IN-SITU THERMAL DESTRUCTION MAKES STRINGENT SOIL AND SEDIMENT CLEANUP GOALS ATTAINABLE

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ABSTRACT

In Situ Thermal Destruction (ISTD) is a remediation process in which heat and vacuum are applied simultaneously to subsurface soils or aboveground soil/sediment piles. Heat flows into the soil primarily by conduction from heaters typically operated at 700-800°C (1300-1500°F). Field project experience at seven ISTD sites and laboratory treatability studies have confirmed that high temperatures maintained over a period of days result in extremely high destruction and removal efficiency of even high boiling point contaminants such as PCBs, pesticides, PAHs and other heavy hydrocarbons. Despite high pre-treatment soil contaminant concentrations, post-treatment soil concentrations have typically been non-detect. ISTD thus offers a cost-effective means to reliably achieve stringent cleanup goals that have not been previously possible by in-place treatment.

1. INTRODUCTION

Contamination of soil, sediments and groundwater by persistent and recalcitrant organic compounds such as chlorinated aromatics, polynuclear aromatics, heterocyclics and nitroaromatics is a widespread legacy of modern industrial, commercial and military efforts. The specific locations where chemicals were spilled or released, even decades ago, tend to remain the places having the highest concentrations of these contaminants. These source areas often give rise to larger contiguous aqueous and vapor plumes. Despite its utility in effecting hydraulic containment at many sites, the failure of pump-and-treat to eliminate subsurface contamination makes it clear that source areas must either be removed or isolated before aquifer restoration is possible.

Until recently, the fastest, most reliable way of cleaning up hot spots was to dig them up, and either treat the soil *ex situ*, or truck it off-site for treatment or disposal. Excavation, however, is intrusive and can expose site workers and nearby residents alike to odors, vapors, dust and traffic. The development of *in situ* technologies, such as soil vapor extraction, surfactant and cosolvent flushing, and in situ oxidation brought the promise of removal of source areas without excavation, but there are no demonstrated instances that they have proven effective with recalcitrant organic contaminants.

These (and most) *in situ* technologies have a common attribute: they rely upon trying to deliver a fluid throughout the subsurface locations where contaminants reside, either by injection, extraction, or both. At the vast majority of sites, however, soil conditions are non-uniform, and it is therefore not possible to fully contact all the contaminants with the treatment fluid. Be it air, liquid or reagent, fluid tends to bypass lower-permeability zones and flow preferentially through higher-permeability zones. Movement of contaminants out of bypassed zones is slow, with diffusion time frames on the order of decades, if not centuries. Freeze and McWhorter (1997) underscored the futility of trying to remediate source areas unless a very high percentage of the mass (e.g., >99.9%) can be removed or eliminated.

Today an innovative *in situ* technology is available that has been proven to effectively remove recalcitrant organic contaminants from soils and achieve the most stringent cleanup standards. *In Situ* Thermal Desorption (ISTD), also known as *In Situ* Thermal Destruction, is a patented remediation process in which heat and vacuum are applied simultaneously to soils. Heat flows into the soil primarily by conduction from heaters operated at approximately 800°C (1500°F). Thermal conduction is the most uniform method of fully sweeping 100% of a contaminated zone, regardless of permeability or degree of heterogeneity.

2. HOW ISTD WORKS

Whichever of the two common modes of application of ISTD are employed, vertical thermal wells for deeper contamination, or horizontal thermal wells, also termed thermal blankets, for shallow contamination, a multiplicity of wells are installed to span the dimensions of the zone requiring cleanup. Typically, electric heaters installed within each well are wired together, with power tapped from utility poles or portable generators. Vapor is extracted from a fraction of the wells, so as to ensure that the boundaries of the heated zone are under vacuum and vapors/steam emanating from the heated zone are contained. The cleaning process and the mechanisms at work are as follows:

1.1 Physical and Chemical Mechanisms

As soil is heated, organic contaminants in the soil are vaporized or destroyed by several mechanisms that come into play as the soil temperature rises.

These mechanisms include:

- evaporation } at ≤ 100°C
- steam distillation
- boiling of contaminant } at > 100°C
- oxidation
- and pyrolysis.

