraged program that matches OST funding with EM site operations funding. This makes the ASTD projects customer driven (supported by DOE Site Managers for EM). It encourages the sites to replace the standard or baseline methods and approaches with innovative ones. The DOE Site Managers share the risk of trying a new technology with OST. Barriers to new technologies are broken down through information transfer and sharing. To further encourage the use of new methods, sites receiving funding to deploy a technology must get a commitment from another site with a similar problem to use the same technology. Multiple site deployments of DOE-supported technologies improve DOE's return on the development investment.

The ASTD Program has expedited more than one hundred deployments of new technologies under 76 projects that focus on a broad spectrum of EM problems. Some examples follow:

- characterization of the subsurface using geophysical and statistical methods;
- characterization of soils contaminated with radionuclides;
- sampling and monitoring of the vadose zone and groundwater contaminated with organics (dense, non-aqueous phase liquids [DNAPLs]) or radionuclides;

- treatment of groundwater contaminated with DNAPLs, metals, or radionuclides; and
- treatment of explosives-contaminated soils, purge water management systems, and landfill covers.

Approximately 40 deployments of 25 technologies have occurred under 25 projects over the last three years. Many more planned or potential deployments of these technologies are expected. At conferences or in publications, DOE sites are sharing their successes and communicating lessons learned so that the new technologies can replace the baseline throughout the DOE complex.

EXAMPLES OF SUCCESS

This paper describes two examples of EM technologies that have been successfully deployed at multiple DOE sites and thus demonstrate the accomplishment of one of the major goals of the ASTD Program. These technologies are:

- Permeable Reactive Barriers: at Kansas City, Monticello, Rocky Flats, and Lawrence Livermore, treating uranium and organics in groundwater; and
- Dynamic Underground Stripping: at Portsmouth and Savannah River, thermally treating DNAPL source zones.

The cleanup accomplishments already realized by these projects are depicted in Table I.

Table I. Examples ASTD Project Accomplishments.

Technology	**Cleanup Accomplishment**
Permeable Barriers	> 10 Million gallons water treated
DUS/HPO	> 70,000 pounds organic solvents removed

Permeable Reactive Barriers

Permeable Reactive Barriers (PRBs) are in situ, passive systems that treat groundwater contaminated with organics, redox-sensitive metals, and radionuclides. These barriers are engineered structures placed in the subsurface to capture and treat an advancing plume of contaminated groundwater. The natural hydraulic pressure gradient drives the plume through the reactive treatment zone, which contains zero-valent iron (or other materials) that react with the contaminants to produce innocuous or immobile products. Contaminant levels are reduced below the regulated maximum contaminant levels. This type of passive treatment requires no external energy sources, no daily operation and maintenance, eliminates secondary wastes, and reduces the long-term EM mortgage when compared to pump-and-treat.

PRB technology can be used to reduce contaminant concentrations in groundwater under a wide variety of site-specific and contaminant-specific conditions. PRBs most commonly are used to treat solvents and redox-sensitive metals. Currently PRBs are constructed in two basic configurations, the funnel and gate and the continuous (or trench) design. Both configurations require some degree of excavation and are limited to fairly shallow depths of 50 feet or less. The funnel-and-gate design uses impermeable walls (skirt pilings, slurry walls, etc.) to funnel or direct the contaminant plume to gates containing the reactive material. The continuous PRB design completely transects the plume flow path with reactive materials

PRB systems have been installed within DOE at the Kansas City Plant, Missouri, Monticello Uranium Mill Tailings Site, Utah, Rocky Flats Closure Site, Colorado, and Lawrence Livermore National Laboratory, California. An additional deployment is planned at the West Valley Demonstration Project in New York.

Kansas City Plant, Missouri

At the Kansas City Plant (KCP), a pump-and-treat system consisting of several interceptor wells and a 250 foot-long interceptor trench has been treating volatile organic compound(VOC)-containing groundwater plume since 1989. Contaminant concentrations were reported as high as 1,400 mg/L dichloroethylene (DCE) and 300 mg/L vinyl chloride (VC). The site geology consists of a four-foot thick, coarse-grained alluvial aquifer (the hydraulic conductivity is approximately 34 feet/day) underlying a low-permeability clay layer and overlying a shale unit. As an alternative to the active pump-and-treat system, DOE made a decision to deploy a permeable reactive barrier to passively treat the organic contaminants. In 1998, the site deployed a PRB that is 130 feet long, 6 feet wide and approximately 30 feet deep. The reactive media is zero-valent iron.

