

# **COST AND PERFORMANCE REPORT**

Dynamic Underground Stripping-Hydrous Pyrolysis Oxidation  
at the Savannah River Site 321-M Solvent Storage Tank Area  
Aiken, South Carolina

June 2003

## SITE INFORMATION

### IDENTIFYING INFORMATION

**Site Name:** Savannah River Site 321-M Solvent Storage Tank Area

**Location:** Aiken, SC

**Regulatory Context:** RCRA

**Technology:** Dynamic Underground Stripping-Hydrous Pyrolysis Oxidation (DUS/HPO)

**Scale:** Field demonstration

### TECHNOLOGY APPLICATION

**Period of Operation:** September 9, 2000 to September 28, 2001

**Type/Quantity of Material Treated during Application:** Source zone - Total volume of 52,000 cubic yards based on a surface area of 100 ft by 100 ft and a depth of 160 ft

### BACKGROUND [1,2,3]

The M-Area Settling Basin Hazardous Waste Management Facility (HWMF) includes the M-Area Settling Basin and associated areas of the U.S. DOE Savannah River Site (SRS), in Aiken, S.C. The HWMF received effluent from various processes at SRS containing high concentrations of tetrachloroethene (PCE), trichloroethene (TCE), and other volatile organic compounds (VOCs). VOC contamination occurred as a result of breaks in the former process sewer line and disposal practices associated with the settling basin. An estimated 3.5 million pounds of residual solvents were released to the sewer leading to the M-Area settling basin and associated outfall. An initial site characterization, conducted in the early 1990's, identified high levels of chlorinated solvents (0.2-0.3% by weight) indicating the presence of DNAPL contamination. Additional site characterization using surface geophysics was performed to further delineate DNAPL contamination and determine chemical composition. Results estimated the composition of the DNAPL as 90% PCE and 10% TCE. Prior to treatment, the total contaminant mass was estimated at 26,800 lbs (total contaminants, not only DNAPLs).

The Solvent Storage Tank Area (SSTA) is located west of Building 321M in the M-Area of SRS. Building 321M operated as a target fabrication facility, primarily housing metallurgical and mechanical processes such as casting, extrusion, hot-die-sizing and welding. Cleaning solvents and caustic solutions were used to prepare the materials for fabrication. The SSTA consisted of a 17,000 gallon storage tank with associated piping and equipment. The tank, located adjacent to a railroad car transfer facility, was used to store chlorinated solvents including PCE and TCE, beginning in 1957. Numerous undocumented spills and leaks were suspected to have occurred in this area. One reported spill released an estimated 1,200 gallons of PCE to the ground. The tanks, part of the railroad track and associated above-ground equipment were removed in the fall of 1997. The concrete pad and two sumps were left in place. The SSTA contains three M-Area SVE wells and the groundwater is maintained under hydraulic control by two M-Area recovery wells.

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## **MATRIX DESCRIPTION**

## **MATRIX AND CONTAMINANT IDENTIFICATION**

**Type of Media Treated with Technology System:** Source zone (saturated and unsaturated)

**Primary Contaminant Groups:** Chlorinated Solvents (PCE and TCE)

## **SITE HYDROGEOLOGY AND EXTENT OF CONTAMINATION [1,2]**

The surficial geology of the SRS consists of Atlantic Coastal Deposits, which is primarily composed of both unconsolidated and consolidated strata, ranging from Late Cretaceous to Miocene in age. Coastal Plain Sediments are comprised of interbedded sand, muddy sand, and mud (clay and silt).

The hydrogeology of the area includes three aquifers of the Floridian-Midville aquifer system which includes in ascending order the McQueen Branch aquifer, the Crouch Branch aquifer, and the Steed Pond aquifer. The Crouch Pond aquifer is the principle water producing aquifer. The vadose zone beneath the

M-Area contains several clay layers interspersed with more transmissive, sandier intervals. A "Green Clay" horizon is located at approximately 160 - 165 ft bgs.

The high concentrations of contaminants suggested the presence of DNAPL in silts and clays in the vadose zone above the water table at depths ranging from 20 to 35 feet bgs, and below the water table in the form of disconnected ganglia (rather than a large, solvent saturated layer).

