

Heat it All the Way - Mechanisms and Results Achieved using In-Situ Thermal Remediation

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ABSTRACT: In situ thermal remediation technologies have been proven to reach very low soil and groundwater concentrations by eliminating the dense non-aqueous phase liquid (DNAPL) source and reducing dissolved and adsorbed chlorinated volatile organic compound (CVOC) concentrations to near non-detect levels. For chlorinated solvents, vaporization is the dominant mechanism, as vapor pressure and Henry's law constants increase most markedly with temperature. For effective treatment, pneumatic and hydraulic control must be achieved during the heating period, and a clear path for the generated vapors to an extraction system must be provided. If remedial goals are stringent, target temperatures shall be the in-situ boiling point of the soil and groundwater system, such that a phase change to the vapor state is forced by the heating. During operation, detailed temperature monitoring and process sampling is conducted and compared to the performance calculated based on mass and energy balances. Interim and final sediment sampling is used to verify remedial progress and performance prior to site demobilization.

INTRODUCTION

Recently, results from sites that were heated and treated using in-situ thermal remediation (ISTR) have indicated impressive removal rates for DNAPL source zones in soil and groundwater. Published results from both a U.S. Department of Energy (DOE) site (Young-Rainey STAR Center; Heron et al. 2005), and an industrial facility in the Midwest (LaChance et al. 2004) have documented mass removal efficiencies in the 99.9% range. Soil concentrations of Contaminants of Concern (COCs) below or near non-detect are reported, and groundwater concentrations near or below Maximum Concentration Limits (MCLs) have been observed inside the original source zones. These results appear almost unrealistic, considering the recalcitrant nature of DNAPLs in the subsurface, long-term diffusion processes, heterogeneity of most source zones, and frequently raised questions about DNAPL capture at thermal sites. Other site reports, particularly from sites where Electrical Resistance Heating (ERH) was used, have reported less impressive results, sometimes less than 90% mass removal (Lowry Landfill, CO: Plaehn et al. 2004; ICN Pharmaceuticals, Portland, OR: USEPA, 2004; Navy Bedford, MA: Francis and Wolf, 2004). As more data are emerging, it is becoming evident that thermal remediation spans a wide range of heating methods, and that applications vary from very robust, effective systems to poorly designed and ineffective systems.

This paper reviews the mechanisms behind ISTR critically, focusing on what happens at the pore and micro-scale, as well as larger scale during heating. It will review ways for the contaminants to be mobilized and extracted, and show the most proper design for vapor recovery and capture systems. Several key design elements will be presented, in an attempt to explain why not all thermal projects have achieved the success made possible by the theory, and how achievement of desired results can be much more widely attained.

THERMAL REMEDIATION METHODS

ISTR is gaining acceptance for restoration of NAPL source zones (Davis, 1997). The following ISTR methods are discussed below:

- Steam Enhanced Extraction (SEE).
- Electrical Resistance Heating (ERH).
- Dynamic Underground Stripping (DUS).
- In-Situ Thermal Desorption (ISTD).

Steam has been used to heat the more permeable zones, which are typically sandy layers with relatively low clay and mineral contents. The in-situ process using steam injection and aggressive fluids extraction was named Steam Enhanced Extraction (Udell et al. 1991), and several field demonstrations and full-scale cleanups have been conducted (Udell et al. 1999; Eaker 2003; EarthTech and SteamTech 2003). Mechanisms used in SEE were reviewed critically (Udell 1996).

Both three-phase and six-phase ERH were developed as robust techniques in the 1990's and demonstrated in the field. ERH involves passing electricity through the soil between electrodes, and heating the soil by Joule heating. Laboratory studies demonstrated that thermodynamic changes induced by ERH can lead to very effective removal of chlorinated solvents from silts and clays (Heron et al. 1998). Since the late 90's, several commercial full-scale implementations of both three- and six-phase ERH were completed, some by the trade name Electro-Thermal Dynamic Stripping Process (ET-DSP) (McGee 2003).

The combination of steam and ERH is named Dynamic Underground Stripping, and was demonstrated at a gasoline spill that had resulted in LNAPL contamination above and below a rising water table at the Livermore Gas Pad (Newmark 1994; Daily et al. 1995). This method was used recently to remediate a DNAPL source area at the Young-Rainey STAR Center (Heron et al. 2005).

