

# Hydrous Pyrolysis Oxidation/Dynamic Underground Stripping

Subsurface Contaminants Focus Area



Prepared for U.S. Department of Energy Office of Environmental Management Office of Science and Technology

February 2000



# Hydrous Pyrolysis Oxidation/Dynamic Underground Stripping

OST/TMS ID 1519/7

Subsurface Contaminants Focus Area

Demonstrated at Visalia Superfund Site Visalia, California



## Purpose of this document

Innovative Technology Summary Reports are designed to provide potential users with the information they need to quickly determine whether a technology would apply to a particular environmental management problem. They are also designed for readers who may recommend that a technology be considered by prospective users.

Each report describes a technology, system, or process that has been developed and tested with funding from DOE's Office of Science and Technology (OST). A report presents the full range of problems that a technology, system, or process will address and its advantages to the DOE cleanup in terms of system performance, cost, and cleanup effectiveness. Most reports include comparisons to baseline technologies as well as other competing technologies. Information about commercial availability and technology readiness for implementation is also included. Innovative Technology Summary Reports are intended to provide summary information. References for more detailed information are provided in an appendix.

Efforts have been made to provide key data describing the performance, cost, and regulatory acceptance of the technology. If this information was not available at the time of publication, the omission is noted.

All published Innovative Technology Summary Reports are available on the OST Web site at http://ost.em.doe.gov under "Publications."

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## SUMMARY

#### **Technology Summary**

#### Problem

At many DOE sites, the most prevalent contaminants in soils and ground water are the common solvents trichloroethylene (TCE) and perchlorethylene (PCE). These chlorinated organic solvents, when present as a separate phase, are categorized as Dense Non-Aqueous Phase Liquids (DNAPLs). Because DNAPLs have low solubility in water, they dissolve slowly over time into flowing ground water and have been very difficult and time-consuming to destroy or recover using traditional methods such as pump-and-treat.

#### How It Works

Dynamic Underground Stripping (DUS) is an innovative thermal remediation technology that accelerates removal of organic compounds, both dissolved phase and DNAPLs, from the subsurface. In DUS, steam is injected into the contaminated zone, and energy, in the form of heat, volatilizes contaminants into the vapor phase and solubilizes contaminants into the ground water. In addition, a portion of the contamination is destroyed in situ by a process called Hydrous Pyrolysis Oxidation (HPO). Because DUS and HPO occur together, this Innovative Technology Summary Report (ITSR) refers to the technology as HPO/DUS.



Figure 1. Schematic showing the principle of Dynamic Underground Stripping. The injection well to the right would be located outside the contaminated area. The extraction well is inside the source zone (modified from Newmark et al., 1994).



HPO/DUS relies on a combination of steam and oxygen injection, electrical heating (where required), in situ bioremediation, soil vapor extraction, electrical resistance tomography, 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.
- Electrical heating of the less permeable sediments (e. g., clays) vaporizes the contaminants and drives them into the more permeable steam zone.
- HPO/DUS also encourages bioremediation by stimulating the growth of microbes that thrive in high temperatures.
- Underground imaging by Electrical Resistance Tomography (ERT) and temperature monitoring track the steam fronts and heated areas.
- The pump-and-treat component of DUS/HPO provides hydrologic control.

This technology, by operating at high temperatures, takes advantage of the rapid reactions that take place at steam temperature, as well as in rapid mass transfer rates, which make contaminants more available for destruction. When the steam injection is stopped, the steam condenses and the contaminated ground water returns to the heated zone. The contaminants in the ground water mix with the oxygen and the condensate, and, with the presence of heat, rapidly oxidize into carbon dioxide and chloride. During the initial (DUS) phase of the process, removal of the contaminants occurs through physical transport to extraction wells with subsequent treatment of effluent vapors, NAPL, and water on site. Simultaneously, and afterwards, HPO converts contaminants in situ into carbon dioxide, chloride ions, and water. Thus, HPO is the chemical process of destroying DNAPLs in place (in the subsurface) that the DUS process has begun.

