APPLICATION OF THERMAL REMEDIATION TECHNIQUES FOR IN-SITU TREATMENT OF CONTAMINATED SOIL AND WATER

RALPH S. BAKER*, JOHN C. LACHANCE AND GORM HERON
TerraTherm, Inc., 10 Stevens Road, Fitchburg, MA 01420 USA

Abstract. In Situ Thermal Remediation (ISTR) refers to technologies including Steam Enhanced Extraction, Thermal Conduction Heating (TCH), and Electrical Resistance Heating that have been demonstrated at >50 sites to be effective options for difficult-to-treat source zones contaminated with organic chemicals. They are well suited to redevelopment and remediation of sites associated with small and medium enterprises (SMEs) in urban areas, as they afford the ability to treat source zones in settings with access limitations, such as adjacent to or beneath buildings, at depth, and in heterogeneous soil, rapidly and completely, without excavation.

In 2005 at the Terminal One Site in Richmond, California, TerraTherm completed a full-scale application of In-Situ Thermal Desorption (ISTD) – a combination of TCH and vacuum – for treatment of chlorinated volatile organic compounds in low permeability (10^{-9} m/s) clay beneath the water table. An array of thermal wells heated the 5,120 m^3, 6.1-m deep target treatment zone (TTZ), both inside and outside a warehouse building, to 100°C in 110 days. Despite the clay's low permeability, steam stripping was the dominant contaminant removal mechanism. Approximately 30% of the pore water present in the TTZ was boiled off and 500 pore volumes of steam were generated and removed, resulting in >99% reduction in tetrachloroethene concentration and achievement of post-treatment concentrations of <100 μg/kg. This Brownfield site was cost-effectively remediated within a 9-month period, for redevelopment as 300 high-value shorefront residential units.

*To whom correspondence should be addressed. Ralph S. Baker, TerraTherm, Inc., 10 Stevens Road, Fitchburg, MA 01420 USA; email: rbaker@terratherm.com

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1. Thermal Remediation Methods

ISTR is gaining acceptance for restoration of non-aqueous phase liquid (NAPL) source zones (Davis 1997), both above and below the water table. The following ISTR methods are briefly reviewed:

- Steam Enhanced Extraction (SEE).
- Electrical Resistance Heating (ERH).
- Dynamic Underground Stripping (DUS).
- ISTD (defined above).

Each of these methods is applied in-situ, i.e., without excavating the contaminated zone. Thus they can be used in hard-to-access locations such as in between buildings, beneath buildings, in deep zones, and at places where there is established infrastructure such as buried utilities and aboveground piping. They are low-impact methods relative to excavation, making them well-suited for use in industrial, commercial and residential locations, and where there are mixed uses. They are also relatively fast, meaning that the source area can be treated and removed in well less than a year if required.

Steam is best applied for heating the more permeable subsurface zones, and has seen extensive use in enhanced oil recovery. Steam is generated aboveground, and injected via wells screened across the zones of interest. SEE (Udell et al. 1991), the ISTR process combining steam injection, aggressive fluids extraction and cyclic depressurization, has been utilized in a number of field demonstrations and full-scale cleanups, including Site 5, Alameda Point, Alameda, CA, and Site 61, Edwards Air Force Base, CA (USEPA 2004). Udell (1996) critically reviewed the mechanisms employed in SEE.

ERH is the process of passing electricity through the soil between electrodes installed in the ground, and heating the soil by Joule heating (Pritchett 1976; Buelt and Oma 1990). Two primary types of ERH, three-phase and six-phase soil heating were developed and later demonstrated in the field. When the temperature achieves the boiling point of water, steam is generated in-situ, and extracted via recovery wells. Laboratory studies demonstrated that thermodynamic changes induced by ERH can lead to very effective removal of chlorinated solvents – also termed chlorinated volatile organic compounds (CVOCs) – from silts and clays (Heron et al. 1998). Since the late 1990s, over two dozen commercial full-scale implementations of both three- and six-phase ERH have been completed (e.g., Francis and Wolf 2004; USEPA 2004), some by the trade name Electro-Thermal Dynamic Stripping Process (ET-DSP) (McGee 2003). Most of these applications have been for treatment of CVOCs, because ERH heating is limited to achieving the boiling point of water. Once the water has boiled off, electrical conductivity becomes negligible and further heating ceases.

