DYNAMIC UNDERGROUND STRIPPING AND HYDROUS PYROLYSIS/OXIDATION OF PCE AND TCE AT SAVANNAH RIVER SITE

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ABSTRACT

DOE-funded technologies developed at Lawrence Livermore National Laboratory and licensed by Integrated Water Resources from the University of California are used for the design, construction and ongoing operation of a thermal remediation system for the removal of the solvents PCE and TCE from a contaminated aquifer at the former Solvent Storage Tank area at Savannah River Site, Aiken, South Carolina. IWR's program for the site involves the application of a suite of complementary thermal remediation technologies:

- Dynamic Underground Stripping – Engineered combination of steam injection and vapor and groundwater extraction;
- Hydrous Pyrolysis/Oxidation (HPO) — Destruction of underground contaminants through oxidation in the presence of injected steam; and
- Electrical Resistance Tomography (ERT) – Geophysical imaging technique for tracking subsurface thermal changes during DUS/HPO operations.

The target zone for steam injection extends over an area of approximately 100 feet by 100 feet, from 20 feet below ground surface to 160 feet below ground surface. Approximately 13,000 kg of the contaminants PCE (90%) and TCE (10%) are estimated to exist throughout this volume. Sands and silts comprise the majority of the subsurface volume, with several thin silt-clay layers.

During the first four months of operation, cumulative PCE and TCE removal is more than 2 tons: 2,400 kg and 300 kg PCE and TCE removed. The highest peak removal rates observed to date are approximately 100 kg/day combined PCE and TCE and removal rates have increased steadily during the first months of operation. Depending on the presence of PCE and TCE mass in excess of the estimate, IWR's active steaming operations will conclude within a few months. The final months of operation will keep the formation both hot and oxygenated to enhance in situ destruction of dissolved phase contaminants by Hydrous Pyrolysis/Oxidation.

INTRODUCTION

The Dynamic Underground Stripping - Hydrous Pyrolysis Toolbox (1, 2), developed at LLNL and UC-Berkeley, and patented by University of California, provides a solution for quickly removing volatile organic contaminants where other technologies may be expected to take many decades or more to succeed. As such, DUS/HPO offers the possibility of solving the "open-ended" remediation process and for reaching stringent cleanup requirements, including reduction of DNAPL contaminant concentrations to drinking water standards. In results from two field-scale applications of DUS/HPO, the technology toolbox has achieved remediation performance in less than one-tenth the time of conventional pump-and-treat methods, both above and below the water table, and at less overall cost.

The advantage of the combined DUS and HPO technologies is their accelerated rate of remediation, achieved by the input of thermal energy in the form of steam injection and direct electrical heating of the subsurface. DUS mobilizes free-product and adsorbed contaminant in the subsurface by volatilizing it through steam injection heating of relatively permeable material. Vapor extraction then removes this volatilized material. The DUS/HPO toolbox technologies are effective in both saturated and unsaturated conditions. Many other technology options available for cleanup cannot change the very low solubilities of these contaminants in water, or cannot mobilize the contaminants for extraction from subsurface regions where they are physically and chemically bound to geologic materials. At the Savannah River Site ("SRS"), where contaminants are contained primarily in permeable materials, contaminants bound in fine-grained layers resistant to direct steam penetration can be mobilized and removed through conductive heating simply by heating the adjacent materials with steam.

HPO uses steam injection to heat and oxidize contaminants in the subsurface to produce benign products. Rather than injecting steam to volatilize and mobilize contaminants, HPO oxidizes contaminants in place by taking advantage of the thermodynamically unstable nature of these organic contaminants. For SRS, IWR's project focuses on volatilization/mobilization of DNAPL for removal to surface, and on maximizing the amount of HPO *in situ* destruction after the bulk of DNAPL mass removal has occurred.

Electrical Resistance Tomography (ERT) is important to DUS operations because it allows near real-time monitoring of the progress and distribution of the subsurface steam front in the subsurface. ERT is used as a primary monitoring tool, and is also used to augment thermal probe data. The monitoring data can then be used to adjust specific controls on steam injection, electrical heating and vacuum extraction for maximum contaminant destruction and recovery.