Table 1 lists the matrix characteristics affecting treatment cost or performance for this application.

**Table 1. Matrix Characteristics [1,2]**

Parameter	Value
Soil Classification	Interbedded sands and clays overlying a clayey aquitard
Depth to Groundwater	143 ft
Porosity	0.3
Presence of NAPLs	Contaminant concentrations suggested the presence of DNAPL
Hydraulic Conductivity	0.4 ft/min - average value from pump tests conducted on 5/4/2000

## TECHNOLOGY SYSTEM DESCRIPTION

### TREATMENT TECHNOLOGY

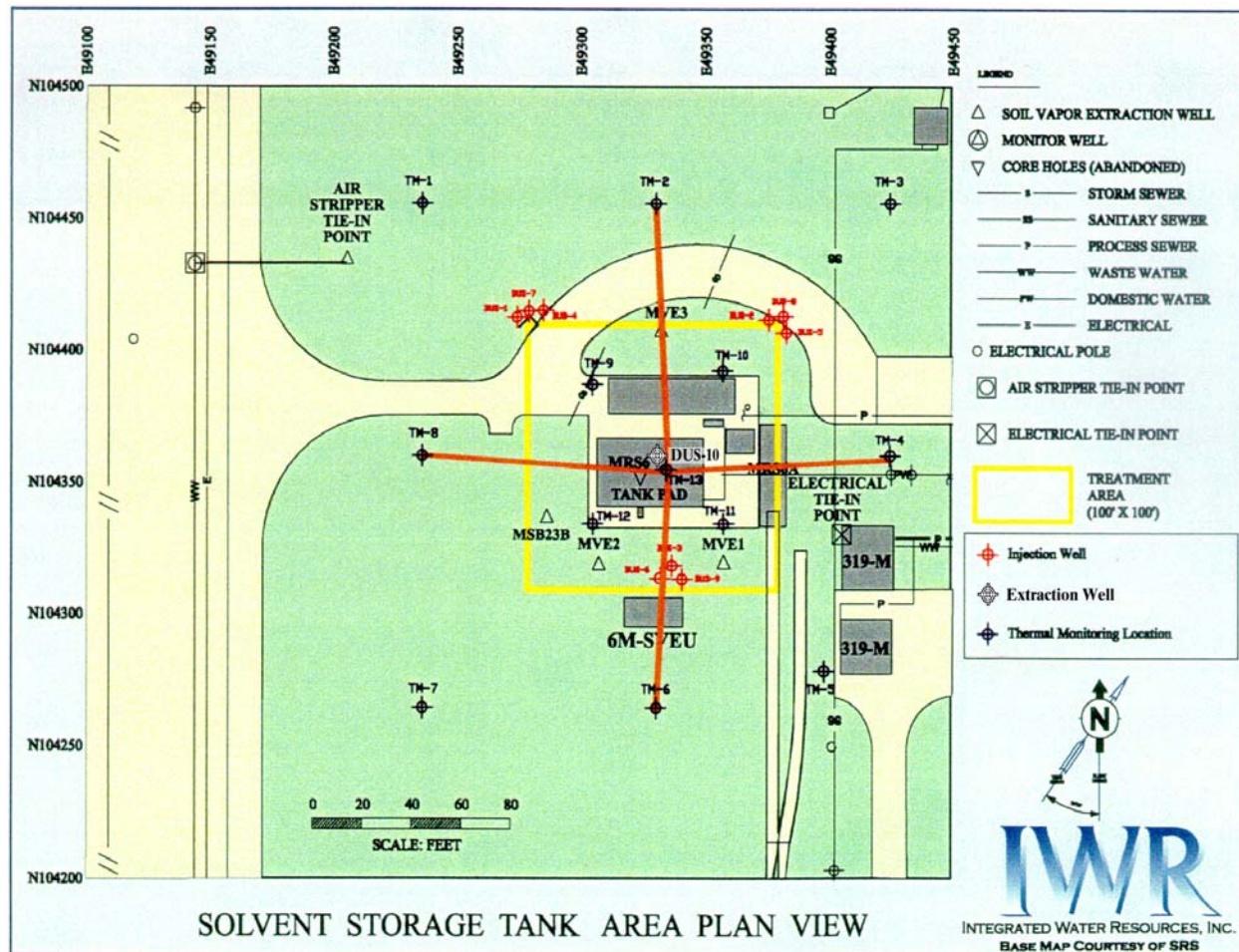
Dynamic Underground Stripping and Hydrous Pyrolysis Oxidation (DUS/HPO)