N.B.: Soils that have attained temperatures greater than 100°C are termed "Superheated."

1.2 Predictability

Compared to fluid injection and extraction processes, the conductive heating process during ISTD is very uniform in its vertical and horizontal sweep. The effectiveness of the process is not limited by the presence of heterogeneous soil conditions, clay or subsurface obstructions, because thermal conductivity is a relatively invariant physical property across a wide range of soil types (e.g., varying by a factor of only approximately ±2 from sand to clay). Thus, conductive heat flows into the soil surrounding the heaters at a very predictable, uniform rate until the heat fronts overlap and 100% of the targeted soil is heated. By contrast, fluid permeability often varies over many orders of magnitude within a site (e.g., varying by a factor of 100,000 or more from sand to clay). During vapor extraction, surfactant flooding, and oxidant injection, for example, fluids flowing preferentially through higher-permeability zones often bypass lower permeability zones, thus failing to cleanse them. With ISTD, as the soil becomes superheated it desiccates, allowing even tight clays to become permeable enough for adequate contaminant volatilization and vapor extraction or destruction.

1.3 Destruction Mechanisms

The vaporized constituents are drawn toward the extraction wells ("heater-vacuum wells"). As vapors move through the superheated zone in the proximity of each heater-vacuum well, they rapidly decompose due to oxidation or pyrolysis reactions. The dilute fraction of gaseous contaminants that remains in the collected air stream is treated aboveground.

1.4 Effectiveness

The combined effectiveness of both heat and vapor flow leaves no area untreated. Field project experience at seven ISTD sites and laboratory treatability studies have confirmed that high temperatures applied over a period of days result in extremely high destruction and removal efficiency of even high boiling point contaminants such as PCBs, pesticides, PAHs and other heavy hydrocarbons.

2. TYPICAL RESULTS

Tables 1 and 2 present a summary of completed field ISTD demonstrations and full-scale projects and results (Stegemeier and Vinegar, 2001).

Table 1. Summary Of Thermal Conduction Field Projects (Stegemeier and Vinegar, 2001).

Location	Project	Soil Type	Depth (feet)	Process	No. of Blankets or Wells
S. Glens Falls, NY	Field Demo	Sand	0 – 0.5	Blanket	5 – 8' x 20'
Cape Girardeau, MO	Field Demo	Clay	0 – 1.5	Blanket	2 – 8' x 20'
Cape Girardeau, MO	Field Demo	Clay	0 – 12	Wells	12
Vallejo , CA	Field Demo	Silt/Clay	0 – 14	Wells	12
Portland, IN	Commercial	Clay	0 – 12	Wells	15
Portland, IN	Commercial	Clay	0 – 20	Wells	130
Tanapag, Saipan	Commercial	Carbonate/Sand	0 – 2	Blanket Box	28 – 8' x 20'
Eugene, OR	Commercial	Sand/Silt/Clay	0 – 11	Wells	761
Ferndale, CA	Commercial	Sand	0 – 15	Wells	53

Table 2. Pre- and Post-Treatment Soil Concentrations for the Projects Presented in Table 1.

Location	Contaminant	Initial Concentration (ppm)	Final Concentration (ppm)
S. Glens Falls, NY	PCB 1248/1254	5,000	< 0.8
Cape Girardeau, MO	PCB 1260	500	< 1
Cape Girardeau, MO	PCB1260	20,000	< 0.033
Vallejo, CA	PCB 1254/1260	2,200	< 0.033
Portland, IN	1,1 DCE	0.65	0.053
Portland, IN	PCE/TCE	3,500/79	< 0.5/0.02
Tanapag, Saipan	PCB 1254/1260	10,000	< 1
Eugene, OR	Gasoline/Diesel	3,500/9,300 + free product	N.D. benzene; 250,000 lbs. free product removed
Ferndale, CA	PCB 1254	800	< 0.17

(Stegemeier and Vinegar, 2001)

Table 1 indicates that ISTD has been employed to treat soil types ranging from sand to clay. Both thermal blankets (for treatment of shallow contamination, up to 2 ft thick) and thermal wells (for deeper contamination) have been deployed. Table 2 indicates that whether ISTD has been used to treat soils heavily contaminated with PCBs, chlorinated solvents, or fuels, post-treatment soil concentrations of the contaminants of concern have typically been non-detect. Often, a large number of confirmatory soil samples were collected. For example, for the thermal well demonstration at the Missouri Electric Works Superfund site in Cape Girardeau, MO, 81 soil samples were collected from within the treatment zone after heating. Of these, 76 were below detection limits (DLs) of 0.033 ppm, and the other five samples were just above the DLs, and well below the remedial goals (Vinegar et al., 1997). Achievement of such stringent remedial goals through in situ treatment of a recalcitrant organic contaminant in clay soil is unprecendented.