#### **Potential Markets**

The potential markets for the HPO/DUS technology include DOE, DOD, and commercial sites with NAPL and dissolved organic contamination of soils and ground water. It can be most cost effectively applied to treat NAPL source zones at sites with contaminants that are difficult to treat due to low solubility, low volatility, and low permeability aquifers.

#### Advantages

HPO/DUS appears to offer significantly faster and more complete remediation of DNAPLs than the baseline pump-and-treat technology.

HPO/DUS also offers substantial cost savings over the baseline pump-and-treat technology. Estimated costs for HPO/DUS are \$75-\$100 per cubic yard.

#### Demonstration Summary

DUS was developed by Lawrence Livermore National Laboratory (LLNL) and was demonstrated at LLNL in 1993-1994 in the cleanup of a gasoline spill. The LLNL spill was remediated with DUS, in about one year instead of 30 to 60 years required for pump-and-treat.

This report describes the implementation of HPO/DUS at the Visalia Superfund Site in Visalia, California, from June 1997 to mid-1999.

The Visalia Steam Remediation Project is being conducted by Southern California Edison Company (SCE), utilizing Steam Tech Environmental Services (the first commercial licensee of DUS) and LLNL technical staff.



For 80 years, the Visalia Superfund Site was used by a southern California utility company to treat utility poles by dipping them into creosote, a pentachlorophenol compound, or both. By the 1970s, these toxic substances had seeped into the subsurface to depths of approximately 100 feet, threatening a drinking water aquifer, which occurs at a depth of 140 feet.

At the Visalia Site, steam and air have been injected to a depth of 80 to 100 feet in paired wells, building a heated, oxygenated zone in which contaminated ground water mixes with the steam and oxygen.

- Some of the dissolved contaminants are destroyed in situ.
- Some of the dissolved contaminants are pumped from the water table to the ground surface, where they are treated to destroy contaminants.
- The vapor-phase contaminants are removed by vacuum extraction to be treated at the surface.

Performance monitoring of the HPO/DUS was conducted using three different approaches.

- ERT has been successfully used at the Visalia Site to monitor the underground movement of steam and the progress of heating.
- Noble gas tracers were used at the Visalia Site to monitor ground water to help verify HPO/DUS in the field.
- The widely-used 3-D ground water modeling code, NUFT, provided predictions of steam and tracer movement during operation.

The HPO/DUS technology was deployed to treat TCE-contaminated ground water at the DOE Portsmouth Gaseous Diffusion Plant (PORTS) beginning in December 1998. A brief description of this deployment, performance results, and costs is included as Appendix B of this report. HPO/DUS is scheduled to be deployed to treat PCE-contaminated ground water at the DOE Savannah River Site and possibly will be used to treat TCE-contaminated ground water at the Lawrence Livermore National Laboratory in FY 2000.

#### **Key Results**

Between June 1997 and June 1999, the Visalia Steam Remediation Project removed or destroyed approximately 1,130,000 pounds of creosote, a rate of about 10,400 pounds per week. The pump-and-treat system, originally installed in 1975 at Visalia, destroyed contaminants at a rate of about 10 pounds per week between 1975 and 1997.

HPO/DUS has been demonstrated to effectively destroy heavier-then-ground water pollutants such as creosote and pentachlorophenol. Laboratory-scale demonstrations show that HPO is effective in treating carbon tetrachloride and PCBs.

#### **Commercial Availability**

Integrated Water Technologies of Santa Barbara, California, recently licensed HPO, DUS, and ERT. The company plans to begin using this suite of technologies to remediate several Superfund sites. At the Visalia Site, SteamTech, Inc. of Bakersfield, California, used this combination of technologies under their license for DUS and ERT.