Monitoring data confirm treatment of contaminants of concern to below regulatory limits. However, groundwater excursions have occurred around the southern end of the barrier (estimated to be approximately five percent of the flow). Several studies have focused on developing a good understanding of this problem with an attempt to remedy it. Oak Ridge National Laboratory has evaluated the hydrogeology and Envirometal Technologies, Inc. has evaluated the hydrogeology and the wall design. They have concluded that installation of the barrier created a smear zone that has caused the groundwater to by-pass the wall in an attempt to seek the pathway of least resistance. The KCP will perform hydraulic fracturing and tracer tests during FY02 to further evaluate the by-pass and its cause. In June of 2001, the KCP installed a phytoremediation system (poplar and willow trees) near the south end of the barrier to treat the by-pass groundwater.

Monticello Mill Tailings Site, Utah

The Monticello Mill Tailings Site (MMTS) is a former uranium and vanadium-processing site that operated from the mid-1940s until 1960. The MMTS was placed on the National Priority List in 1989 and is currently being remediated under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). At the MMTS, groundwater contaminated with radionuclides and heavy metals flows through a shallow alluvial aquifer that is underlain by impermeable bedrock (Figure 1). The groundwater is funneled naturally through a narrow valley less than 500-feet wide. The major contaminants of concern at MMTS are arsenic, uranium, vanadium, selenium, lead-210, and manganese.

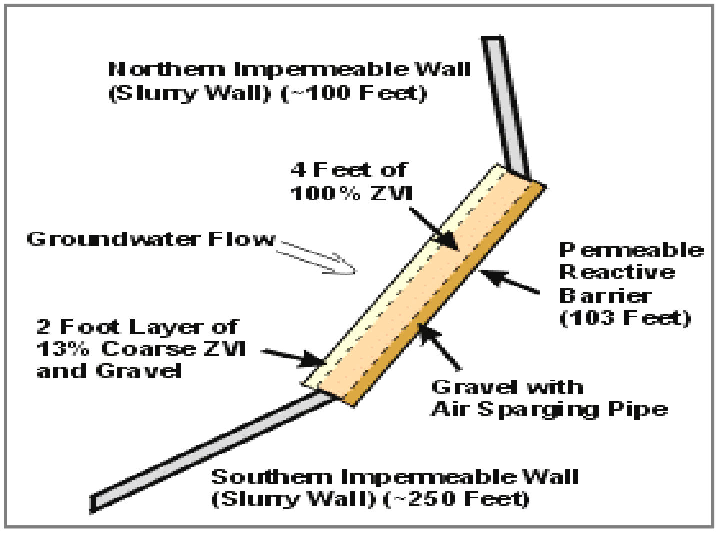

Fig. 1. Geologic Cross-Section of Monticello PRB.

In June 1999, construction of a funnel-and-gate PRB was completed at the MMTS (Figure 2). The permeable reactive gate was constructed by driving steel sheet piling down into the bedrock, forming a rectangular box about 103 feet long by 7.6 feet wide to a depth of 12 to 24 feel. The zero-valent iron reactive media was placed in a box and the sheet pilings perpendicular to groundwater flow were removed to allow groundwater to flow through the reactive portion of the wall. The impermeable walls were also installed by driving sheet piling to bedrock. On the downstream side of the treatment media, an air sparging system was installed to treat elevated levels of iron or manganese should they occur.

An extensive monitoring network was installed in the summer of 1999 to evaluate performance. The results from monthly and quarterly sampling show that concentrations of arsenic, selenium, uranium, and vanadium have been reduced to near non-detectable levels within the wall (Table 2) to meet remediation goals.