A robust method for heating soils and groundwater is thermal conduction heating, also named In-Situ Thermal Desorption (ISTD; Stegemeier and Vinegar 2001). ISTD is a soil remediation technology in which heat and vacuum are applied simultaneously. Heat flows into the soil primarily by conduction from heaters typically operated between 500 and 800°C, with the target soil volume being heated to 100°C for VOC removal. As the soil is heated, water is boiled and DNAPL constituents in the soil are vaporized. The resulting steam and vapors are drawn toward extraction wells for in-situ and aboveground treatment. Compared to fluid injection processes, the conductive heating process is very uniform in its vertical and horizontal sweep.

Other thermal methods such as hot water flooding, hot air sparging, and radio-frequency heating were not considered during this review. This review focuses on volatile compounds, and therefore on the methods for which heating to the boiling point of water is sufficient. The higher temperature version of TerraTherm's ISTD technology, used for treatment of semivolatile organic compounds (SVOCs) such as polychlorinated biphenyls (PCB) and coal tar, will not be discussed.

REMEDICATION MECHANISMS FOR CVOC CONTAMINANTS

For thermal treatment of VOC DNAPL, the dominant mechanism is vaporization, as illustrated in Figure 1, showing how boiling leads to steam formation and gas flow rich in contaminant vapors out of the pore matrix. Note the continuous gas phase in the right image where pore fluids are boiling and creating steam, which sweeps out to recovery wells. Boiling occurs at DNAPL-water interfaces and throughout.

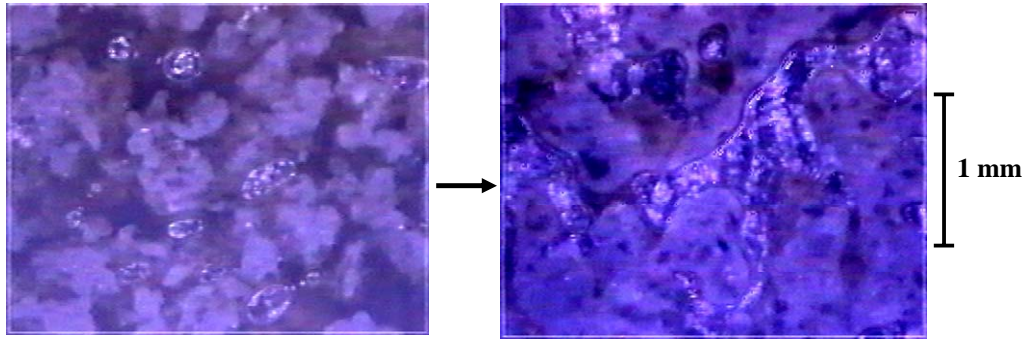


Figure 1. Conceptual illustration of the difference between ambient temperature (left) and boiling temperature conditions (right) at the pore scale

Figure 2 summarizes the physical property changes occurring during heating for water, trichloroethene (TCE), and tetrachloroethene (PCE). While DNAPL density, viscosity, surface tension, and solubility varies slightly, vapor pressure and Henry's law constants increase dramatically with temperature.

