

A DESCRIPTION OF THE MECHANISMS OF IN-SITU THERMAL DESTRUCTION (ISTD) REACTIONS

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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 even today with high contaminant concentrations. 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. Sale and McWhorter (1) 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

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cleanup standards. *In-Situ* Thermal Desorption (ISTD), also known as *In-Situ* Thermal Destruction, is a patented soil and sediment remediation process in which heat and vacuum are applied simultaneously to soil, waste and/or sediments. Heat flows into the soil primarily by conduction from heaters operated at approximately 800°C. Thermal conduction is the most uniform method of fully sweeping 100% of a contaminated zone, regardless of permeability or degree of heterogeneity. This paper summarizes how the ISTD technology works, and elucidates the underlying destruction reaction mechanisms and rates, showing that most of the unique efficacy of this in-situ remediation technology may be attributed to in-situ destruction reactions.

IN-SITU THERMAL DESTRUCTION (ISTD) DESCRIPTION

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. Electric heaters installed within each well are wired together, with power tapped from utility poles or other power sources. Vapor is extracted from a fraction of the wells, so as to ensure that the boundaries of the heated zone are under vacuum. The cleaning process works as follows [Stegemeier and Vinegar (2)]:

1. As soil is heated, volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs) in the soil are vaporized and/or destroyed by several mechanisms that come into play as the soil temperature rises, including:

- evaporation
 - boiling (H₂O, VOCs)
 - steam distillation
 - boiling (SVOCs)
 - oxidation
 - and pyrolysis.
- } at ≤ 100°C
- } at > 100°C (termed the “Superheated” Range)

2. 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 or clay, 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 radially into the soil surrounding the heaters at a very predictable, uniform rate until the heat fronts from neighboring heaters 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 vapor extraction.

3. 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, reactions such as oxidation and pyrolysis rapidly decompose them.

The dilute fraction of gaseous contaminants that remains in the collected air stream is treated aboveground.

4. The combined effectiveness of both heat and vapor flow leaves no area untreated. Laboratory treatability studies and field project experience at seven ISTD sites 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 polychlorinated biphenyls (PCBs), pesticides, polynuclear aromatic hydrocarbons (PAHs), and other heavy hydrocarbons.

Typical Results

Despite high pre-treatment soil contaminant concentrations, post-treatment soil concentrations have typically been non-detect (Table 1). Nearly all of these sites underwent extensive regulatory agency scrutiny, and are documented in the literature [e.g., Stegemeier and Vinegar (2)].

Table 1 goes near here.

IN-SITU DESTRUCTION MECHANISMS DURING ISTD

Most of the contaminants (95-99% or more) are destroyed in the soil before reaching the surface. Thus, the mass of contaminant in the vapor requiring treatment aboveground is greatly diminished. The high fraction of the contaminant mass that is destroyed in the soil is attributed to the exposure of the contaminants to elevated 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. Hydrolysis, pyrolysis and oxidation data have been compiled for chlorinated hydrocarbons from the literature (3, 4, 5, 6, 7 and 8).

Figure 1 goes near here.

These data show that only 1,1,2-trichloroethane and chlorophenol (Figure 1, left) decompose at a rate high enough to be destroyed quickly in water at a temperature below water's atmospheric pressure boiling point (~100°C). It is important to note that both of these chemicals are less volatile than water. Thus, they will not be vaporized quickly from a zone that is near its boiling point and condensed into a cooler zone where the reaction is quenched. Trichloroethylene (TCE - boiling point [bpt] 87°C), on the other hand, is vaporized below the atmospheric pressure boiling point of water. This means that hydrolysis at steam distillation temperatures cannot effectively destroy TCE or other more volatile chemicals like *trans*-1,2-dichloroethylene (EDC bpt 80°C) or tetrachloromethane (carbon tetrachloride; CCl₄ bpt 78.5°C), since they are both readily transported out of the advancing high temperature zone. Similar data have been compiled for PAHs, benzo(a)pyrene (BaP) and coke (Figure 2) from a search of the petroleum, combustion and pyrolysis literature (9, 10, 11, 12, 13, 14, 15 and 16).

Figure 2 goes near here.