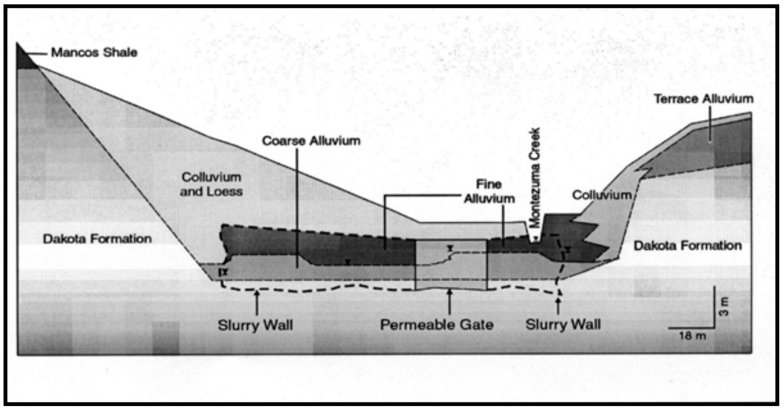

Fig. 2. Map View of PRB at Monticello.

Table II. Contaminant Concentrations and Remediation Goals.

ANALYTE	UPGRADIENT (µg/L)	EXITING (µg/L)	GOAL (µg/L)
Arsenic	10.3	<0.2	50
Selenium	18.2	0.1	10
Uranium	396	<0.24	44
Vanadium	395	1.2	260

Rocky Flats Closure Project, Colorado

In FY98, a PRB was successfully installed at the Mound Site at Rocky Flats to treat VOCs and radionuclides in a groundwater plume generated by buried leaking drums (Trench 1). Groundwater at Rocky Flats crops out to the surface in the incised valleys that cut through the site. A collection system was installed adjacent to the Mound Site at the edge of the valley before outcrop of the groundwater. The collection system was installed in a 270 foot-long trench lined on the downhill side with high-density polyethylene. At the bottom of the trench, the water enters a perforated pipe, which gravity feeds into two ten-foot diameter tanks containing iron filings. The reactive media remain flooded at all times. Monitoring has shown that concentrations of carbon tetrachloride, tetrachloroethylene (PCE), trichloroethylene (TCE), VC, uranium, and americium have been reduced to non-detectable levels in the effluent from the treatment tanks.

As a result of the success of this project, FY99 ASTD funding was awarded to install PRB's to treat two other groundwater plumes: at the Solar Pond and the East Trenches sites.

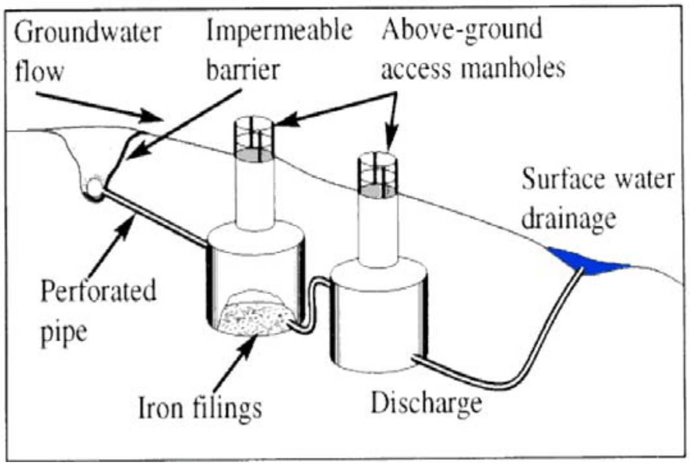

Fig. 3. Permeable Reactive Barrier System Design at Rocky Flats.

The East Trenches Plume at Rocky Flats was formed as a result of leaching of waste from disposal trenches containing sanitary sewage sludge, non-aqueous phase liquids (NAPLs), crushed drums, and miscellaneous waste. These trenches were remediated in FY96. Contaminants of concern in groundwater in the East Trenches Plume include TCE, PCE, carbon tetrachloride, chloroform, and DCE. The East Trenches Plume PRB works by collecting groundwater in a 1,200-foot long collection system lined on the downhill side with high-density polyethylene. At the bottom of the collection trench, the water enters a perforated pipe and is gravity-fed into two ten-foot diameter tanks containing iron fillings. Treated groundwater is then passively discharged into South Walnut Creek. Sampling results from FY00 show that contaminant concentrations in effluent from the treatment tanks are all below remediation goals, and many are non-detectable.