Contacts

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#### Licensing

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#### Other

All published Innovative Technology Summary Reports are available online at http://em-50.em.doe.gov. The Technology Management System, also available through the EM50 web site, provides information about OST programs, technologies, and problems. The OST reference number for HPO is 1519; for DUS, the number is 7.



## **TECHNOLOGY DESCRIPTION**

#### Process Description

A schematic diagram of the HPO/DUS process is shown in Figure 2. HPO/DUS combine steam and air injection, electrical resistance heating, and underground imaging and monitoring techniques to treat contaminated areas below the water table.





Figure 2. A Schematic Diagram of the HPO/DUS Process



Major elements of the technology may include steam injection, air injection, vacuum extraction, electrical heating, ground water extraction, and surface treatment of vapors and ground water. Use of the various elements of the HPO/DUS technology depend upon site conditions, particularly site geology. The major elements of the HPO/DUS technology are described below:

#### Steam Injection And Vacuum Extraction

Injection wells are drilled around the area of concentrated contamination, i. e. the source zone, to supply steam and electric current. Vacuum extraction wells in the center of the contaminated area remove contaminants. A steam front develops in the subsurface as permeable soils are heated to the boiling point of water, and volatile organic compounds are vaporized from the hot soil. The steam sweeps the permeable zones between the injection and the extraction wells. Steam injection ceases while vacuum extraction continues once the front reaches the extraction wells. The vapor is pulled through the extraction wells to the surface where it is treated. Ground water removed via the extraction wells is also treated above surface. When the steam zone collapses, ground water reenters the treatment zone and the steam/vacuum extraction cycle is repeated in a process termed "huff and puff."

#### **Electrical Resistance Heating**

Electric current is used to heat impermeable zones. Water and contaminants trapped in these relatively conductive regions are vaporized and forced into the permeable zone being swept by the steam and then subjected to vacuum extraction. At Visalia, electrical resistance heating was not required, because the subsurface consisted of relatively permeable sediments through which the steam could be effective.

#### **Underground Imaging And Monitoring**

An integral component of the technology is the sophisticated imaging system known as ERT, which allows real-time 3-D monitoring of the subsurface (Figure 3). ERT is based on a cross-hole tomography system that maps changes in resistivity over time. Changes in resistivity both laterally and vertically can be related to the migration of steam through various zones between the injection and extraction wells. ERT can be utilized to make process adjustments to optimize the performance of the system.



Figure 3. Progression of heated zone during thermally enhanced remediation

#### Hydrous Pyrolysis Oxidation

Steam and air are injected in paired wells, building a heated, oxygenated zone in the subsurface. When the injection is stopped, the steam condenses and contaminated ground water returns to the heated zone where it then mixes with the condensed steam and oxygen, which destroy dissolved contaminants in situ. HPO occurs after contaminants are removed during the DUS phase.



#### Process Equipment

Equipment required for this combination of technologies includes steam generation and transfer equipment, extraction well equipment, ERT/monitoring equipment, and surface treatment equipment. The extraction wells include large vacuum pumps capable of running at 2,500 standard cubic feet per minute. At Visalia, four steam boilers provide the steam; each boiler can generate 50,000 pounds of steam per hour.

#### **System Operation**

#### Steam Injection/Vacuum Extraction Phase

Continuous steam injection into permeable zones that contain contaminants occurs over a period of weeks or months to vaporize trapped liquids, which are then removed through vacuum extraction. At Visalia, continuous injection occurred over a period of 4 to 5 months in order to achieve an average temperature of approximately 60° Celsius and a maximum temperature of about 140° Celsius. Ground water is extracted at a rate of 350 to 400 gallons per minute (gpm). Twenty-nine ERT wells, plus thermocouples, are used to track the steam front.

Originally, the offgas vapor from vapor extraction was scrubbed using carbon. Because this proved to be very expensive, the offgas is now dried and incinerated in the steam boilers, at the same time supplementing heat content for the production of steam. Free product is collected in tanks for future disposal. Extracted ground water is treated via gravity filtration and is discharged offsite to a public wastewater treatment facility.