3. IN SITU DESTRUCTION

Most of the contaminants (95-99% or more) are destroyed in the soil before reaching the surface. Thus, the mass of vapor requiring treatment aboveground is greatly diminished. The significant fraction of the contaminant mass that is destroyed in the soil is attributed to the exposure of the contaminants to high temperatures for long residence times. As vapors are drawn through the superheated soil in the proximity of heater-vacuum wells, there is ample opportunity for destructive chemical reactions to occur. Kuhlman (2001) compiled reaction rates for oxidation and pyrolysis of 3-ring polynuclear aromatic hydrocarbons (PAHs), benzo(a)pyrene (BaP), tar and coke (Figure 1) from a search of the petroleum, combustion and pyrolysis literature. Although some destruction of PAHs by hydrous pyrolysis oxidation has been reported (Leif et al., 1998), Figure 1 suggests that steam distillation temperatures (~100°C) are too cool to result in significant in-situ destruction rates of the higher-molecular weight PAH compounds within practical remediation timeframes. By contrast, ISTD affords rapid in-situ destruction by these mechanisms. Interwell temperatures (Figure 1, center) of 300 to 500°C, which occur within the cooler locations midway between heater wells, are sufficient to allow many oxidation half-lives to elapse over the course of days or weeks. Note for comparison that 20 half-lives would need to have elapsed to achieve a final concentration of <0.033 ppm from an initial concentration of 20,000 ppm if all the treatment seen at the Cape Girardeau, MO site were due to in situ destruction. Moreover, in the proximity of heater-vacuum wells, soil temperatures of 600 to 700°C (Figure 1, right) constitute, in effect, a packed-bed reactor that is hot enough to accomplish rapid decomposition by either pyrolysis, if oxygen is deficient, or by oxidation, if oxygen is available.

