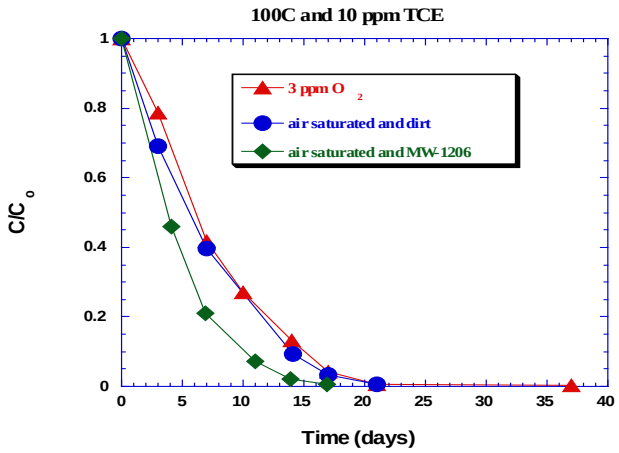
Dynamic Underground Stripping with Hydrous Pyrolysis Oxidation -
An *In Situ* Destruction of DNAPLs and Dissolved Contaminants in Groundwater

Groundwater contaminated with chlorinated solvents, either as dense non-aqueous phase liquids (DNAPLs) or dissolved components, are a widespread problem at several hundred DoD installations. The EPA has estimated there may be over 5,000 DoD, DOE, and Superfund sites contaminated with chlorinated compounds. Currently, pump-and-treat is the most commonly used and accepted groundwater treatment method. However, this technique leads to a remediation project where the total time and cost for cleanup are not well defined. Cleanup efforts can proceed for decades because of the occurrence of contamination in the fine-grained sediments. Additionally, pump-and-treat preferentially cleans the coarser grained soils and more permeable units, while leaving contamination in the finer grained units. Unfortunately, it is in the fine grained source regions for contaminant plumes, where the concentrations are the usually the greatest. Using the pump-and-treat method for remediating groundwater plumes can lead to an open-ended solution and it is virtually impossible to know when or if an aquifer will reach regulatory standards. Also, the cost per mass of contaminant treated by pump-and-treat dramatically increases over time because of large volumes of groundwater with increasingly small contaminant concentrations is being extracted. In contrast, a remediation method which destroys the contamination *in situ* by volumetric techniques can be a more effective solution in terms of total cost and cleanup time.

Dynamic Underground Stripping (DUS) combined with Hydrous Pyrolosis Oxidation (HPO) are innovative processes for the destruction and removal of DNAPLs and dissolved organic components in the soil and groundwater without surface treatment (*insitu*). DNAPLs and dissolved organic contaminants are rapidly oxidized to form carbon dioxide and non-toxic ions when heated to temperatures near the boiling point of water (thermal treatment technology). The DUS/HPO method utilizes the proven experience of heating large volumes of soil and groundwater for the *in situ* destruction of volatile organic compounds (VOCs). Steam and oxygen are injected together, building a heated oxygenated zone in the subsurface. When injection is halted, steam condenses and contaminated groundwater returns to the heated zone. The contaminated groundwater then mixes with the heated condensate and oxygen, destroying the dissolved contaminants. This remediation method takes advantage of more rapid chemical reactions, which occur at steam temperatures, as well as the large increase in mass transfer rates, which make the contaminants more available for destruction. Most environmental processes cannot be observed while operating. Electrical resistance tomography (ERT) gives the operator detailed views of the hot and cold zones at their site on a daily basis. Heating soil and groundwater produces such a large change in electrical properties that it is possible to obtain images between wells (inverted from low voltage electrical impulses passed between wells) of the heated volumes by ERT imaging, similar to a CAT scan.

Experimental work with VOCs at LLNL has suggested that *in situ* thermal oxidation of these compounds by HPO forms the basis for a new remediation method (Knauss, 1997). The results of hydrothermal oxidation uses both dissolved O_2 gas and mineral oxidants naturally present in the soils (e.g., MnO_2) to demonstrate that PCE, TCE, and TCA can be rapidly and completely degraded to benign products at moderate conditions in thermal remediation. Polycyclic aromatic hydrocarbons (PAHs) also have a large thermodynamic driving force favoring oxidation amenable to *in situ* destruction. DUS/HPO is a process that can also be used for the *in situ* destruction of solvents, including DNAPLs and dissolved contaminants. DUS/HPO is quite capable of remediating contaminants to below MCLs, including TCE, TCA, PCE, toluene, MTBE, pentachlorophenol, and PAHs. DUS/HPO offers the promise of rapid cleanup and closure of contaminated sites on the order of a few months to a few years.