#### Hydrous Pyrolysis Phase

When the steam and air injection is stopped, the steam condenses and contaminated ground water returns to the heated zone. The contaminants in the ground water mix with the oxygen and condense. With the presence of heat, they rapidly oxidize into carbon dioxide, chloride, and water. At Visalia, monitoring indicates that HPO accounts for about 17% of the total destruction of creosote.

It is anticipated that once the steam is turned off, residual heat will dissipate slowly. The rate of contaminant destruction decreases with diminished temperature, but the ground can be expected to retain warmth for years.



## PERFORMANCE

#### **Demonstration Plan**

This section of the report documents the HPO/DUS demonstration at the Visalia Poleyard in Visalia, California where the aquifer was contaminated with heavy petroleum hydrocarbon compounds, namely creosote. A subsequent deployment of HPO/DUS has recently occurred at a site contaminated with chlorinated solvents at the DOE PORTS facility in Ohio. A description of the deployment, the performance of the technology, and associated costs are included as Appendix B.

#### Background

The four-acre Visalia Poleyard in California's Central Valley was the site of a wood preservation treatment plant for power poles, since the 1920's. Contamination of soil and a shallow, confined aquifer by creosote, pentachlorophenol (PCP), and diesel fuel led to the designation as a Superfund Site in 1975. A pump-and-treat system was installed in 1975 and several years later a slurry wall was constructed to contain the plume at its leading edge. The pump-and-treat system has been effective as a hydraulic barrier for plume containment (preserving a drinking water aquifer located at a depth of 140 feet), but was ineffective and costly for long-term site remediation.

#### **Implementation Plan**

HPO/DUS has integrated thermal, chemical, physical, and biological treatment methods in a rapid and highly effective remediation at the Visalia Site. It utilizes DUS, HPO, Soil Vapor Extraction (SVE), In Situ Bioremediation (ISB), Pump and Treat, and ERT to conduct a rapid and effective remediation.



#### Figure 4. Cross section (approximately northeast-southwest) through the Visalia site, showing the lithology and current prediction of DNAPL location (Geraghty and Miller, 1992). Depth to water is about 60 ft today (the shallow aquifer is unsaturated). Drinking water is produced from the uncontaminated deep aquifer.

At the Visalia Pole Yard, there are three distinct water-bearing zones, as shown in Figure 4. Several shallow aquifers are considered as one unit, from about 35 to 75 feet below ground surface; the intermediate aquifer is present from about 75 to 105 feet below ground surface. The shallowest contamination is not being treated with thermal methods, because in situ bioremediation is working well enough at this depth. The most sensitive ground water resource is the deep aquifer below about 120 feet.



The thermal remediation system has been designed and targeted to remove contaminants from the intermediate aquifer without disturbing the deep aquifer.

Figure 5 shows the approximate locations for the 11 injection and 8 extraction wells at the Visalia Site.



Figure 5. Approximate locations for steam injection wells and extraction wells, Visalia Pole Yard, Southern California Edison Company

#### Results

During twenty-five months of operation a total of 1,130,000 pounds of creosote were removed or destroyed (a rate of about 10,400 pounds per week). Figure 6 shows the rate of contaminant destruction over approximately twenty-five months at Visalia. ERT provided near real-time images that reflect progress in remediation of the subsurface between pairs of monitoring wells. Monitoring the progress of the heating fronts ensured that all of the aquifer was treated.

Field methods were developed for sampling and analysis of hot water for contaminants, oxygen, intermediate products, and products of reaction.



During the twenty-five months of operation, approximately 50% of the contaminants were removed in the free phase, 16% as hydrocarbon vapors, 16% in the aqueous phase, and 17% were destroyed by HP in situ. Free-phase product was collected in tanks for eventual disposal.

In order to maximize extraction rates, several wells were converted to dual use, allowing steam injection in the center of the treatment zone.