### TREATMENT SYSTEM DESCRIPTION AND OPERATION [1,2,3]

Figure 1 shows a plan view of the DUS/HPO system used at the SSTA. Three steam-injection well clusters were installed around the perimeter of the 100 ft by 100 ft treatment area (at the northwest corner, northeast corner, and southern boundary). Each well cluster consisted of three injection wells with screen intervals at 50-70 ft bgs, 110-130 ft bgs, and 150-160 ft bgs. One dual-phase groundwater and vapor extraction well (DUS-10) was installed in the center of the target zone with a screen interval from 20-160 ft and used to extract both groundwater and vapor from the subsurface. Groundwater was extracted from the well using a high-temperature electric-submersible pump, located 25 to 35 ft below the static groundwater elevation (143 ft bgs). The extracted groundwater was collected in a tank, with final discharge through an air stripper.

Vapor extraction was performed using DUS-10 and three existing vadose zone soil vapor extraction wells (MVE-1, -2, and -3), located along the perimeter of the target zone. The steam for the system was supplied from other industrial operations at SRS. Steam pressure was reduced to 100 psi prior to entering the DUS/HPO system.

Figure 1. Plan View of DUS/HPO System [1]



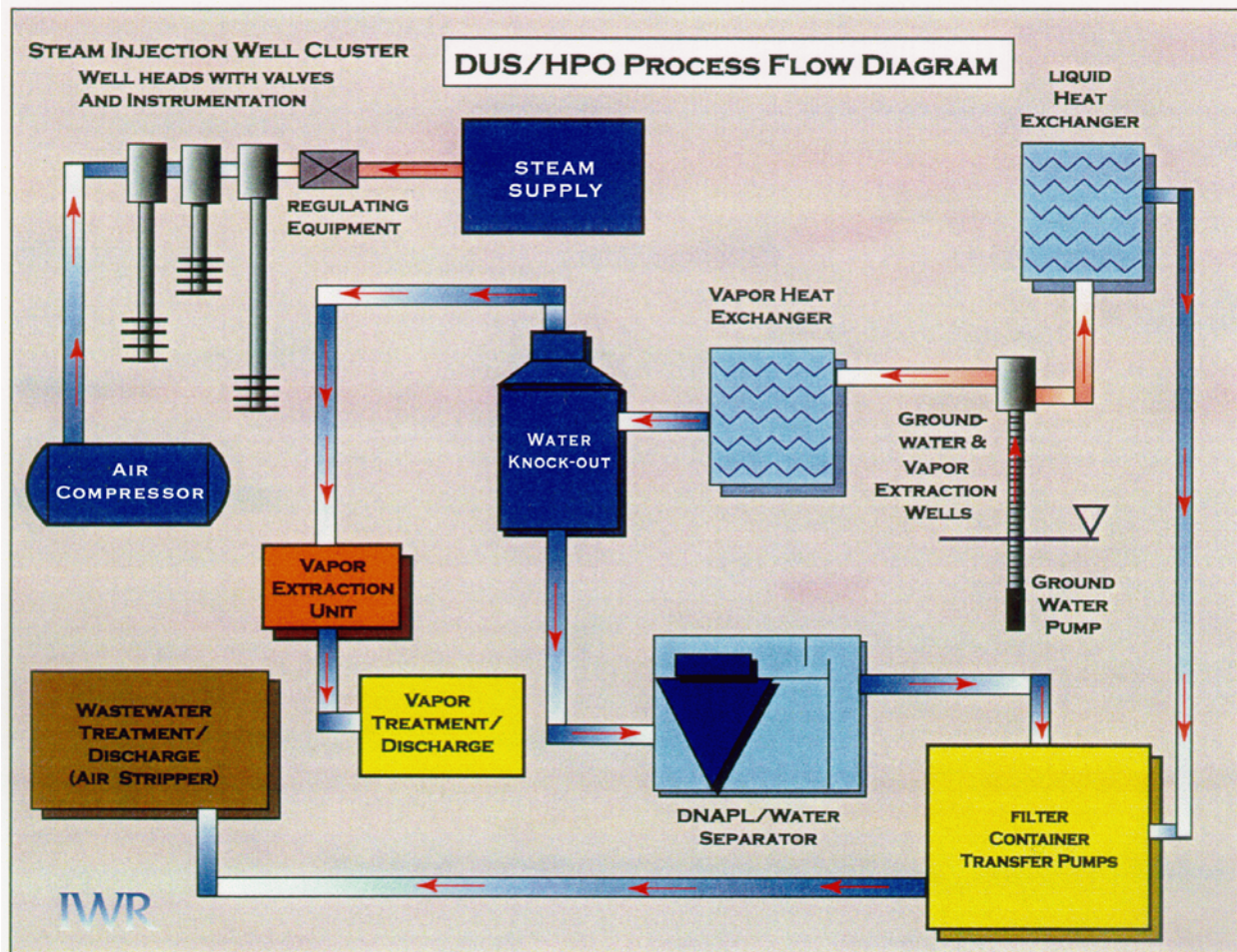
SRS's 6M Soil Vapor Extraction Unit (6M-SVEU) was used to extract vapors from wells DUS-10 and MVE-1, 2, and 3. The vapor flow input of the unit was about 500 scfm. The hot extracted vapors were cooled through a heat exchanger, and condensed liquids were separated from vapors in a knockout tank. The condensate was routed through a DNAPL-water separator (DWS), which separated DNAPL droplets for collection and removal. Figure 2 shows a process flow diagram of the DUS/HPO system, with vapor and wastewater treatment. The 6M-SVEU was operated to keep levels of contaminants in the vapor discharge was below air emissions limits.