SAVANNAH RIVER SITE SOLVENT STORAGE AREA DUS/HPO DEPLOYMENT

The IWR/IT deployment of DUS/HPO technologies at Savannah River Site meets key criteria for success, including:

- Successful source area contaminant mass removal;
- Applicability to both saturated and unsaturated subsurface materials from clayey-silt to sand, applicability to DNAPL contaminants PCE and TCE, together with dissolved and residual contamination;
- Successful subsurface monitoring of remedial actions and processes; and

- Acceptance and approval by state and federal regulatory agencies.

Design Overview

The IWR/IT design approach reflects several principles and technology deployment choices important to cost-effective success of the DUS/HPO/ERT program at SRS (refer also to Figure 1):

- Team qualifications necessary for thermal modeling, system design, construction, operation, monitoring and permitting of a high-temperature, high peak flow-rate remediation system.

- Iterative process for incorporating site characterization data from injection well borings into final design modifications.

- Injection well clusters. IWR's design incorporates 3 deep injection wells near the perimeter of the target zone, each screened in the lowermost 10 or 20 feet of the formation overlying an aquitard that forms a base of the treatment zone. Our thermal modeling shows that this design optimizes heating of the full saturated region, creating a kind of hot plate to mobilize contaminants both up and in toward the central system extraction well.

- The vadose zone and contaminants within it are heated from below (from steaming in the saturated zone) and by direct injection of steam at higher levels within the stratigraphy – using an intermediate and a shallow injection well in each of the injection well clusters. Screen locations were determined by thermal modeling of the steam front, specific targeting of fine-grained layers, and operational considerations.

- One central extraction point, with a groundwater pump at the bottom of the well to remove DNAPL product and contaminated groundwater, and for hydraulic control of the target zone; this ensures that all mobilized contaminants and contaminated groundwater are directed to the center of the treatment zone and away from clean areas outside the target zone. Vapor-phase contaminants mobilized from the saturated zone are captured by the vacuum extraction system through extraction well screens.

- The surface treatment system is designed to accommodate the large volumes of effluent which are mobilized as increasing formation temperature mobilizes liquid DNAPL, increases dissolved concentration of NAPL in groundwater, and produces vapor-phase NAPL as temperature rises to the PCE-water azeotrope (88 °C). Because contaminants are recovered in all 3 forms, the system includes components to cool and separate the waste stream, and to divide NAPL product from contaminated wastewater. The IWR/IT system routes NAPL to surface storage tanks, contaminated water to the SRS treatment facility, and vapor to the SRS SVE unit.

- IWR's monitoring system is an integrated program of chemical and physical monitoring of the surface treatment system, subsurface imaging of thermal energy distribution using Electrical Resistance Tomography ("ERT") and subsurface monitoring of temperature from direct thermocouple measurements. Each of these monitoring techniques has significantly greater value when used in combination with the other techniques.

- Industrial safety elements are integral and important, and the DUS/HPO thermal methods require special focus on industrial safety and effluent handling.

Thermal modeling and hydrogeological analysis are the basis for IWR's project design for subsurface well installation, and for steam injection rates and pressures. We draw also from our experience with other DUS/HPO/ERT projects, and from the 10-year history of thermal remediation expertise of the IWR/IT team-members.

Because the region surrounding the treatment zone is uncontaminated, operations started with heating just outside the impacted area, driving contaminants inward to a centrally-located extraction well. Over time, the thermal front migrates inward so that the entire volume of saturated and unsaturated material in the target zone is brought to steam temperature. For this project, maximum steam injection rates, distributed to multiple points in the well clusters is 20,000 pounds/hour

Thermal Modeling

Thermal model calculations provide information necessary for developing injection and extraction parameters, and for operations guidance. IWR analytical thermal analysis estimated that during approximately 60 days of steam injection, the steam zones will advance through the saturated portion of the treatment zone to a radius of about 50 feet around each injection well. This model result is corroborated by the observed migration of steam zones (see "System Performance" section below).

IWR's analytical model utilizes equations from Prats (3), which was based originally on Marx and Langenheim (4), with modification to include heat loss to adjacent formations. The model of the steam front shape is taken from van Lookeren (5). These models have been developed over the last several decades for use in subsurface oil recovery operations, and portions of the work are applicable to, and can be specifically modified for, detailed application to DUS/HPO projects. The analysis is made using conservative estimates and provides a guideline for the project's scale.