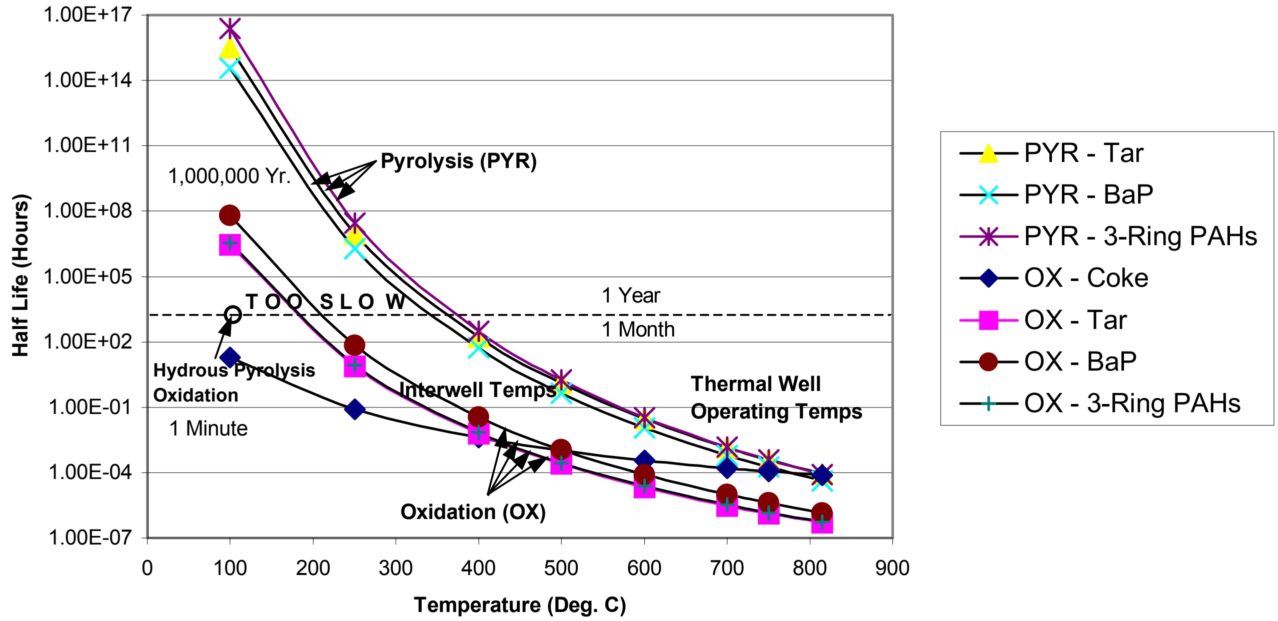

Figure 1. Oxidation and pyrolysis reaction rates (after Kuhlman, 2001).

4. OFF-GAS TREATMENT

A treatment train that typically includes some or all of the following components accomplishes aboveground treatment of the off-gas produced during ISTD (Figure 2): cyclone separator; thermal oxidizer; heat exchanger; granular activated carbon (GAC) adsorber; and dry acid gas scrubbing media (if required). Stack sampling has demonstrated that emissions of toxic air pollutants including contaminants of concern and dioxins have consistently been substantially below standards (Stegemeier and Vinegar, 2001). In some cases, where allowed by emission requirements, the thermal oxidizer may be cost-effectively replaced with GAC for organic off-gas treatment, due to the typically dilute extracted vapor concentrations seen with ISTD.

5. CONCLUDING REMARKS

ISTD offers a cost-effective means to reliably achieve stringent cleanup goals for recalcitrant organic contaminants in heterogeneous and/or low permeability soils that has not been previously possible by in-place treatment. Thorough source removal, as with ISTD, makes monitored natural attenuation of the associated dissolved plume attainable within a relatively short timeframe. Also, liabilities associated with capping, excavation and/or off-site disposal can be eliminated, and the full asset value of a property can be quickly restored.

REFERENCES

Freeze, R.A., and McWhorter, D.B., "A framework for assessing risk reduction due to DNAPL mass removal from low-permeability soils," *Ground Water*, 35(1):111-123, 1997.

Kuhlman, M., *Simulation of In Situ Thermal Desorption and Destruction of Town Gas Residuals at the North Ryan Street Superfund Site*, Prepared for TerraTherm, Inc. by MK Tech Solutions, Inc., Houston, TX, January 12, 2001.

Leif, R.N., Chiarappa, M., Aines, R., Newmark, R.L., Knauss, K.G., and Eaker, C., "In Situ Hydrothermal Oxidative Destruction of DNAPLs in a Creosote Contaminated Site," In G.B. Wickramanayake and R.E. Hinchee (eds.), *Remediation of Chlorinated and Recalcitrant Compounds: Physical, Chemical and* Thermal Technologies, pp. 133-138, 1998.

Stegemeier, G.L., and Vinegar, H.J., "Thermal Conduction Heating for In-Situ Thermal Desorption of Soils," In: Chang H. Oh (ed.), *Hazardous and Radioactive Waste Treatment Technologies Handbook*, CRC Press, Boca Raton, FL, Ch. 4.6-1, 2001. Table 2 reprinted by permission of CRC Press.

Vinegar, H.J., deRouffignac, E.P., Rosen, R.L., Stegemeier, G.L., Bonn, M.M., Conley, D.M., Phillips, S.H., Hirsch, J.M., Carl, F.G., Steed, J.R., Arrington, D.H., Brunette, P.T., Mueller, W.M., and Siedhoff, T.E., "In Situ Thermal Desorption (ISTD) of PCBs", *Proceedings of the HazWaste/World Superfund XVIII Conference*, Washington, DC, December 2, 1997.