Beginning in December of 2000, air was injected into the deep saturated zone injection wells to enhance the HPO process. Air injection was implemented over one 10-hour period at a rate of approximately 5 scfm. According to the vendor, air injection occurred whenever deep injection of steam occurred. During the later stages of the effort, this injection into the deep wells was implemented intermittently during periods of steam injection into the shallow wells.

Initial steam injection to the deep vadose zone was at a maximum design pressure of 60 psig and a temperature of 152°C; and 40 psig and 143°C for the intermediate vadose zone. In addition, initial heating was performed in the saturated area to set up a "hot plate" at the base of the treatment area, and followed by steam injection heating in the vadose zone. According to the vendor, this approach helped to drive contaminants towards the recovery system while limiting potential for dispersal in the subsurface. Approximately 50% - 90% dilution air was used prior to contaminant entry into the SVE unit (6M) so that vapor emissions remained within permitted discharge limits.



Figure 2. Simplified Process Flow Diagram [1]



Thermal monitoring of the subsurface conditions included temperature profiles from 14 downhole thermocouple arrays and electrical resistance tomography (ERT) images which displayed changes in subsurface resistance caused by differences in temperature. For ERT monitoring, 6 electrode strands were placed through narrow boreholes: 4 on the perimeter of the treatment zone, one in the middle, and one in an abandoned groundwater monitoring well. Each borehole with an electrode also housed a thermocouple string. Eight additional thermocouple strings were installed: four outside and four inside the target area. In addition, one thermocouple was installed at the base of each steam injection well and at the base of the main vapor extraction well. Thermocouples ranged in depth from 3 ft bgs to 163 ft bgs, and were vertically spaced 6 ft apart on each thermocouple strand.

For the pilot demonstration, data collected included: steam flow; steam injection at each well-head; vapor extraction information from the SVE unit, including concentration data; extracted vapor temperature and pressure collected at the wellhead; cooling system data; and wastewater stream data (total flow and temperature). In addition, regular vapor (Tedlar bag) and water samples were collected to track system performance. Groundwater was heated to a temperature of approximately 100 °C, while the source zone reached a temperature of approximately 87°C. Table 2 provides a summary of operational data for the DUS/HPO pilot demonstration.