Although some destruction of PAHs by hydrous pyrolysis oxidation has been reported by Leif et al. (17), Figure 2 suggests that atmospheric pressure steam distillation temperatures are too low to result in significant in-situ destruction rates of the higher-

molecular weight PAH compounds in less than a year. For instance, Kuhlman (18) shows that 45% of the BaP at the Visalia, CA Superfund site was destroyed by hydrous pyrolysis in two years. Even lower fractions of the smaller, more volatile PAHs were mineralized.

By contrast, ISTD affords rapid in-situ destruction by pyrolysis or oxidation. Two combinations of destruction conditions are possible. If volatile organic compounds like TCE are being remediated, it is only necessary for water to approach 100°C between wells to mobilize these chemicals. TCE, EDC or CCl₄ that are dissolved in water or adsorbed on the soil can be desorbed when water is at or below its boiling point if sufficient flux of gas is available. Thus, VOCs are primarily destroyed by pyrolysis or oxidation in the 500 to 700°C region near the heater-vacuum well (Figure 1, right). In contrast, if high boiling point compounds like PAHs are to be remediated, interwell temperatures (Figure 2, 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 between wells. As in the previous VOC example, in the proximity of heater-vacuum wells, soil temperatures of 500 to 700°C (Figure 1 or Figure 2, 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 2, right).

SIMULATION OF ISTD PHYSICAL AND CHEMICAL PROCESSES

The ISTD process is routinely modeled using thermal simulators developed and proven by decades of use in the petroleum industry. TerraTherm uses STARS* to design its projects. Figure 3 is one example of information that STARS can generate.

Figure 3 goes near here.

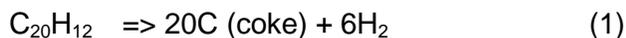
Figure 3 presents the calculated mole fraction of water, air, and BaP produced by desorption of BaP from a former manufacturing site in the southern United States. The figure shows that the effluent from the project is largely water during the first 40 days of the project. The concentration of oxygen (air) in the off-gases gradually decreases because a larger volume of steam is produced as the in-situ temperature rises. Then when the interior of the well pattern is over 100°C, water production decreases and the effluent begins to contain a significant amount of oxygen (air) that is drawn into the pattern by the slight vacuum at the heater-vacuum well. As the site becomes even hotter, BaP production begins, but the ratio of BaP to the reactants (H₂O and O₂) is very small. Thus, high boiling contaminants like BaP (or PCB) are desorbed when the effluent contains a large excess of oxygen and water. VOCs are desorbed when the effluent contains less oxygen and a large excess of water. As the following equations show, both water and oxygen contribute to the destruction of recalcitrant contaminants.

For BaP the following reactions can be written to summarize the destruction mechanism:

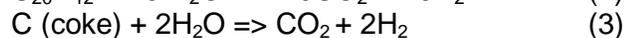
* Developed and marketed by CMG, Ltd of Calgary, Alberta, Canada

Baker and Kuhlman
Description of ISTD Reaction Mechanisms

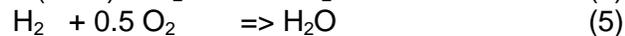
Pyrolysis



Hydrolysis

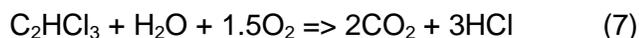


Oxidation



For a chlorinated chemical like TCE the reactions can be summarized as

Oxidation



Pyrolysis



The ISTD reactions of TCE have been written with water as a reactant in order to convert the chlorine in TCE into HCl. It should be recognized that each reaction as written only summarizes the mass balance of a series of hundreds of reactions that have been shown to be in the complete mechanism of each of these reactions. Thus, coke formation and destruction could have been included in the TCE destruction reactions if a large concentration of contaminant were present. Even with these simplifications a simulation can include dozens of destruction reactions in order to model the ISTD process for multiple components.

The example shown in Figure 4 illustrates the result of including a series of 17 ISTD reactions to model destruction of three PAH components at a former manufacturing site in the southern United States. Figure 4 reports the mass of BaP produced when no reactions are included in the simulation, and the mass of BaP produced when reactions are included.

Figure 4 goes near here.