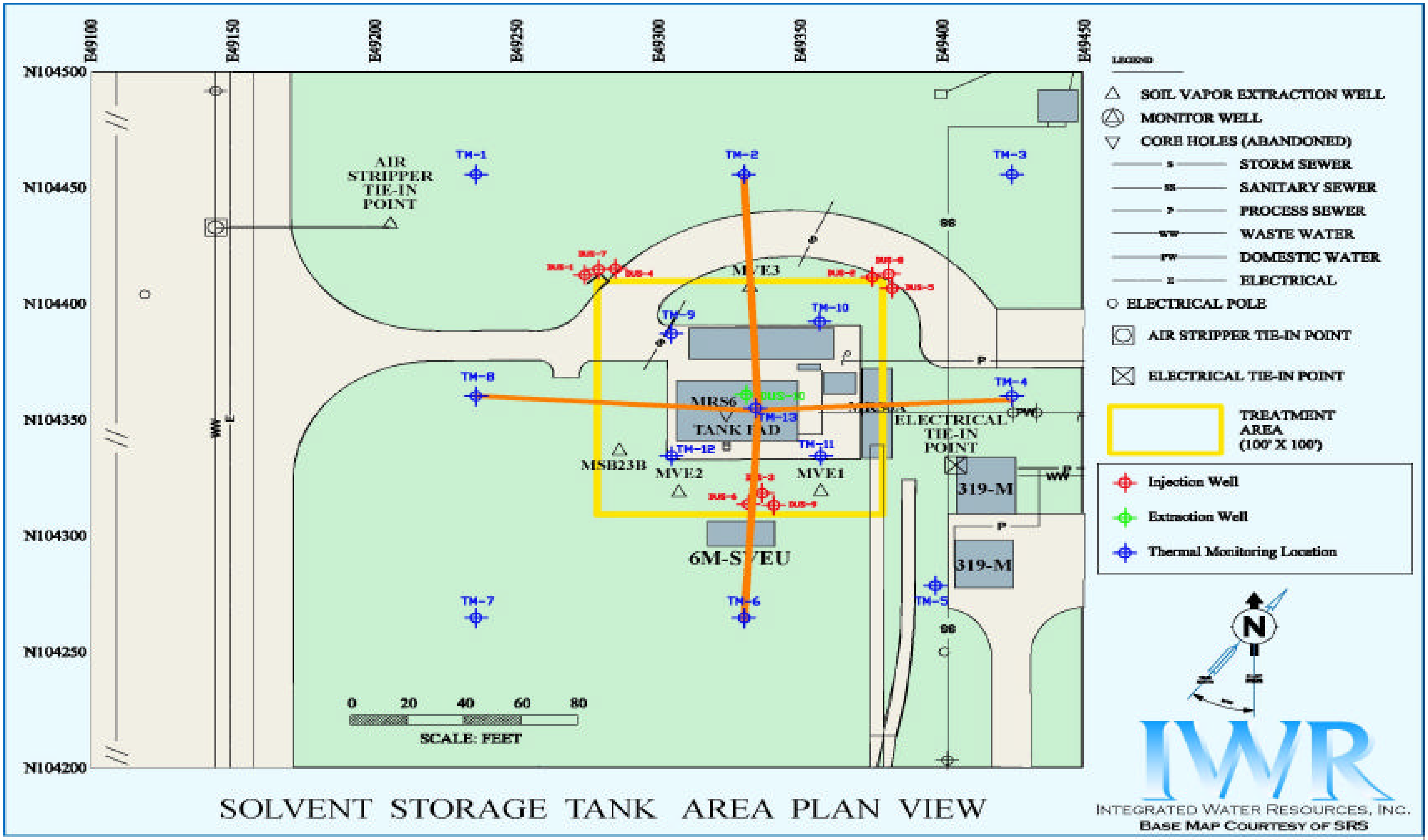

Fig. 1. Map of Savannah River Site Dynamic Underground Stripping project site.

Monitoring and Controls

Monitoring is a critical component of IWR's design for the SRS project. Monitoring includes devices for measuring subsurface thermal changes and steam migration (thermocouples and Electrical Resistance Tomography electrodes) as well as water quality sampling.