**Table 2. Operational Data from SRS DUS/HPO Pilot Demonstration [1,2]**

Parameter	Value
Source zone temperature	87 °C
Operating pressure/vacuum	5.1 in of Hg
Weight of injected steam	45,400,000 lbs
Heat content of injected steam	4.5 x 10 <sup>10</sup> BTUs
Total time for steam injection	3,226 hours (134 days)
Total time for effluent treatment system operation	7,020 hours (293 days)
No. of pore volumes extracted	420
Total volume of extracted air	176,000,000 ft <sup>3</sup>
Volumetric equivalent flow rate of extracted steam	698 scfm
Average non-condensable extraction rate	300 scfm

**TIMELINE [1,2]**

- September 9, 2000 Demonstration system operations began
- December 2000 Air injection for enhancing HPO began
- March 8, 2001 Performance objective met; operational period extended to meet revised mass removal goals
- September 28, 2001 System shutdown; began cold standby
- October 2001 Began demobilization

**TECHNOLOGY SYSTEM PERFORMANCE****PERFORMANCE OBJECTIVES [1,2]**

The following performance objectives were identified for the pilot demonstration:

- Contaminants must be extracted from the target source zone
- The target source zone must be heated to the applied boiling point
- Air to support HPO must be injected into the treatment area

In addition, discharge limits were established for vapor emissions and water discharge, however specific values were not provided.

**TREATMENT PERFORMANCE [1,2]**

Concentrations of PCE and TCE were provided for the four vapor extraction wells (DUS-10, MVE-1, MVE-2, and MVE-3) from August 2000 to February 2001, and for the 6M-SVEU from March 2001 to July 2002. During the first six months of operation, concentrations of PCE and TCE from the dual-phase extraction well (DUS-10), located in the target zone, increased to 4,200 ppmv and 230 ppmv, respectively, while concentrations in wells MVE 1, 2, and 3 varied. From March 2001 to July 2002, vapor contaminant concentrations for 6M-SVEU ranged from 963 to 5,733 ppmv for PCE and 25 to 99 ppmv for TCE.

**Table 3. Contaminant Concentrations in Extracted Vapors August 2000 to July 2002 [1]**

Date	6M-SVEU			DUS-10		MVE-1		MVE-2		MVE-3	
	PCE	TCE	Flow (scfm)	PCE	TCE	PCE	TCE	PCE	TCE	PCE	TCE
8/22/00	NR	NR	NR	160	42	NR	NR	3.6	1.1	NR	NR
9/14/00	NR	NR	474	120	19	9.5	1.9	10	7.4	160	49
10/11/00	NR	NR	468	190	48	86	15	2.3	0.76	3.5	4.3
11/15/00	NR	NR	645	160	34	57	17	3.9	1.2	22	2.1
12/13/00	NR	NR	578	570	73	17	4.1	25	3.1	120	4.4
1/30/01	NR	NR	545	1,500	120	47	36	2.2	0.52	5.6	0.93
2/14/01	NR	NR	554	4,200	230	12	3.4	310	8.7	NR	NR
3/19/01	5,733	66.3	500	NR	NR	NR	NR	NR	NR	NR	NR
4/3/01	5,320	99.1	306	NR	NR	NR	NR	NR	NR	NR	NR
5/7/01	963.1	25.2	301	NR	NR	NR	NR	NR	NR	NR	NR
6/11/01	3,471	38.7	272	NR	NR	NR	NR	NR	NR	NR	NR
7/9/02	1,256	35.9	288	NR	NR	NR	NR	NR	NR	NR	NR

NR - not reported

Figure 4 shows the cumulative removal of PCE and TCE from September 2000 through September 2001. During this time, a total of 30,000 kg of PCE and 1,000 kg of TCE were removed for a total of 31,000 kg of mass of contaminant removed.

By March 2001, over 62% of TCE mass had been removed compared to 26% of PCE mass, attributed to the lower boiling point of TCE. According to the vendor, after March 2001, concentrations and daily removal rates decreased more rapidly for TCE than for PCE, likely due to removing the majority of TCE during initial heating and the relatively higher rate of destruction of TCE by HPO.