Figure 4 is a conservative estimate of the BaP destruction when reactions are included and shows that a maximum of 0.3 pounds/day would be produced at around 60 days of heating from a 7 well hexagonal pattern before the amount of oxygen at the heater-vacuum well (Figure 3) is high enough to accelerate the destruction reactions. As an example, pyrolysis (reaction 1) produces coke which deposits near the heater-vacuum well. Coke oxidizes easily (reaction 4 and Figure 2) releasing enough energy to raise the temperature and accelerate other decomposition reactions (move to the right in Figure 2). In the example shown in Figure 4, 25% of the energy needed to desorb the PAHs was generated by in-situ oxidation of these fuels.

CONCLUSION

Off-Gas Treatment

Baker and Kuhlman
Description of ISTD Reaction Mechanisms

Stegemeier and Vinegar (2) summarize the approach (Figure 5) that is typically used to treat ISTD off-gases at projects under stringent emissions limits. Stack sampling has demonstrated that emissions of toxic air pollutants including dioxins are substantially below standards [Baker and LaChance (19), elsewhere in this volume].

Figure 5 goes near here.

Optionally, certain off-gas treatment unit processes may be omitted, depending on the contaminants and discharge standards. For example, use of activated carbon alone may be sufficient for treatment of ISTD off-gases at sites with VOCs or heavy hydrocarbons in an attainment area.

Heating Costs

Subsurface heating, on average, costs between about 10 and 30% of the ISTD project price, depending mostly on project size, cost of power, water content, and treatment temperature.

General Remarks

ISTD offers a cost-effective means to reliably achieve stringent cleanup goals that have not been previously possible by in-place treatment. Thorough source removal makes monitored natural attenuation of the dissolved plume attainable within the near term. ISTD eliminates liabilities associated with capping or excavation, restoring the full asset value of the property.

Patent Notice: ISTD is covered by one or more of the following U.S. patents: 4,984,594, 5,076,727, 5,114,497, 5,169,263, 5,190,405, 5,193,934, 5,209,604, 5,221,827, 5,229,583, 5,233,164, 5,244,310, 5,271,693, 5,318,116, 5,553,189, 5,656,239, 5,660,500, 5,674,424, 5,997,214, 6,102,622 and 6,419,423. Additional Patents Pending. Within the U.S.: All rights reserved by the University of Texas at Austin and TerraTherm, Inc. Outside the U.S.: All rights reserved by Shell Oil Co. and TerraTherm, Inc. International Patents Pending.

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Baker and Kuhlman
Description of ISTD Reaction Mechanisms

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List of Tables

Table 1. Summary Of ISTD Field Projects [after Stegemeier and Vinegar (2)]. Reprinted with permission from *Hazardous and Radioactive Waste Treatment Technologies Handbook*; Chang H. Oh (Ed.); 2001. Copyright CRC Press, Boca Raton, Florida.

List of Figures

- Figure 1 – Hydrolysis and Pyrolysis Half-Lives for Several Chlorinated Hydrocarbons
- Figure 2 – Pyrolysis and Oxidation Half-Lives of Polycyclic Aromatic Hydrocarbons
- Figure 3 – Mole Fractions of Water, Air, and BaP Produced without ISTD Reactions
- Figure 4 – Mass of BaP produced with and without ISTD Reactions
- Figure 5 – Typical Off-Gas Treatment Train used for ISTD of PCBs and TSCA Wastes

Tables

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
	PCB1260	20,000	< 0.033
Vallejo, CA	PCB 1254/1260	2,200	< 0.033
Portland, IN	1,1-DCE	0.65	0.053
	PCE/TCE	3,500/79	< 0.5/0.02
Tanapag, Saipan	PCB 1254/1260	10,000	< 1
Eugene, OR	Benzene Gasoline/Diesel	33 3,500/9,300 + free product	<0.044 250,000 lbs. free product removed
Ferndale, CA	PCB 1254	800	< 0.17

Figure 1:

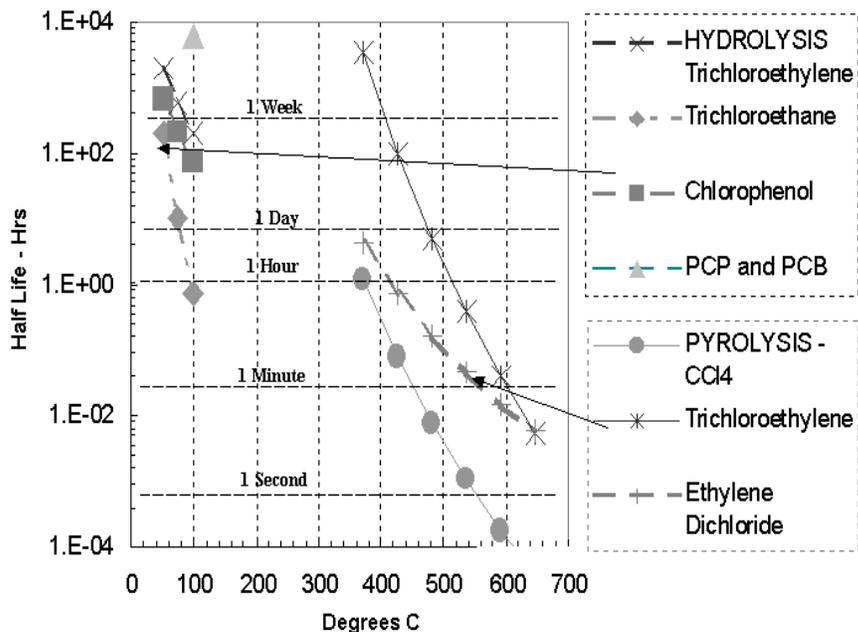


Figure 2:

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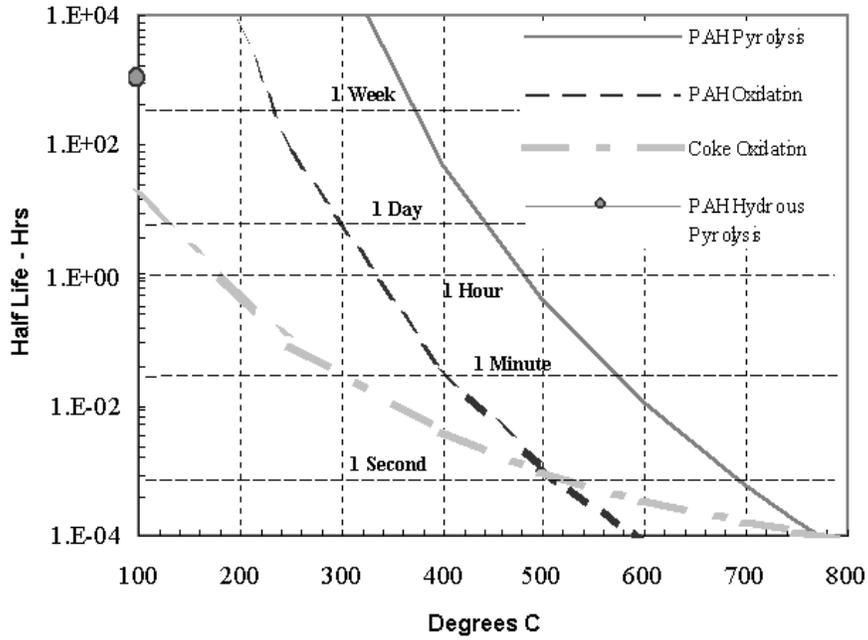


Figure 3:

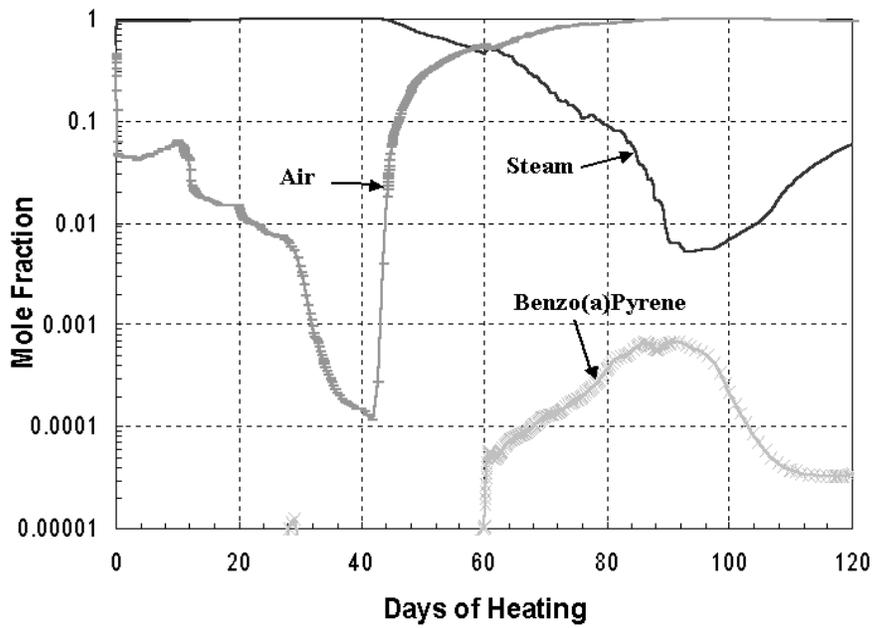


Figure 4:

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Description of ISTD Reaction Mechanisms

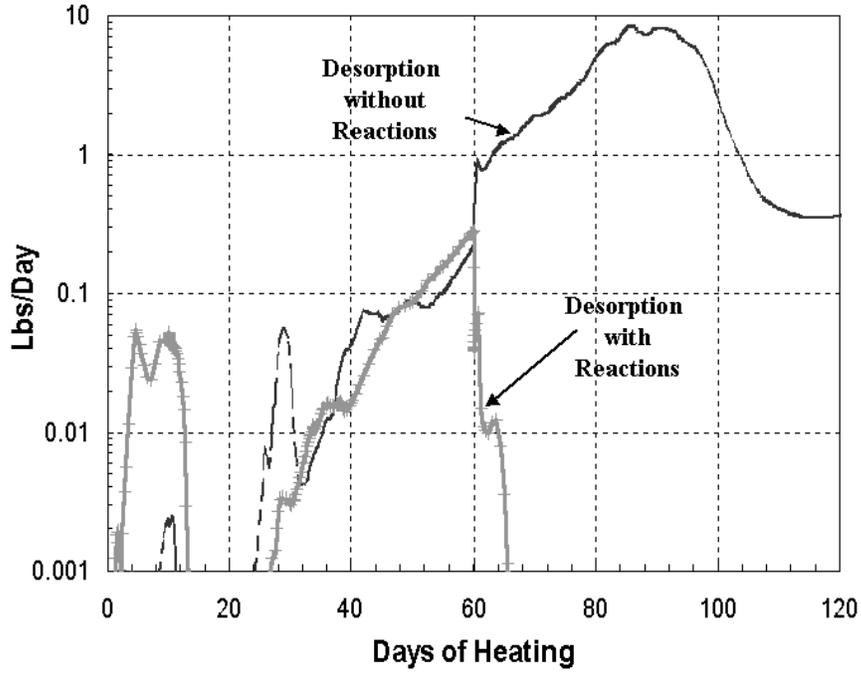
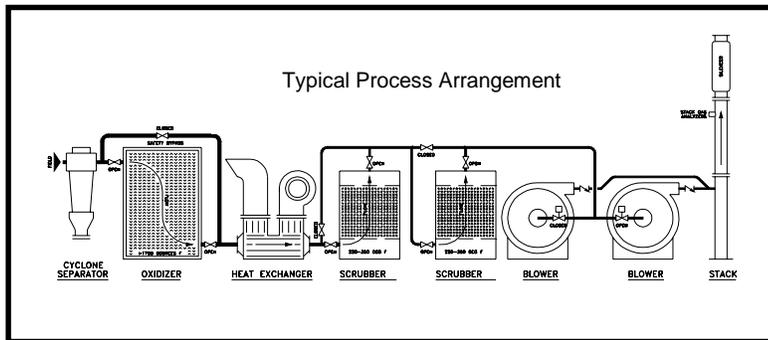


Figure 5:



Process trailer components may include a particle separator, thermal oxidizer, carbon canisters, discharge blowers, back-up generator, control cabin, thermal monitoring system and continuous emission monitoring system (CEM).