Process monitoring such as rates and chemistry of recovered effluent are also designed into the system. Robust monitoring is important because it provides a near real-time means of tracking steam front migration in the subsurface. This allows detailed and timely adjustment of operational parameters, to ensure that heating occurs only where and when it is desired, and to ensure that surface systems are meeting performance demands.

For Electrical Resistance Tomography monitoring, IWR emplaced 5 vertical electrode arrays through narrow-diameter boreholes – 4 at the periphery of the site and one in the middle (Figure 1). The peripheral locations are outboard of the steam injection wells and the boreholes were grouted after emplacement of the ERT equipment.

In addition to the ERT electrodes, each borehole with an electrode string also includes a thermocouple string. Having these two instruments together in the same borehole does not change the performance of either device. IWR's design also includes 4 additional thermocouple strings placed in intermediate locations at the site, and thermocouples at the base of the steam injection wells (Figure 1).

The surface effluent system contains ports and equipment to acquire samples and measure pressures, temperatures and volumes within storage vessels. Such information serves the dual purpose of important operational control for the treatment system itself, and for interpreting subsurface data and processes within the thermal treatment zone.

Effluent flow through the surface system provides important information for system performance and NAPL recovery from the subsurface. IWR's design capitalizes on this information capacity by using a variety of low-cost monitoring devices such as thermocouples, effluent sampling ports and flowmeters at key locations in the surface treatment system. Such devices also provide important controls and warnings for system safety.

SYSTEM PERFORMANCE

During the first 4 months of system operation, IWR/IT's DUS/HPO deployment has successfully heated large portions of the target region to temperatures at or in excess of the azeotrope for PCE and TCE in water (88 °C and 73 °C, respectively). Steam temperatures of 100°C or more (dependent upon depth) are observed within specific geological strata at significant distance from the injection wells (Figure 2). In addition, the groundwater pumping and vapor extraction system has removed over 2,400 kg of PCE, together with approximately 300 kg TCE as of December 21, 2000 (Figure 4).

As the full target volume increases in temperature, higher recovery rates are expected. In addition, chemical data suggests that HPO is occurring, even during early stages of the deployment.

Heating of the target volume is occurring as expected. Monitoring wells at intermediate distance from the injection well clusters (Monitoring points #9 and 10) have shown progressive heating of: (1) the lower saturated unit, which in places is also relatively higher permeability; (2) intermediate unsaturated units; (3) intermediate fine-grained layers which have heated conductively over several weeks in response to more rapid heating of the permeable layers above and below; and (4) the uppermost unsaturated units.

Monitoring of the central target zone (Monitoring point #13) also shows the impact of extraction on heating of the unsaturated zone, with relatively slower temperature increases, compared with the intermediate or exterior (Monitoring point #8) monitoring points. Detail of these trends is provided by the ERT monitoring (Figure 3), which provides higher resolution of the stratigraphic differences within both the unsaturated and saturated portions of the target zone.

The thermocouple and ERT data combined provide a detailed view of subsurface processes during the DUS/HPO deployment. For example, relatively higher permeability units which reached temperatures in excess of 100ºC during active steaming operations (December 17 profiles in red on Figure 2) gave up energy relatively quickly as the steam front collapsed in the weeks that followed, when steam injection was halted temporarily. In temperature profiles recorded in early January (black lines on Figure 2), before renewed January steam injection operations, more fine-grained layers increased in temperature during the shutdown period. Viewed in concert with heating rates and vapor extraction patterns during active operations, the post-shutdown heating of the fine-grained layers shows how conductive heating is also an important component of the Dynamic Underground Stripping process.

Differences in the rate and distribution of subsurface heating is also shown in the ERT images. Figure 3 shows 2 ERT cross-sections through the treatment zone; TM2 - TM13 - TM6 is oriented north-south; TM8 - TM13 - TM4 plane is oriented west-east. Locations of injection wells are projected onto the ERT planes, with notation indicating the steam injection screen intervals. Stratigraphic control over thermal migration and heating rates in the subsurface are indicated by the varying electrical resistivity. A relatively prominent fine-grained layer ("clay" layer annotation in Figure 3) is shown to heat more slowly than the surrounding materials. The ERT and thermocouple data are used together to help guide operations and achieve efficient and controlled heating of the target zone.