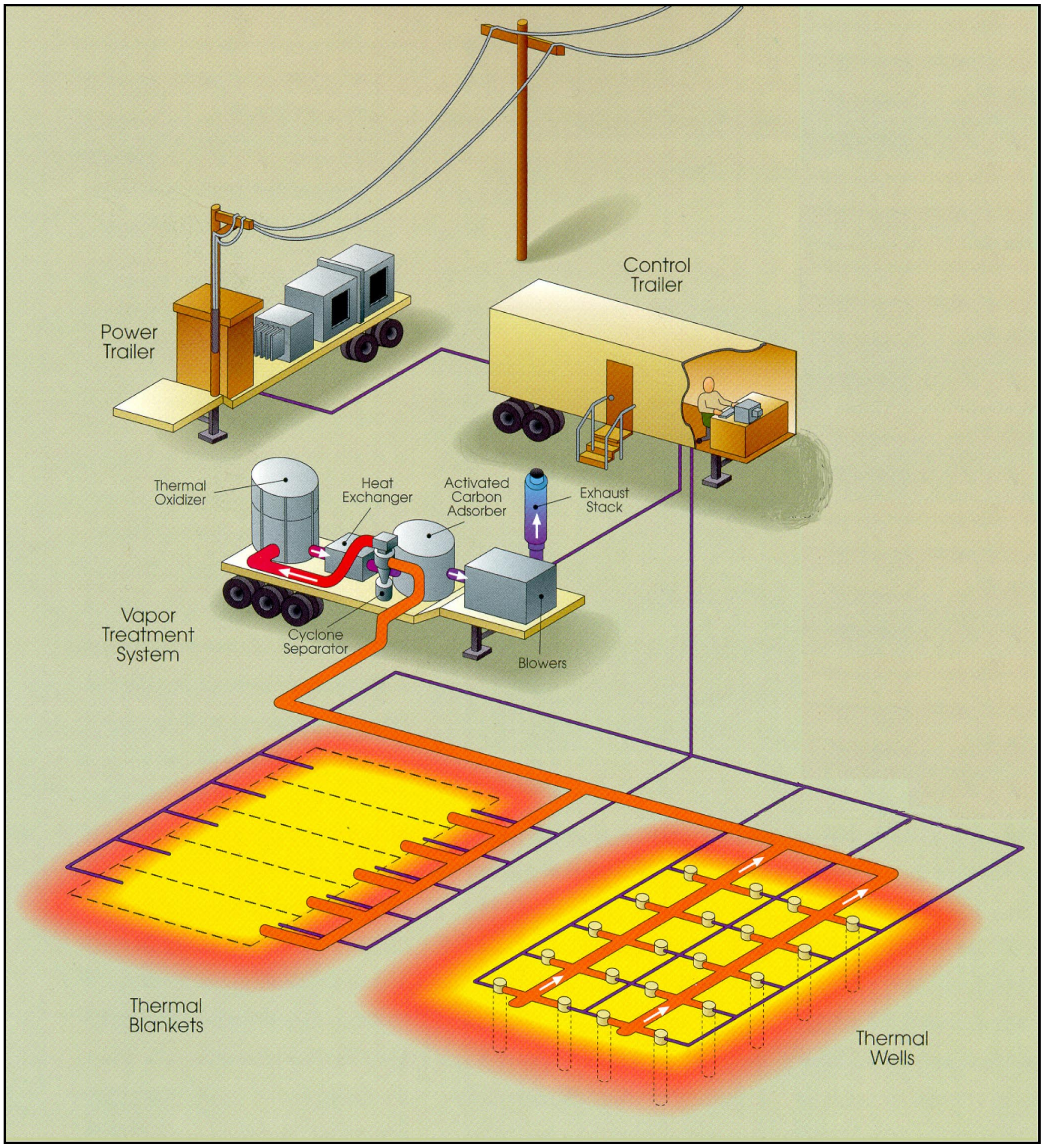

Figure 2. ISTD process schematic.

Subsurface conductive heating and vapor extraction are applied either with horizontal heaters ("Thermal Blankets") for shallow contamination, as shown in foreground at left, or with vertical heaters ("Thermal Wells") for deeper contamination, as shown in foreground at right. Vapor Treatment System consists of the following trailer-mounted components: Cyclone Separator, Thermal Oxidizer, Heat Exchanger, Activated Carbon Adsorber, Blowers and Exhaust Stack. Power and Control Trailers (background) provide electrical power distribution and process control/monitoring, respectively.