The Solar Ponds Plume at Rocky Flats contains low levels of nitrate and uranium, derived from storage and evaporation of radioactive and hazardous liquid wastes in the Solar Evaporation Ponds (drainage and sludge removal of the Evaporation Ponds was completed in 1995). An 1,100 foot-long collection system and passive treatment cell, which has two compartments, organic sawdust mixed with iron filings to remove nitrates and reactive iron as a final polishing step, was installed.

The design of the Solar Ponds system is different than the other two systems due to constraints related to an endangered species problem. In this case, the treatment cell is located immediately adjacent to the collection trench, which requires approximately 11 feet of groundwater in the trench to develop sufficient hydraulic head for the groundwater to flow into the treatment cell.

The treatment cell is performing as designed, however, fluctuating water levels in the collection trench may have caused some of the groundwater to by-pass the treatment system. However, water quality in North Walnut Creek continues to be well below applicable standards for nitrate and uranium.

Lawrence Livermore National Laboratory, California

Since July 2000, Lawrence Livermore National Laboratory (LLNL) has been using another variation of PRB, similar to that used at Rocky Flats. At the LLNL Site 300, the contaminated groundwater contains TCE, perchlorate, and nitrate. The LLNL Site 300 PRB system uses three artesian wells for collecting water that rises to the surface by internal hydrostatic pressure. These artesian extraction wells have flow rates of five to eight gallons per minute, and are located at an elevation approximately 300 feet high and at a point approximately 400 feet up-gradient from the treatment system. Groundwater flows passively from the artesian wells through a polyethylene collection system to four drums filled with zero-valent iron. In addition to the iron, the system includes two drums containing granular activated carbon, and aerators and sand beds for removing iron oxides. Accelerated bioremediation is used as a final treatment to remove nitrate, with acetate used as the carbon source for the microbial community.

DYNAMIC UNDERGROUND STRIPPING

Dynamic Underground Stripping (DUS) is a technology that uses injection and extraction enhanced with steam to accelerate the removal and oxidation of VOCs, both the dissolved phase and the DNAPLs. DUS injects steam into the contaminated zone. The steam volatilizes the contaminants into the vapor phase and solubilizes contaminants into the groundwater. Then, soil vapor extraction (SVE) removes contaminant vapors, while pumping removes contaminated groundwater. In addition, a portion of the contamination is destroyed in situ, in a process called hydrous pyrolysis oxidation (HPO). DUS/HPO offers significantly faster and more complete remediation of DNAPLs.

DUS/HPO is a two-phase process that relies on a combination of steam and oxygen injection, electrical heating (where required) in situ bioremediation, SVE, electrical resistance tomography (ERT), and conventional pump-and-treat technologies.

Steam and oxygen are injected below the water table to build a heated, oxygenated zone at the periphery of the contaminated area to drive contaminants to centrally-located extraction wells. If a site contains less permeable zones interlayed between permeable zones, electrical heating can be used within the less permeable sediments (e.g., clays) to vaporize the contaminants and drive them into the more permeable zones where they can be easily removed. DUS/HPO also encourages microbial degradation of contaminants by stimulating the growth of indigenous microbes than thrive in high temperatures. The stream fronts are tracked using ERT and temperature monitoring. The pump-and-treat component of DUS/HPO provides hydrologic control.