At current extraction rates (recovered, condensed effluent is consistently in excess of 500 ppm PCE), PCE and TCE removal is limited as much by the surface treatment system discharge permit (for cost savings, some existing SRS surface treatment equipment was used in the treatment compound) as by the subsurface conditions that now produce contaminant to the central part of the target zone and the extraction well.

With nearly all of the target zone at or above steam temperature within a few months, ever-increasing rates of contaminant recovery and over 2 tons of recovered PCE and TCE in 4 months of operations (Figure 4), the IWR/IT project at Savannah River provides an excellent example of successful DUS/HPO deployment for source removal of chlorinated solvents.

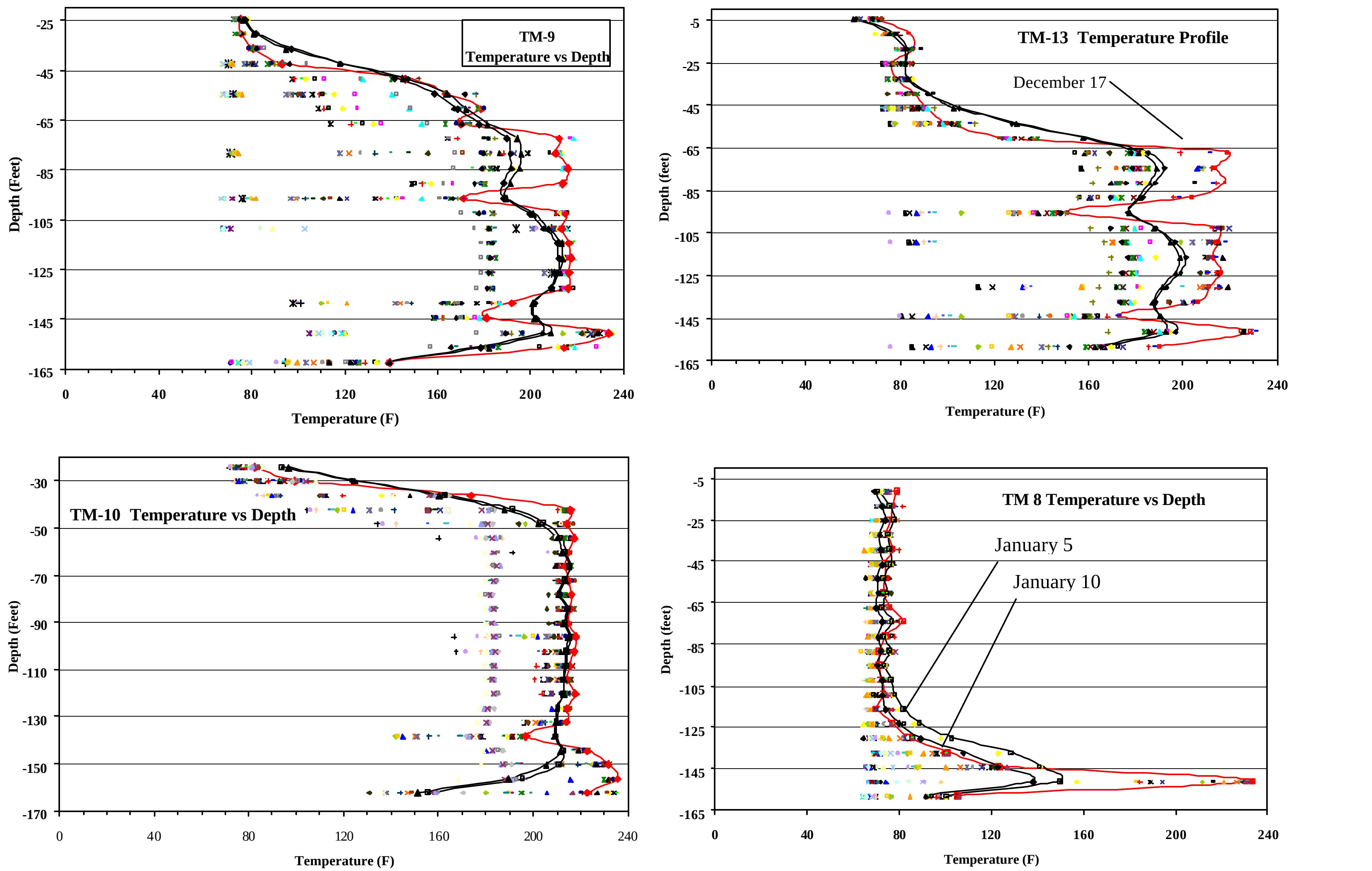

Fig. 2. Plots of temperature data from thermocouple arrays; refer to Figure 1 for locations.