Oxidation rate experiments in with comparable oxygen and TCE content, showing the minimal effects of the addition of LLNL site groundwater and site soil. TCE is destroyed to below 5 ppb in less than four weeks at 100° C; the reaction is about 2 ½ times faster for each increase in temperature of 10° C.

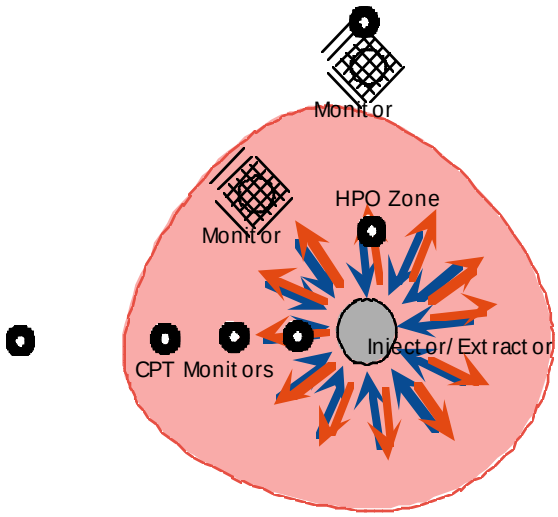
LLNL completed the cleanup and closure of a moderately sized VOC (primarily BTEX) spill site in which thermal cleanup methods, and the associated control technologies, were used to remediate over 10,000 gallons of gasoline trapped twenty feet below the standing water table (Newmark, 1992, 1994a). The spill originated from a group of four underground tanks, from which an estimated 17,000 gallons of gasoline migrated into the soil, eventually reaching the water table, where it spread out. The water table was located at about 100 ft below ground surface. Rises in the water levels from changes in agricultural use trapped considerable free product below the water table. Soils at the site are alluvial, ranging from very fine silt/clay layers to coarse gravels. The site was prepared for long-term groundwater pump-and-treat with vapor extraction. Product recovery rates were about 2.5 gal/day. Six steam injection/electric heating wells were placed around the free product in an irregular circle as was determined by the shape of the free product; and three additional electric heating wells were placed near the center of the spill. Eleven monitoring and ERT imaging wells were placed within and outside the target area to provide control of the heating processes. In an 1 year operational period, followed by a monitoring period of two years, a volume of soil of approximately 100,000 yd^3 was cleaned and the extraction and treatment operations were terminated. Following removal of more than 99% of the contaminant and achievement of MCLs in groundwater for five of the six contaminants, the site is now being passively monitored under an agreement with the Cal-EPA and US EPA Region 9. The purpose of the this demonstration was to utilize previous LLNL experiments in heating soil for remediation of gasoline and other PAHs, coupled with the knowledge of *in situ* reaction chemistry to destroy VOCs, and to show that contaminated soil and groundwater can be cleaned quickly at a low cost.

The DOE LLNL is currently operating a DUS/HPO demonstration project at the Southern California Edison (SCE) pole yard in Visalia, CA, for the remediation of creosote, dioxins, and some secondary contaminants (solvents). In 1997, a pilot-scale steam injection groundwater and vapor extraction system was installed and consisted of 14 steam injection wells surrounding the plume of soil and groundwater contaminants. Steam is injected into the ground at a depth of 80-100 ft, forcing groundwater, creosote, and other hydrocarbons towards central extraction wells. In the first 9 months of operation, about 240 million pounds of steam were injected and about 540,000 pounds of contaminants were removed from the subsurface. DUS/HPO has increased the rate of contaminant recovery more than 1000-fold over the existing pump-and-treat system (EPA, 1998). SCE now predicts the site will be cleaned up in years instead of decades. The DOE subsurface contaminants focus area (SCFA) plans to complete this effort in the next year, pending the preliminary results of the project, which have been very successful. After steam injection and extraction is stopped, SCE will continue to inject air into the subsurface to enhance oxidation by HPO and biological degradation processes.

HPO builds upon the past success of DUS (steam injection), which is used to remediate fuel hydrocarbon sites. As such, the basic process of steam injection for remediation has been accepted by both the

stakeholder and regulatory communities. Also, the ability to inject steam in a controlled and engineered manner in a heterogeneous aquifer has also been established. The HPO process relies on getting heat, adequate oxygen, and contaminant in the same place at the same time. One feasibility check is to assess the ability of the site soils to consume oxygen, and thereby reducing its availability to destroy contaminants by the oxidation of organic matter. Bench scale experiments with site soils and groundwater will reduce this risk, as will a thorough site characterization.