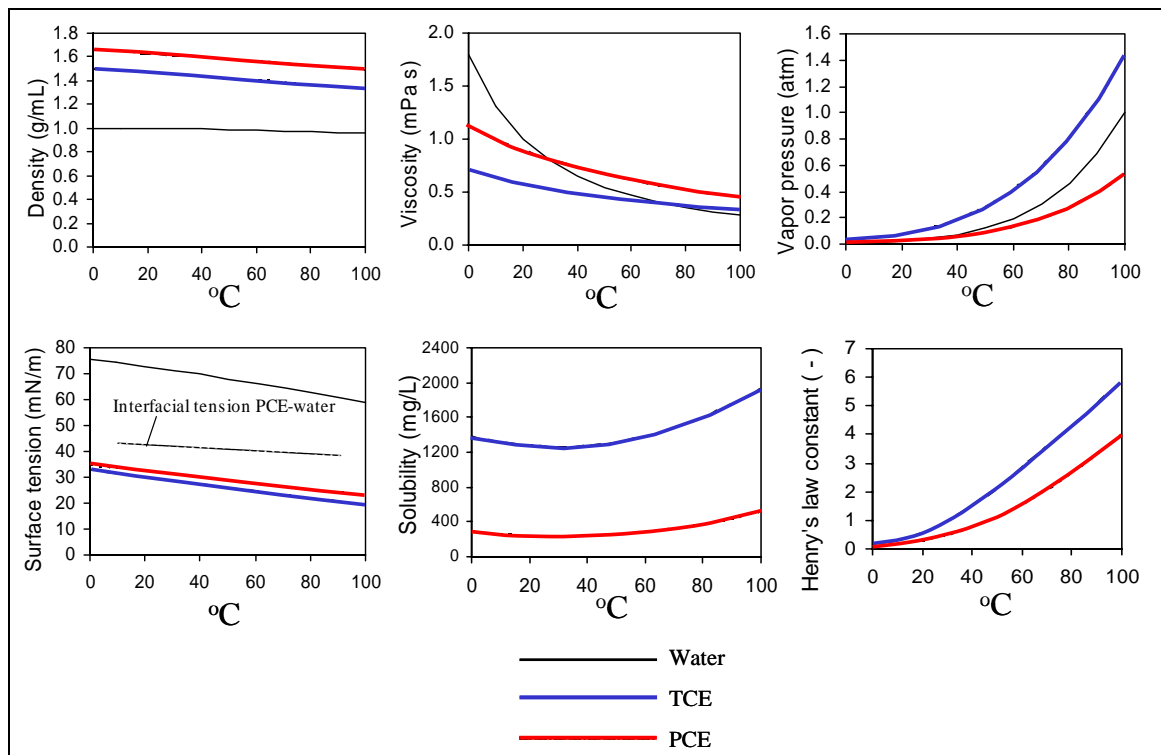


Figure 2. Properties of water, PCE and TCE as a function of temperature.

Other mechanisms include enhanced dissolution, hydrolysis, and aqueous phase oxidation. However, vaporization is dominant for most chlorinated solvents.

HOW CLEAN CAN IT GET?

Table 1 shows the results achieved using DUS combined with detailed flexible monitoring, sampling, energy balance calculations, and careful pneumatic and hydraulic control. Removal efficacies of 99.9% or better were achieved.

Table 1. Treatment efficiency based on mass estimates from soil sampling before and after DUS treatment at the Young-Rainey STAR Center, Largo, FL (Heron et al. 2005).

	Number of samples	TCE (µg/kg)	<i>cis</i> -1,2-Di-chloroethene (µg/kg)	Methylene Chloride (µg/kg)	Toluene (µg/kg)
Before, maximum	231	250,000	68,000	650,000	72,000
Before, average		2,753	1,239	3,444	825
After, maximum	80	110	120	8.2	420
After, average		3.3	4.4	0.8	21
Removal efficiency (%)		99.99	99.85	99.99	99.89

Table 2 shows similar contaminant mass reduction achieved using ISTD to heat a tight saturated clay to 100°C and vaporizing 40% of the groundwater.

Table 2. Comparison of COC concentrations before and after ISTD treatment at the Terminal 1 site in Richmond, CA (Geomatrix and TerraTherm 2005).

	Number of samples	PCE (µg/kg)	TCE (µg/kg)	<i>cis</i> -1,2-Di-chloroethene (µg/kg)	Vinyl chloride (µg/kg)
Before, maximum	64	510,000	6,500	57,000	6,500
Before, average		34,222	1,055	6,650	932
After, maximum	44	44	< rep.limit	1,500	24
After, average		12	< rep.limit	65	4.7
Removal efficiency (%)		99.96	99.63	99.03	99.49

These results illustrate the dramatic reduction in source zone CVOC concentrations when the technology is used to reach boiling point temperatures and operated with a sufficient energy input to vaporize more than 30% of the soil moisture.

CRITICAL DESIGN AND IMPLEMENTATION ISSUES

Select the Most Appropriate Heating Technology. Often site owners or consultants fail to consider all the options for thermal treatment and rely on one concept and cost when making a decision. It is important to realize, for instance, that ERH and ISTD often apply to the same sites, and that sometimes one method is more appropriate. Key issues for the selection includes treatment size (ERH often is cheapest for small sites with modest remedial goals), treatment depth (ISTD is simpler and more cost-effective for deep sites), treatment goals (ISTD is often used for sites with very stringent cleanup goals), and site permeability (SEE may be more applicable to deep permeable formations). Therefore, clients and consultants should not restrict themselves to working with a single thermal vendor, but ought to request evaluations from more than one for each site.

Establish Hydraulic and Pneumatic Control. Before heating, inward flow of fluids (vapor and water) must be ensured. During SEE and DUS, inward flow of groundwater and vapor must also be ensured. Detailed calculation of necessary rates must be performed (steam can rapidly displace large quantities of fluids). During ERH and ISTD, vapor capture must be ensured by a robust vacuum extraction system that allows a flow pathway for the steam and

CVOC vapors to extraction points. One cannot rely on steam bubbles migrating upward to the vadose zone, or on clay drying to create permeability – the generated vapor must flow readily to extraction wells screened in the right zones. During ERH and ISTD, hydraulic control must be maintained, either by boiling sufficient amounts of groundwater to create capture, pumping, or through use of a hydraulic barrier.