Performance objectives were met on March 8, 2001, however system operation was continued until September 26, 2001 for additional contaminant mass removal. Once the treatment area had reached the target temperatures in March, only intermittent steam injection was needed to maintain steam temperatures. After March, the majority of steam injection was targeted at maintaining temperature in the shallow sections which tended to cool more rapidly. Contaminant removal patterns also indicated that much of the contaminant mass was being removed from the shallowest portion of the treatment area.



Figure 3. Average Concentrations in Extracted Vapors for PCE and TCE [1]

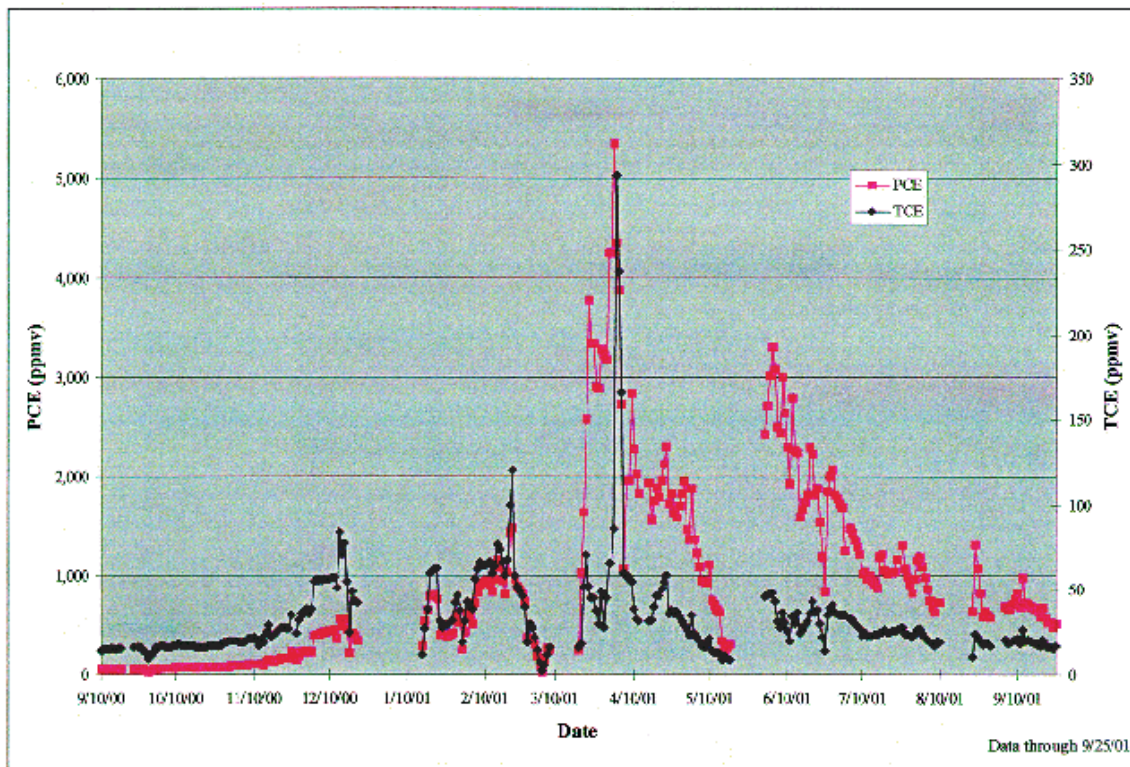
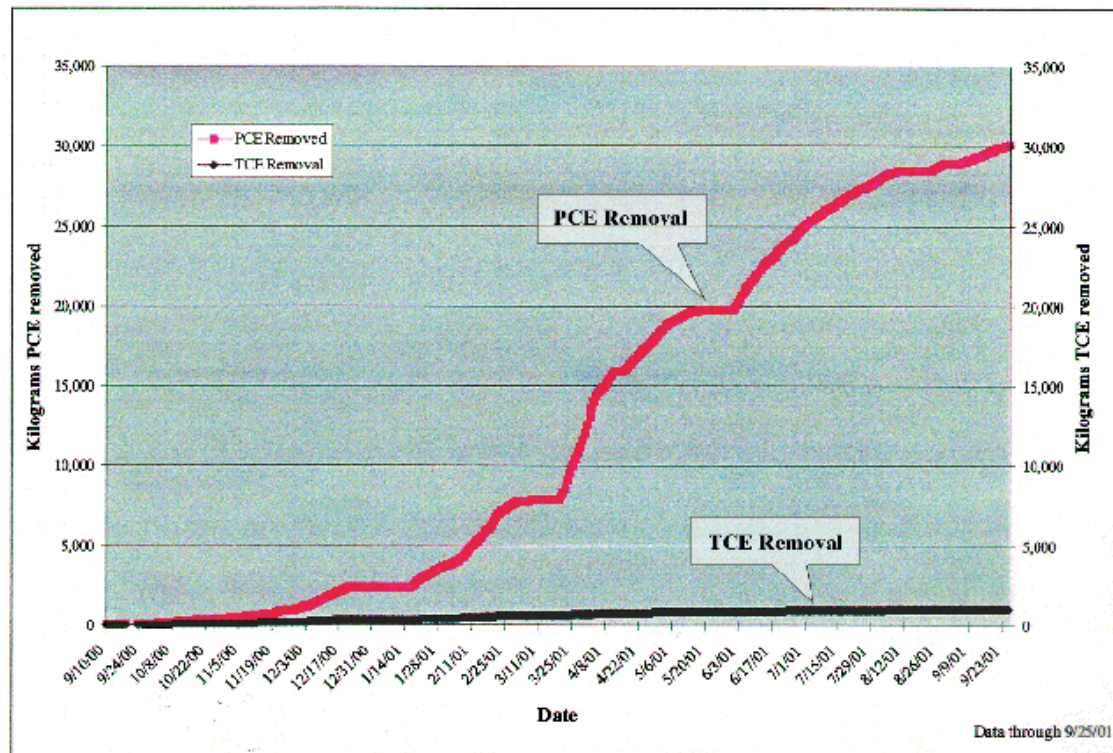