The NFESC proposed DUS/HPO project will focus primarily on remediating DNAPLs and dissolved chlorinated solvents. A preferred small-scale implementation for demonstration of steam and air will be injected into a steel-cased well to build a steam zone in the subsurface. DUS injection will be stopped, allowing the groundwater to return to the heated zone, where the HPO destruction reaction can rapidly occur. Some ground water will be pumped out of the injection well, removing the condensed steam and any additional native groundwater in which the HPO reaction has removed all contamination. This water will be used to feed the boiler for the next injection cycle. The injection is monitored so that more water is always extracted than injected to guarantee that no contaminants are further dispersed.



This demonstration's goal would be cleanup of TCE and/or other chlorinated solvents from a moderately permeable aquifer. Proof of cleanup would be principally by water chemistry. About 20,000 yd^3 of aquifer material would be targeted for a deep site or 5,000 yd^3 of for a shallow site. About 2 months of set-up and 1 year of operation would be required. The test will be run in a single, steel well using an injector assembly. The test will be optimized for *in situ* destruction (no surface removal contamination). Existing wells will be used for chemical analysis of groundwater. Control of steam injection will be maintained by cone-penetrometer (CPT) emplaced temperature and ERT imaging probes.

This demonstration project would need to use steel extraction wells for use in testing; at least two steel-screened monitoring wells in a treatment zone; natural gas or plant steam; disposal or allowed reinjection of any produced water; characterization (zone thickness, initial concentrations, hydraulic parameters); and normal water quality monitoring to confirm cleanup effectiveness over time. The site must be addressable by a CPT rig.

To evaluate success, it will be necessary to have had a thorough site characterization to define the initial contaminant concentrations and their distributions in the targeted aquifer. In a test steam injection process it is also necessary to measure how much the contaminated groundwater was displaced by the injection process and where the injected steam actually went. This is accomplished through the use of a monitoring network of piezometers, thermocouples, and electrodes for ERT imaging. Data from these can be used to establish mass and thermal fluxes in the contaminated aquifer. In addition, a high temperature fluid extraction system has been developed that enables direct measurement of fluid chemistry under all expected conditions. Using this and tracers injected with the steam, it will be possible to quantify reduction in contaminant mass and attribute it to the DUS/HPO process and not some other mechanism.

HPO provides a means to rapidly destroy contamination in situ through-out the entire aquifer. Because it works by heating the entire subsurface, it's costs are scaled volumetrically. Similarly, total cleanup time is estimated as the total time to heat and destroy contaminants in the designated contaminated volumes. Current commercial implementation costs for soil cleanup ranges from about \$100 to \$500/m^3. By using

DUS/HPO, it is estimated that soil and groundwater remediation could be completed at about $75/m^3 of soil, which equates to about $50/kg of contaminant. This can yield a cost savings ratio of up to 1000 times the current pump-and-treat costs. Using the DOE's cost estimates for the HPO technology at Visalia, the total costs for groundwater cleanup using pump-and-treat would be about $45M over 50 years. By using HPO, it was estimated that the groundwater cleanup could be accomplished at a cost of $14M over 2 years with a savings of about 1/3 of the total estimated costs. With the DoD having several hundred sites with solvent contaminated groundwater, it is estimated that several $$ Billion could be saved by using the DUS/HPO technology, versus using the long-term pump-and-treat systems. The cost of remediation has been found to be dependent on the volume of soil or groundwater to be cleaned. This is readily comparable with a method such as excavation, but is difficult to compare to the primary used pump-and-treat method. Pump-and-treat may address wide areas but generally only affects a few narrow sections of soil that permit the passage of large amounts of water. Where groundwater flows readily, the soil is typically cleaned, and less porous soils often remain contaminated for longer periods.

Proposed project tasks, deliverables, and estimated time after receipt of funding from ESTCP:

Task 1: Select DUS/HPO technology demonstration site(s) (3-months).
Deliverables: Demonstration project and execution work plans.

Task 2: Install CPTs with monitoring equipment and chemical monitoring systems in wells (6-months).

Task 3: Install steam systems and injector/extractor (12 months).

Task 4: Initiate and complete DUS/HPO field demonstration test (18 months).

Task 5: Complete test data evaluation and reporting (24 months).
Deliverables: Final DUS/HPO Technology Demonstration Report & Cost and Performance Report.

It is anticipated that one of the currently licensed firms in thermal remediation technologies, including the DUS described above, would participate as a partner in this demonstration. DUS and its HPO component technologies are available for licensing from the University of California and LLNL. After the ESTCP demonstration project reports and deliverables have been reviewed and finalized by the proposal partners, they will be transitioned with various DoD ESTCP, DOE SCFA, EPA TIO & ORD, academia, and private interests.