Heat to Target Temperature High Enough to Accomplish the Remedial Objectives. For most CVOCs, except those which degrade readily by hydrolysis such as Methylene Chloride (MeCl_2), 1,2-Dichloroethane (1,2-DCA), and 1,1,1-Trichloroethane (1,1,1-TCA), the target treatment temperature should be the boiling point of the pore water or groundwater. Heating to 100°C or slightly lower where vacuum is applied ensures that all DNAPL is vaporized and removed, and that steam stripping will reduce dissolved and adsorbed concentrations (Udell, 1996). One mistake is to rely on the psychrometric effect (air mixing with steam and lowering the boiling point), since typical heterogeneity makes it impossible to distinguish whether a zone heated to 85°C is being cleaned due to air flow or whether it is stagnant and by-passed by the heating (Heron et al. 2005). Ultimately this reduces the certainty of reaching cleanup goals in a timely manner.

Below the water table the target temperature increases with depth due to the increased pressure. At a depth of 10 m below the water table, the groundwater boils at approximately 120°C . Target temperatures must be the boiling temperature to ensure steam stripping.

During operation, subsurface temperature monitoring is essential (e.g. Heron et al. 2005). For heterogeneous sites, thermocouples should be placed no more than 1.5 m apart vertically, and a network of monitoring wells should cover the target area and the zones around it.

Mass and Energy Balance Calculations and Data Management. A key to a good thermal project design and execution is careful energy management and monitoring of the progress in different ways – an example of the use of a detailed energy balance for finding problems is presented in Figure 3. At this site, the energy balance indicated that a cool zone was present (average site temperature was $80\text{-}90^\circ\text{C}$, but the thermocouples showed $100\text{-}110^\circ\text{C}$), and subsequent drilling revealed a recalcitrant zone, which was then targeted for more intense treatment. The results were encouraging, showing the importance of complete heating, and the value of careful monitoring and engineering checks.

Use Pressure Cycling during Steam Enhanced Extraction. During SEE and DUS, steam breaks through to dedicated extraction wells (Udell et al. 1991). The principle of pressure cycling is illustrated in Figure 4. The steam stripping is enhanced during the depressurization step, where the pressure in the steam zone is reduced. This leaves the pore fluids in the steam zone and the surrounding condensation zones at slightly superheated conditions since the equilibrium temperature is lower than the actual temperature (see the inserted steam pressure curves at the top of the figure). The zones respond by releasing energy to get to a lower equilibrium temperature – this happens by boiling pore fluids. The generated steam and BTEX-vapors migrate in the steam zone towards recovery wells. This was documented to lead to large increases in vapor-phase recovery during full-scale remediation (Heron et al 2005). Failure to conduct pressure cycling will prolong the heating period and reduce treatment efficiency.