Several pumps were specifically developed for use in wells where temperatures exceeded the boiling point. Additional injection wells were installed and completed in the deep aquifer to allow steam injection below the confining layer for the contaminant plume; this allowed heating from below the plume.



Figure 6. Daily Removal Rates at the Visalia Steam Remediation Project



## TECHNOLOGY APPLICABILITY AND ALTERNATIVES

#### Competing Technologies

The baseline against which HPO/DUS can be compared is pump-and-treat. The pump-and-treat technology has been used at the Visalia Superfund Site for more than 20 years.

A variety of in situ thermal treatment technologies have been either demonstrated or developed through DOE, DOD, and EPA programs. Full-scale demonstrations of these related technologies include the following for DOE: Six-Phase Soil Heating; Thermal Enhanced Vapor Extraction; and Radio Frequency Heating. For DOD/EPA, the following technologies have been demonstrated: Contained Recovery of Oily Wastes; HRBOUT Process; In Situ Steam and Air Stripping; In Situ Steam Enhanced Extraction Process; Radio Frequency Heating; Steam Enhanced Recovery System.

#### Technology Applicability

HPO/DUS has been used successfully to remediate DNAPLs (creosote and pentachlorophenol). Laboratory studies have been successful for the contaminants TCE, carbon tetrachloride, and PCBs.

HPO/DUS is effective in the presence of free-phase and dissolved-phase organic contaminants. It is applicable to sites with contamination both above and below the water table.

The minimum depth for application of HPO/DUS is 5 feet. At greater depths, the steam injection pressure can be increased, producing higher efficiencies.

A key competitive advantage of HPO/DUS is the speed of cleanup relative to conventional technologies.

HPO/DUS has a potential market at sites where conventional technologies have failed to produce acceptable results.

HPO/DUS is best suited to treat DNAPLs and strongly sorbed contaminants in heterogenous or fractured formations. Unlike most competing technologies, it can directly treat contamination in complexly interbedded sands and clays.

#### Patents/Commercialization/Sponsor

Numerous patents covering the major aspects of DUS, ERT, and HPO are either pending or have been granted to DOE and the University of California. Integrated Water Technologies of Santa Barbara, California, has recently become the first nationwide licensee of the DUS, ERT, and HPO technologies package. SteamTech, Inc., of Bakersfield, California, is also a licensee of the DUS, ERT, and HPO package. These cleanup technologies are licensable through the University of California Office of Technology Transfer.



## COST

#### Methodology =

Information in this Section is summarized from a report prepared by MSE Technology Applications (MSE) using real data from the deployment of the HPO/DUS technology at the Visalia Superfund Site in California. MSE was tasked to perform cost analyses as an independent team for the DOE Office of Science and Technology. Cost information on the HPO/DUS deployment at the DOE PORTS site is included in Appendix B.

The conventional pump-and-treat technology was used as the baseline technology against which HPO was compared.

A Life-Cycle Cost Model (LCCM) was developed to provide cost estimates for using HPO/DUS to remediate sites contaminated with organic compounds. This model is based on a limited amount of data, which are used to build a scalable cost-estimating tool. Because the data are very limited, the model has a high level of uncertainty.

Because only general data were available from the Visalia Site, where the largest mass of contaminant is creosote, the model has been set up to estimate the costs associated with removal of contaminants with boiling points of less than 100 degrees Celsius, such as trichloroethylene (TCE). While capital and setup costs would be similar for either compound, the main difference is in operating costs, because creosote has an average boiling point of 300 degrees Celsius and requires a larger amount of energy input.

Data input requirements for the model include:

- the length, width, and maximum depth of the plume;
- the mass of the contaminants;
- the soil type (to determine whether electrical heating is necessary to supplement the steam) for clay conditions;
- the time the steam-injection system is operating;
- the pump and treat capacity;
- the estimated time pump and treat would be required to operate; and
- the discount rate.