Figure 4. Cumulative Mass Removal Rates for PCE and TCE [1]



From May to September 2001, vapor extraction data indicated that the majority of the contaminant mass removal was coming from within the periphery of the target zone (DUS-010 consistently recorded the highest concentrations of vapor). The vendor indicated that the residual contaminant removal pattern may have resulted from the volatilization of PCE and TCE bound in clay horizons above 20 ft bgs (above the DUS/HPO remedial target zone). The vendor also indicated that the data from the last two months of operation suggested that the source of this contaminant had not been heated much, supporting the interpretation that it was volatilized from horizons above the target zone.

The mass of contaminants destroyed in the subsurface by HPO was not quantified. However, based on estimates from other projects and experimental work at Lawrence Livermore National Laboratory, the vendor indicated that the amount of dissolved phase contaminants expected to be destroyed by HPO would be at least 10% (6,800 lbs) and could be as high as 30% (20,000 lbs) of the contaminant removed by DUS. Information was not provided about any potential indicators for the amount of contaminant removed by HPO.

The following information about wastewater stream totals, steam injection rates/pressure, vapor extraction temperatures, and subsurface thermal monitoring were provided by the vendor.

#### Wastewater Stream Totals:

At the beginning of the pilot demonstration, groundwater accounted for the majority of the wastewater collected. Following steam breakthrough in the saturated zone, condensate increased and at times exceeded the groundwater production rates. In comparison to the vapor stream, the wastewater stream produced a very small amount of contaminant. This was because PCE has a solubility limit of 150 ppm, which would only be sustained in condensate when the vapor stream was saturated with PCE. Low wastewater production rates combined with a low solubility contaminant like PCE yielded a modest amount of contaminant removed via groundwater extraction (about 75 lbs PCE and 10 lbs TCE).

#### Steam Injection Rates/Pressures:

Steam injection rates regularly increased from startup to a maximum rate of 20,000 lb/hr in February 2001 and continued at that level through March 2001 and most of May 2001. Injection pressures never reached the design injection pressures (design injection pressures were 60, 40, and 26 psig), particularly in the deep and intermediate wells (DUS-004 through DUS-009). Injection pressures remained constant over the life of the project, indicating a lack of blockage in the wells that might require well maintenance.