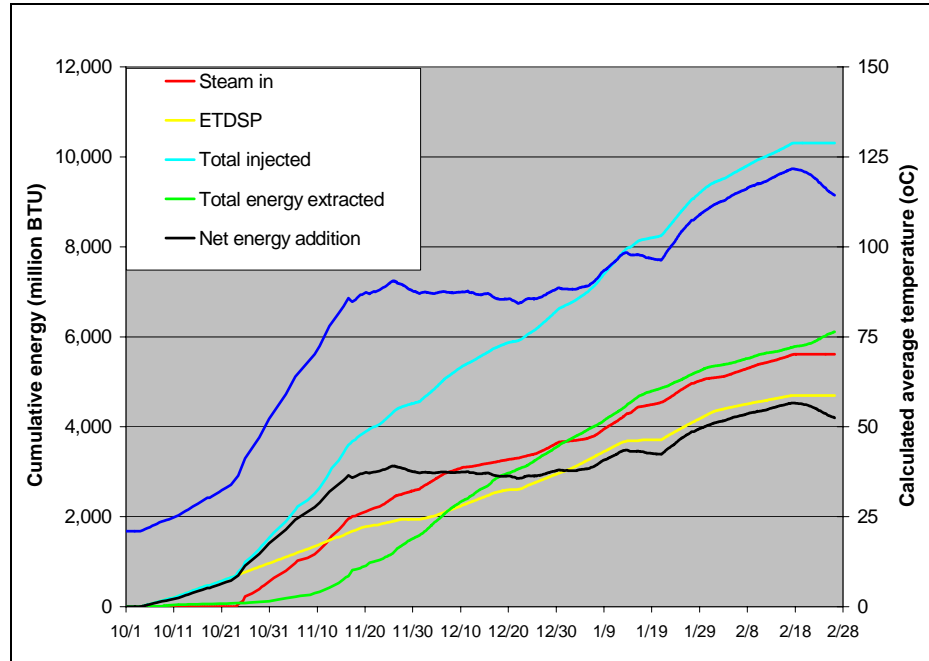


Figure 3. Energy balance for the steam and ERH project at Young-Rainey STAR Center Area A. The blue curve is calculated average treatment zone temperature (Heron et al. 2005).

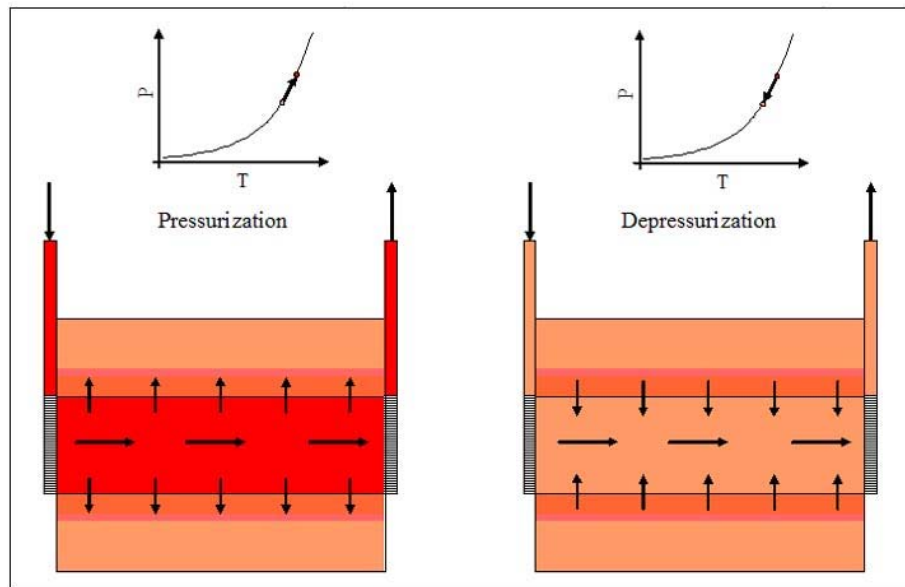


Figure 4. Illustration of pressure cycling during steam injection and extraction. The left figure illustrates the pressurization and heating stage, the right the situation during de-pressurization.

Use Process Stream Sampling to Document Mass Removal Rates over Time. A flexible approach to sampling and data collection can not only enhance the operation of the thermal system, it can shorten the time to reach remedial goals and lower overall costs. Extraction

wells and manifolds are hot and under vacuum – no standard EPA methods exist for collection and sample analysis. However, screening-level sampling can reveal areas where problematic compounds persist and reveal area where treatment is complete (diminishing returns). Examples are published by US DOE (2003).

Use Interim Soil Sampling to Document Remedial Progress. Interim drilling during thermal remediation can be performed safely when not drilling into significant steam zones (Gaberell et al. 2002). The data can be used to document remedial progress and final performance before operation is completed. It is useful for gathering information in zones where contaminant extraction continues despite a sense that heating is complete, as shown by Heron et al. (2005).

Soil and sediment sampling is particularly useful since potential rebound after cooling would be the result if partitioning of contaminants from the sediments to groundwater. Since the sampling represents the potential source for rebound, it is preferred over waiting for cooling and then performing groundwater sampling.

CONCLUSIONS

This review revealed how effective thermal remediation can be for CVOC sites if designed and implemented well. It identified these critical design elements:

- CVOC sites with stringent treatment goals must be heated to the boiling point of water, and a significant amount of energy spent on boiling groundwater.
- Pneumatic and hydraulic control must be maintained, and a path for the generated steam to extraction wells must be included.
- Pressure cycling is important on steam projects – it shortens remediation time and increases effectiveness.
- Mass and energy balance calculations are useful for overall process verification, troubleshooting, and assurance that site heterogeneities are addressed.
- Interim process and soil sampling are important for tracking remedial performance and verifying treatment prior to cessation of operations.

Remedial standards of below 1 mg/kg have been consistently met by properly engineered ISTR systems.

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