Steam cannot be injected in greater volumes than the groundwater is extracted from the site without expanding the contaminant plume, the pump and treat system capacity is the limiting factor for how much steam can be injected into the subsurface. The input for the pump and treat capacity is the maximum total amount of ground water that can be extracted and treated at the site. From this value, the model can calculate the total amount of steam to be injected.

Output values from this model include:

- operating time;
- capital and startup costs;
- operating and disposal costs;
- total costs;
- net present value costs;
- unit costs per cubic yard; and



• cost savings or loss over the pump and treat system.

If economies of scale apply in this case, larger sites might be less expensive on a per unit cost basis, while unit costs for smaller sites would be higher. Total costs are calculated for each technology using the capital costs, the operating and maintenance costs, and the total operating time. While this model assumes the capital necessary to cover the costs to provide the equipment for the complete cleanup of one site, this equipment could be moved from one site to another. (This would increase the total time for remediation but would reduce the capital costs, which may result in an overall cost savings.)

#### **Cost Analysis**

The inputs and outputs of the model using the Visalia Site data are shown in Table 1 below.

#### Table 1. Visalia Site input and output data

#### Inputs

Estimated Mass of Contaminants to be Treated, lbs	635,000
Length of plume, ft	525
Width of Plume, ft	150
Maximum depth, ft	100
Estimated % time Steam Injection to be Operating	80
Maximum Pump and Treat Capacity, gpm	350
Estimated Length of Pump and Treat Operation, year	30
Discount Rate	3.80%

#### Outputs

Output	Р8	T System	HPO/DUS
Total Operating Time, yrs		30	0.44
Total Capital/Startup Costs	\$	5,500,000	\$ 8,444,005
Annual O & M/Disposal Costs	\$	1,500,000	\$ 6,449,692
Total Costs	\$ !	50,500,000	\$ 11,305,736
NPV Costs	\$ 3	32,079,702	\$ 11,229,590
Unit Costs, \$/cubic yard	\$	110	\$ 39

#### Cost Conclusions

While capital and startup costs for HPO/DUS are typically larger than for pump and treat alone, it is usually a more cost-effective solution to DNAPL cleanup because of the reduction in time and operating and maintenance costs. Conversely, pump and treat is a slow process requiring many years of operation before the contaminant is removed, because it is limited by rates of dissolution as well as extraction and treatment capacity.

The capacity of the pump and treat system is the limiting factor for the HPO/DUS technology, because the amount of steam injected cannot exceed the amount of ground water removed. For sites with very low ground water extraction rates or limited water treatment capacity, pump and treat may be more economically feasible. A system with a maximum ground water extraction capacity of 100 gallons per minute (gpm) or less would be more cost effectively remediated using pump and treat. For ranges of about 150 gpm or more, HPO/DUS would be more cost effective, because the site can be remediated at a faster rate, thereby reducing the total operating costs.



HPO/DUS is a cost-effective solution for the removal of DNAPL contaminants in the subsurface over a wide range of soil volume. In cases where the total volume of soil is very large, pump and treat may be more cost effective, assuming the cleanup time and total extraction rate does not change. However, it is doubtful that pump and treat could clean up a larger volume without increasing the extraction rate or requiring more time to complete. Holding the data inputs in the table constant and varying only the total volume, HPO/DUS becomes more costly than pump and treat on a cubic yard basis when the total volume is somewhere between one-half and 1 million cubic yards.



## **REGULATORY AND POLICY ISSUES**

#### Regulatory Considerations

HPO/DUS at the Visalia Superfund Site is proceeding under CERCLA regulation. CERCLA requirements have been met to accomplish the remediation.

Permit requirements for future applications of this combination of technologies (HPO, DUS, and ERT) will likely include:

- air permits for operation of steam generation equipment and discharge from surface treatment equipment (i.e., air stripper, GAC units, or internal combustion engine);
- liquid effluent discharge permits from aboveground treatment systems;
- NEPA documentation for Federal facilities.