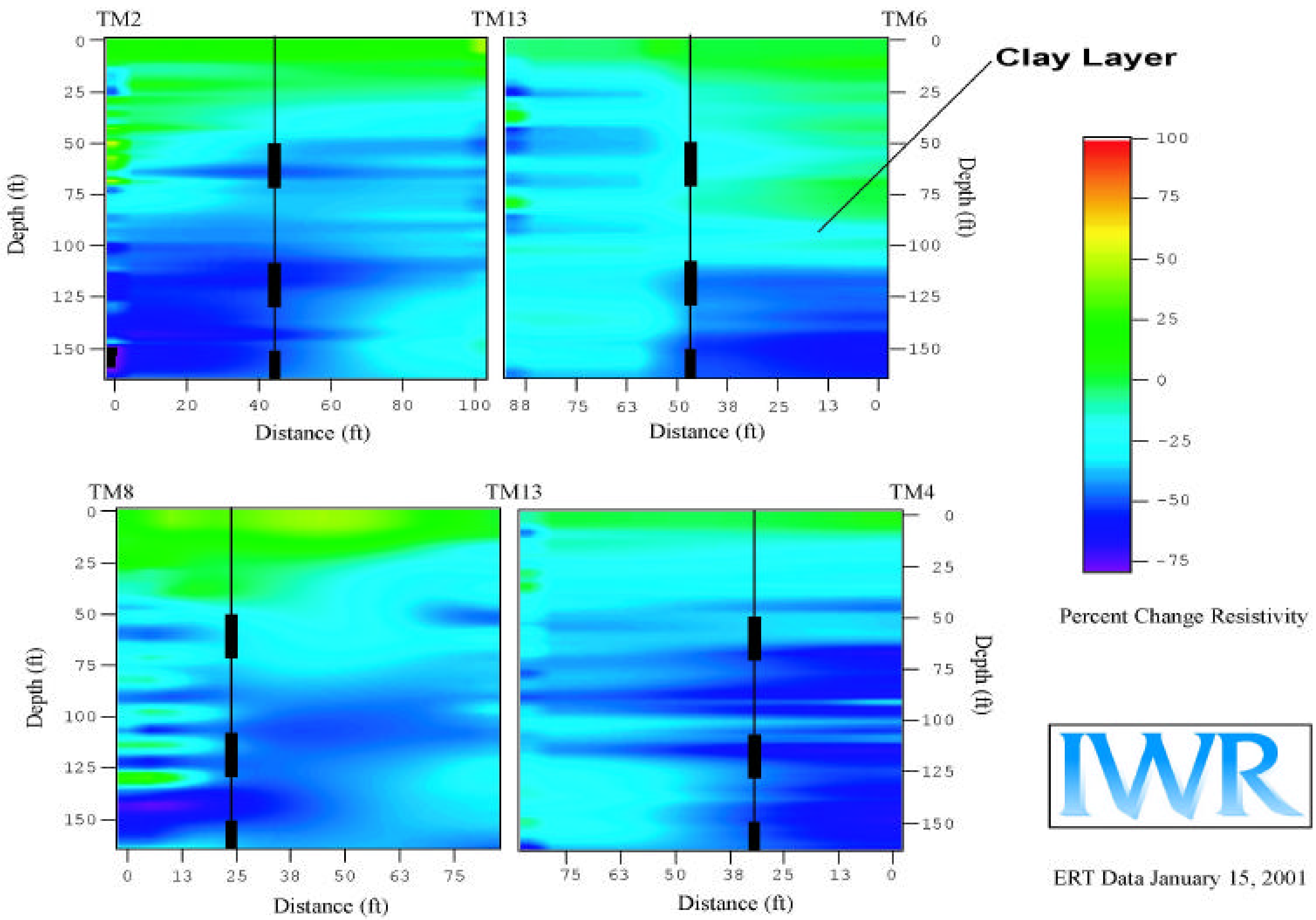

Fig. 3. ERT percent change in resistivity between data collected 1/15/01 and background collected 8/24/00.