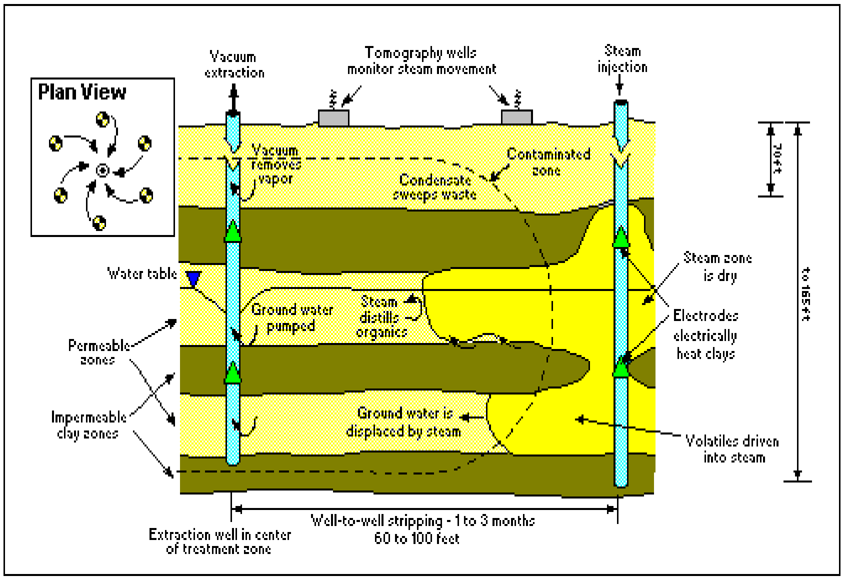

Fig. 4. DUS/HPO Process.

Continuous steam injection into permeable zones occurs over a period of weeks or months to vaporize VOCs, which are then removed through vacuum extraction. Effective removal of contaminants from the subsurface requires repeated creation of the steam zone by successive phases of steam injection and vacuum extraction. Above-ground treatment systems must be sized to handle anticipated peak extraction rates and the expected distribution of VOCs in the extracted vapor and liquid streams.

HPO is the chemical process of destroying NAPLs in place after DUS. This technology takes advantage of the rapid reactions and mass transfer rates that take place at steam temperature, making contaminants more available for destruction. When the stream injection is stopped, the steam condenses and the contaminated groundwater returns to the heated zone. The contaminants in the groundwater mix with the oxygen and the condensate, and, in the presence of heat, rapidly oxidize into carbon dioxide and chloride. During the initial phase of the process, removal of contaminants occurs through physical transport to extraction wells with subsequent treatment of effluent vapors, NAPLs, and water on site. Simultaneously, and afterwards, HPO converts contaminants in situ into carbon dioxide, chloride ions, and water.

Portsmouth Site, Piketon Ohio

DUS/HPO was deployed within the source area of the X-701 Plume at the DOE Portsmouth Site near Piketon, Ohio, from July 1998 through August 1999. The treatment area at Portsmouth was approximately 120 feet wide and 180 feet long. The contaminant of concern is TCE, and concentrations in the groundwater within the treatment zone were as high as 970 mg/L.

Treatment system design included:

- 19 vertical wells, screened across the Gallia Formation, the site aquifer, for steam injection (up to 16 wells were used for steam injection, with typically 8 to 12 wells used at a given time);
- generation of steam by heating pre-treated water in a diesel-fired steam generator;
- distribution of steam to the injection wells through an above-ground piping network;
- regulation of steam pressure at the well head to the desired injection pressure (typically between 12 and 16 psig);
- extraction of fluids using positive-displacement pneumatic pumps (typical rates of 1 to 4 gpm per well with a combined extraction rate of up to 15 gpm);
- extraction of vapors through wells screened in the Gallia aquifer and the overlying Minford silt by applying a vacuum of 5 psig (typically 100 to 500 scfm);
- cooling extracted fluids and condensing water and TCE vapors;
- treating the separated liquid phase by air stripping and discharging to the existing ground- water treatment facility; and
- treating the separated vapor phase by using activated charcoal and discharging to the atmosphere.

During treatment operations:

- Steam was injected outside the zone of DNAPL contamination driving the contaminants toward the center of the area where liquids and vapors were extracted.
- After the entire area reached steam temperature, steam was injected in a cyclic manner with continuous vapor and liquid extraction. Cycling was conducted to:
    - Expand the treatment volume to include the underlying Sunbury Shale and the overlying Minford silts, and
    - Reduce aqueous-phase concentrations and assist in desorption of contaminant from the soil.
- During final stages of steam injection, air was co-injected to supply oxygen to the ground water to stimulate HPO reactions.
- Progression of the heated zone was monitored daily using a network of 314 thermocouples and electrodes for three-dimensional ERT measurements.