For applications in some states, underground injection permits may be required for system application.

#### **Other Considerations**

Waste forms, including air and liquid discharges, as well as spent activated carbon (from filtration) are generated by the DUS technology. The carbon can either be regenerated or placed in a landfill and poses no unusual regulatory or permitting burden.

HPO allows certain contaminants to be destroyed in situ, thereby eliminating sources of secondary waste.

#### Safety, Risks, Benefits, and Community Reaction

#### Worker Safety

Operational safety procedures were used to address DUS-specific safety issues. Areas of concern included hazards posed by the steam-generating equipment, electrical hazards from the large currents utilized, and pressurized steam injection wells.

Although large amounts of contaminants are more quickly extracted from the ground with DUS than with conventional technologies, safety measures for handling extracted liquid and vapor streams are similar to those for the conventional technologies.

#### **Community Safety**

Although DUS involves handling extracted vapor and liquid streams with higher concentrations of contaminants than conventional technologies, the dramatically increased speed of cleanup reduces long-term risks to nearby populations.

HPO/DUS employs real-time monitoring controls that greatly reduces the likelihood of accidents or offsite migration of contaminants.

#### **Environmental Impact**



HPO/DUS speeds cleanup relative to conventional technologies, thereby freeing land for beneficial reuse.

#### Socioeconomic Impacts and Community Reaction

Unlike some other long-term remedial alternatives, HPO/DUS will require a staff for only a limited period of time. Selection of HPO/DUS can reduce the amount of time an environmental restoration work force is needed at some installations.

HPO/DUS has received positive support from the general public at the LLNL Community Work Group Meetings. The basic principles of the technology have been readily understood by both technical and nontechnical audiences.



## **LESSONS LEARNED**

#### Implementation Considerations

- Above-ground treatment systems must be sized to handle anticipated peak extraction rates and the expected distribution of volatile organic compounds (VOCs) in extracted vapor and liquid streams.
- Above-ground treatment systems must be located so as not to interfere with access to the subsurface treatment zone.
- Effective removal of contaminants from the subsurface requires repeated creation of the steam zone by successive phases of steam injection and continuous vacuum extraction. The pressure changes created by this oscillatory approach distill contaminants from pore spaces in both saturated and unsaturated sediments.
- Extraction rates can vary greatly depending upon the amount of steam injected, the total vacuum applied, and cycle times.
- Permitting of air discharges from both above-ground treatment units and equipment to supply steam energy is an issue requiring early attention.
- HPO/DUS is a labor-intensive process requiring significant field expertise to implement.
- ERT has proved to be the most effective method for monitoring the steam remediation process in real-time.

#### Technology Limitations and Needs for Future Development

Treated soils can remain at elevated temperatures for months and even years after cleanup. This could impact site use plans. Soil venting can greatly accelerate the cooling process. The capacity of the pump and treat system is the limiting factor for the HPO/DUS technology because the amount of steam injected cannot exceed the amount of ground water removed.



## APPENDIX A

### REFERENCES

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## APPENDIX B

## DOE PORTSMOUTH DEPLOYMENT

#### Background and Objectives

A dynamic underground (steam) stripping and hydrous pyrolysis/oxidation (DUS/HPO) deployment was conducted within the source area of the X-701B plume at the DOE PORTS Site near Piketon, Ohio. The project was conducted in three phases during July 1998 through August 1999:

- Phase I conceptual design,
- Phase II site characterization, and
- Phase III system design, onsite construction, operations, post steaming drilling and soil sampling, and demobilization.

The purpose of this project was to deploy DUS/HPO for remediation of trichloroethylene (TCE)contaminated soil and ground water. This was the first application of DUS/HPO where the primary contaminant was chlorinated solvents, namely TCE. Specific objectives included:

- Evaluate the ability of steam to flow to the water-bearing unit and heat it to steam temperature, the geological controls on steam flow, and the range of acceptable injection pressures;
- Assess the ability to remove TCE;
- Assess changes in the contaminant concentrations during and after operations; and
- Obtain cost and other design information for future applications at PORTS and other DOE sites.