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

The third frequently used method, ISTD, is also known as Thermal Conduction Heating (TCH). Because the thermal conductivity of a wide range of soil types varies only by a factor of about three, TCH is a robust and highly predictable method for heating soils and groundwater, even in heterogeneous settings. Compared to fluid injection processes, which in heterogeneous soil tend to be limited by preferential flow through high permeability zones and bypassing of lower permeability regions, the TCH process is very uniform in its vertical and horizontal sweep. When TCH is applied in combination with vapor recovery, it is termed ISTD (Vinegar et al. 1993, 1994; Stegemeier and Vinegar 2001; de Rouffignac et al. 2005). Heat flows into the soil primarily by thermal conduction from electric resistance heaters typically operated between 500 and 800°C. For volatile organic compound (VOC) removal, the entire TTZ is typically heated to 100°C, generating steam in-situ. For thorough treatment of semi-volatile organic compounds (SVOCs) such as polychlorinated biphenyls (PCBs) and high-boiling polycyclic aromatic hydrocarbons (PAHs), the target temperature in the soil between heaters is typically 325°C, meaning that the water must be entirely boiled off. Over 15 ISTD field demonstrations and full-scale projects have been completed. This paper focuses on the use of TCH/ISTD for treatment of CVOCs. As the soil is heated, water is boiled, steam is generated and DNAPL constituents in the soil are vaporized. The resulting steam and vapors are drawn toward extraction wells for in-situ and aboveground treatment.

Other in-situ thermal methods such as hot water flooding, hot air sparging, radio-frequency and microwave heating are not in common commercial use and will not be discussed further.

2. Remediation 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. The left image shows the quiescent condition prior to heating, with NAPL “blobs” and ganglia (dark color) trapped within an otherwise water-filled porous medium, along with a few gas bubbles. Note the continuous gas phase in the right image indicating that pore fluids are boiling and creating steam, which sweeps out to recovery wells. Boiling occurs at DNAPL-water interfaces and throughout.

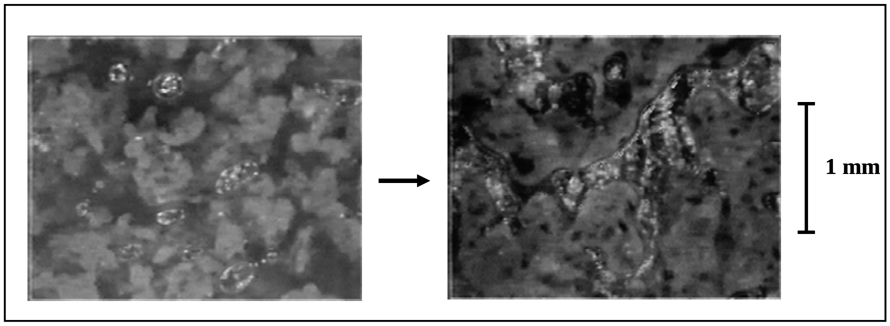

Figure 1. Conceptual illustration of the difference between ambient temperature (left) and boiling temperature conditions (right) at the pore scale (Heron et al. 2006, reprinted with permission).

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.