#### Vapor Extraction Temperatures:

Vapor extraction temperatures can be found in Figure . The vendor reported that maintenance of very high vapor temperatures in the extracted vapor stream (+93°F) would have required almost continuous steam injection. The reduced steam injection rates used in June to September 2001 caused only minor decreases in vapor extraction temperatures, indicating that considerable latent heat remained in the subsurface.

#### Subsurface Thermal Monitoring Data:

ERT images identified several lithologic layers, particularly a zone at approximately 100 ft bgs that was slower to heat than surrounding layers. Boring logs indicated that those layers are fine-grained clay horizons and were slow to show changes in electrical resistance and heat up or cool down. For example, during a shutdown period, more permeable horizons cooled slightly but the finer grained layers showed increasing temperatures caused by.

## COST OF THE TECHNOLOGY SYSTEM

### COST DATA [2]

For this pilot demonstration, the Interstate Technology Regulatory Council (ITRC) reported a project cost of \$29/cu yd, but did not indicate what was included in the cost or how it was calculated. The ITRC stated that cost for steam generation and treatment of vapor and dissolved phase contaminants were not included in this cost, because these services were provided by SRS.

Information was not provided about the projected cost for using this technology on a full-scale basis at SRS.

## OBSERVATIONS AND LESSONS LEARNED

### OBSERVATIONS AND LESSONS LEARNED [1,2,3]

A one-year pilot demonstration of steam injection lead to the removal of 31,000 kg (68,000 lbs) of PCE and TCE. The target treatment area was heated to near 90 °C and air was injected to support HPO, leading to an additional, unquantified amount of contaminant destroyed in situ by HPO.

The following lessons learned were provided by the vendor:

- During the DUS/HPO process, steam was injected through wells that were specially designed to withstand elevated pressures and temperatures. It was important that existing and new monitoring wells be similarly designed or removed prior to steam injection. If non-high temperature wells are left in place, then DNAPL likely would have condensed and collected within the target region.
- During the later stages of system startup and testing, the jet pump designed for groundwater extraction was not performing well. Using steam as the motive fluid combined with the depth to groundwater was not sufficient for pumping. Other fluids such as air or water were determined not to be cost effective. To address these concerns, a 15 gpm high-temperature electric submersible pump was installed in November of 2000.
- During the span of system operations, there was little loss of injection capability, which would have resulted in increasing pressures for constant injection rates. High injection rates with low injection pressures indicated that the formation had the ability to receive large volumes of steam. Consequently, the steam injection rate was limited only by the amount of steam that could be delivered.
- The most difficult region of the target zone to heat was the shallow portions at the center of the treatment area. The most likely reason for this was the circulation of air from the surface to the shallow zone. Restricting vapor extraction and continuous long-term steam injection sufficiently heated this portion after five months of steam injection.
- Removal rates could have been considerably higher had there been the capability for contaminant destruction in the vapor stream. However, the SRS SVE unit was not configured for contaminant destruction.

- During system operations, both thermocouple and ERT systems experienced shutdowns due to lightning ground strikes in the immediate vicinity of the project area. The ERT experienced fewer but more prolonged shutdowns from the lightning strikes due to its complexity.
- On November 26, 2000, the knockout tank was reported to be physically rocking on its base and the SVE unit was shut down. It was determined that the concrete pad supporting the knockout tank was not level and the support used to stabilize the tank was no longer in place. The restarting of the SVE system disturbed water in the tank causing the water to slosh and the tank to rock. The support was relocated to the base of the unit and checked daily; there was no recurrence of the problem over the remainder of the project.

## REFERENCES

1. Integrated Water Resources. "Deployment of a Dynamic Underground Stripping-Hydrous Pyrolysis/Oxidation System at the Savannah River Site 321-M Solvent Storage Tank Area, Final Report. September 2002.
2. ITRC DNAPL Team Case Study Report: 321 M Solvent Storage Tank Area, Savannah River Site, Aiken, South Carolina. September 2002.
3. Project Descriptions, Integrated Water Resources. Savannah River Site- 321-M Solvent Storage Tank Facility. Savannah River, South Carolina.