#### Site Description and System Design

The treatment area was approximately 120 ft wide and 180 ft long, located within, but not encompassing, the primary source area of the X-701B plume. The X-701B plume extends downgradient (eastward) approximately 1,900 ft with TCE concentrations as high as 970 mg/L. Prior to steaming, the mass of TCE within the treatment area was estimated to range between 674 and 1181 lbs.

Treatment system design was comprised of (Figure B.1):

- 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;
- distributing steam to the injection wells through an above-ground piping network;
- regulating 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 8 to 15 gpm);
- extraction of vapors through well screens 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.





## Figure B.1. Map of X-701B site showing distribution and type of wells with surface piping layout (SteamTech 1999)

#### **System Operations**

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 treated soil layers 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 hydrous pryolysis/oxidation reactions.
- Progression of the heated zone was monitored daily using a network of 314 thermocouples and electrodes for three-dimensional ERT measurements.



#### Performance

Steam injection began in late January 1999 and continued at desired rates and pressures for approximately 4 months with less than 1% downtime.

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



Heating of the area was monitored daily. The hotwater/steam front appeared to remain within the lower Gallia, closely following the interface between the Gallia and the underlving Sunbury (bedrock). The majority of the site had been heated by early April with the exception of the northeast and western areas of the site (Figure B.2). Monitoring wells in these areas were converted to injection wells in order to deliver steam to these areas (Figure B.3).

Figure B.2. Map view of the top of the lower Gallia Formation. ERT data from April 7, 1999 showing differences in resistivity (> 15% decrease) occurring as a result of steam injection (SteamTech 1999).

Although difficult to estimate because only a portion of the source plume 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 ground water treatment facility.
- Approximately 38 lbs of TCE were recovered by the air emissions treatment system.



Figure B.3. Map view of the top of the lower Gallia Formation. ERT data from June 3, 1999 showing differences in resistivity (>15% decrease) occurring as a result of steam injection (SteamTech, 1999).



- 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 soil samples such that the HPO reaction could still occur further reducing the overall TCE mass.

Lessons learned included:

- Most of the TCE in the treatment area was within the top of the Sunbury shale as opposed to the Gallia, which required alternative steam delivery approaches (i.e., cycling).
- Steam flow rates were lower than anticipated (averaged ~200 lb/hr) and can be increased somewhat by increasing injection pressures (up to 18 psig).
- Well spacings of ~40 ft should be used for the final design to optimally deliver steam to the finer grained materials.

#### Cost i

The total approximate cost of this deployment was \$6,212,000 including PORTS site support. Table B.1 is a breakdown of these costs.

Activity	Estimated Cost (\$K)	% of Total Cost
Technology provider (design, construction,	3,014	49
operations, demobilization)		
Well installation	256	4
Laboratory analyses	125	2
Field services support	151	2
Waste management (excluding waste disposal)	106	2
Other site support (engineering, QA, health and	589	9
safety, health physics, project management, etc.)		
Overhead	1,971	32
TOTAL	6,212	100

#### Table B.1. Estimated Pilot Project Costs

Based on the findings from the first deployment, a cost estimate for remediation of the entire source area plume (west of the perimeter security fence) is summarized in Table B.2.

#### Table B.2. Estimate for Remediation of the X-701B Plume

Task	Estimated Cost
Design	\$62,380
Equipment	\$1,774,580
Well Installation	\$1,117,089
Monitoring System	\$940,600
Field Piping and Pumps	\$1,272,450
Operations	\$2,753,050
Demobilization	\$149,780
Subtotal	\$8,069,929
Indirect costs	\$1,792,532
TOTAL	\$9,862,461