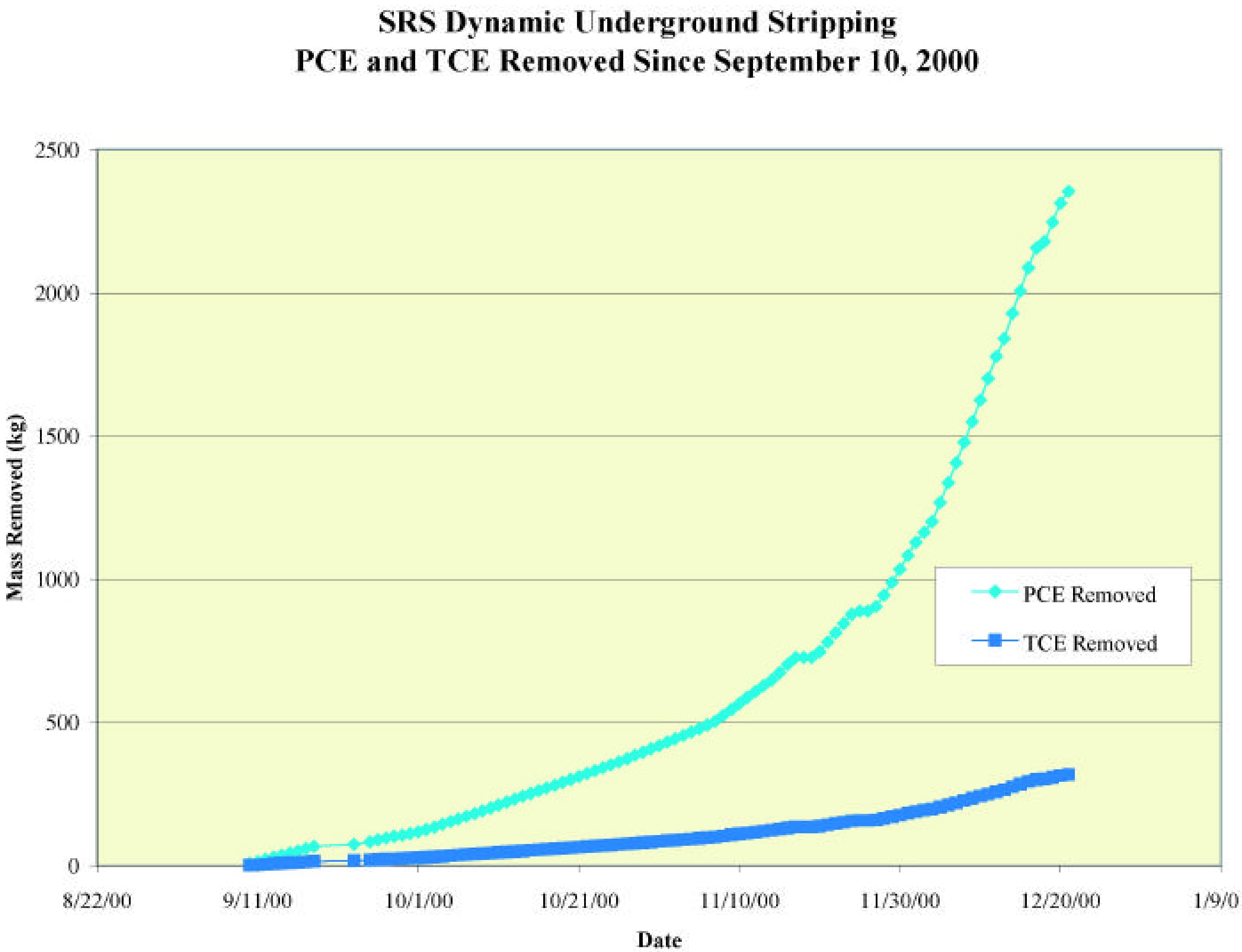

Fig. 4. Plot of contaminant mass removal from September 10 through December 21 for the DUS project at SRS.

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