Steam injection began in late January 1999 and continued at desired rates and pressures for approximately four months with less than 1% downtime.

- Approximately 7.5 million pounds of steam were injected.
- The average injection rate was 2100 lbs/hr with the highest rate of 5500 lbs/hr.
- Injection rates for individual wells ranged from 50 to 600 lbs/hr, averaging 200 lbs/hr.

Heating of the treatment volume was monitored daily. The hot-water/steam front appeared to remain within the lower Gallia, closely following the interface between the Gallia and the underlying Sunbury (bedrock). The majority of the site had been heated in just over two months, with the exception of the northeast and western portions of the treatment volume. Monitoring wells in these areas were converted to injection wells to better deliver steam to these areas.

Although difficult to estimate because only a portion of the source zone was treated, approximately 80% of the estimated TCE mass was removed from the treatment area, based on mass recovered and system losses:

- Approximately 30 lbs of TCE were recovered by the groundwater treatment facility.
- Approximately 38 lbs of TCE were recovered by the air-emissions treatment system.
- Approximately 760 lbs of TCE were recovered by the treatment system (based on carbon dioxide concentration increases measured in off-gas, where an estimated 1700 lbs of organic matter was destroyed).
- Sufficient TCE levels were detected in post-treatment soils samples such that HPO reactions could still be occurring, thus further reducing the overall remaining mass of TCE.

Savannah River Site, Aiken South Carolina

The DOE Savannah River Site (SRS) produced special nuclear materials for the DOE between 1952 and 1988. The manufacture of fuel and target assemblies for nuclear weapons occurred in the SRS M Area where large quantities of industrial cleaning solvents were used. Over a 20-year period, approximately 2 million pounds of spent solvents entered the soil and ground water via the unlined M Area Settling Basin, while another 1.5 million pounds were released via the A-014 outfall. Additional releases occurred at the 321-M Solvent Storage Tank and other areas. These solvents have migrated below the water table and comprise a groundwater plume of approximately 1500 acres.

A pump and treat system has been operated to treat the M Area groundwater plume since 1984. New technologies have been applied to treat portions of the source zone. DUS/HPO was deployed to treat the source zone associated with the M-Area Solvent Storage Tank in 2000. The initial steaming and startup testing occurred in May 2000 and full operational steaming and extraction occurred from September 2000 through March 2001. The DUS/HPO system consisted of nine injection and three extraction wells. Steam pressures of 40-60 psi were used in the vadose zone while pressures of 100 psi were used in the below the water table. More than 70,000 pounds of total VOCs were removed by the DUS/HPO system.

LLNL with the University of California at Berkeley originally developed the Dynamic Underground Stripping (DUS) process. After successful demonstrations at LLNL and the Visalia Superfund Site, the process was licensed to two California firms for commercial deployment, SteamTech Environmental Services, Inc. and Integrated Water Resources.

LESSONS LEARNED

Lessons learned related to site characterization, remediation design, system installation and operation, and vendor contracting have been obtained from each of the projects described in this paper. A few examples follow:

- The contaminated site must be fully characterized so that system installation and remedial design can be optimized.
  - Using the KCP example, the low permeability of the host formation and incomplete knowledge of site hydrogeology affected system installation and later performance. Technology to install the wall had to be modified because of problems. Remedial design resulted in a wall that was not extended sufficiently to capture the entire plume.
  - At the Portsmouth site, the remedial design did not initially include the underlying Sunbury Shale, which contained a large percentage of the contaminant mass. Because a robust understanding of subsurface permeabilities did not exist, the remedial design was not optimized. More thorough site characterization could have significant impact remedial design and performance.
- The SRS vendor contract was written to end when a target temperature was reached in the subsurface. However, this approach did not take into account the need for continuing vendor support after steam injection has been terminated but VOCs are still being recovered from the subsurface. A contract detailing two phases of operation that include first steaming to a target temperature and then continued recovery until production levels are reduced to a certain target level is now preferred.
- All of the example projects have valued the conduct of bench-scale testing before full deployment so that remedial design and installation can be optimized.