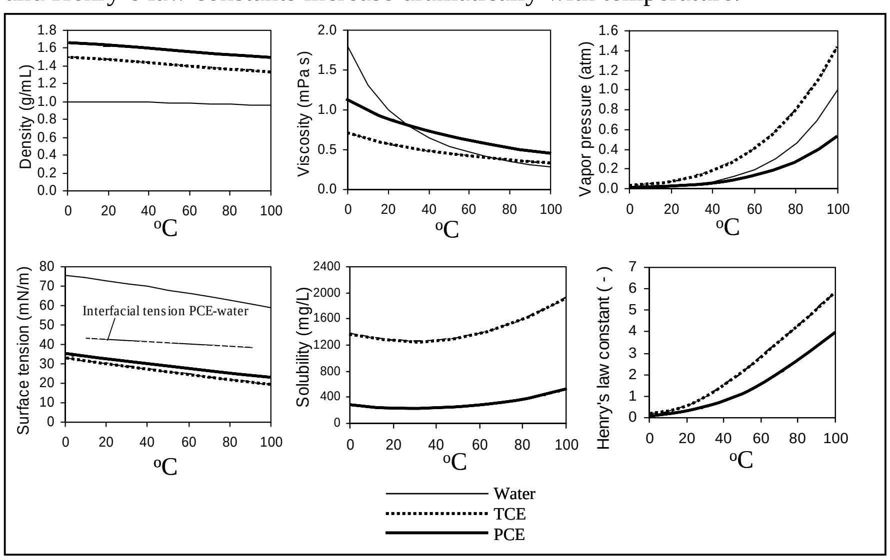

Figure 2. Properties of water, PCE and TCE as a function of temperature (Heron et al. 2006, reprinted with permission).

Removal mechanisms for organic contaminants during ISTR can be summarized as follows:

- For treatment of VOCs, SEE and ERH target the boiling point of water (as does low-temperature ISTD).
- All changes in contaminant properties as a function of temperature favor contaminant removal from the subsurface.
- Vaporization is the dominant removal mechanism for VOCs including CVOCs.
- Viscosity reduction can be utilized to aide removal of large NAPL volumes.
- Degradation reactions may be important – this is very specific to the contaminant and the environmental conditions.
- Downward mobilization is not favored (Davis 2006).

Prior to selection of a heating method, it is strongly recommended that one obtain the services of an ISTR expert to perform a site-specific analysis.

3. Richmond, CA In-Situ Thermal Desorption Case Study

3.1. INTRODUCTION AND SITE BACKGROUND

A full-scale field application of ISTD treatment of CVOCs in saturated low permeability soils (i.e., 10^{-9} m/s) was recently completed at the Terminal One Site in Richmond, CA. The site was operated as a shipping and bulk storage terminal from about 1915 to the 1980s. The portion of the property that is the subject of this case study is known as the “Southwestern Tank Farm”, where chlorinated solvents, petroleum and other chemicals were stored in large aboveground tanks. Site investigations indicated that the land at the site had been created decades earlier by placement of hydraulically dredged sediments from the adjacent San Francisco Bay. Although the aboveground tank structures were removed several years ago, a large warehouse building remained on the shore of the Bay, and a portion of the contaminated zone extended beneath the building.

The owner of the property, the City of Richmond Redevelopment Agency, decided to prepare this Brownfield site for sale to a developer who plans to construct approximately 300 high-value shorefront condominium residences. Concerns about the potential for human exposure to vapors drove the cleanup goals, which were established at 2.0 mg/kg for PCE, the primary contaminant of concern (COC). Goals for the other COCs were 2.0 mg/kg for TCE, 17.0 mg/kg for *cis*-1,2-dichloroethene (*cis*-1,2-DCE), and 0.230 mg/kg for vinyl chloride (VC). Excavation of the soil was ruled out because of high disposal costs and concerns of potential vapor release. The owner's engineering firm, Geomatrix Consultants, Inc. selected ISTD as the best available option to achieve the desired goals in the required short timeframe, and under a performance guarantee offered by TerraTherm.

3.2. NATURE AND EXTENT OF CONTAMINATION

Soil sampling had been used to determine the ~840-m^2 areal extent and 6.1-m depth of the CVOC-contaminated target treatment zone (TTZ) both outside and beneath the building. Maximum and average soil concentrations of PCE within the TTZ were measured to be 510 mg/kg (indicative of DNAPL), and 34.2 mg/kg, respectively. For the other COCs, these values were 6.5 and 1.05 mg/kg for TCE; 57.0 and 6.65 mg/kg for *cis*-1,2-DCE; and 6.5 and 0.93 mg/kg for VC. The site stratigraphy consisted of about 1 m of unsaturated sandy fill, overlying more than 20 m of saturated Bay Mud, a dark greenish gray lean clay with minor amounts (<5%) of sand. Thin interbedded layers (a few cm thick) with abundant shell fragments were observed within the Bay Mud. The water table is present at, or just above the top of the Bay Mud. Figure 3 provides a plan view of the site showing the extent of the 5,120 m^3 (6,700 yd^3) TTZ, the ISTD heater well layout, and the locations of the horizontal soil vapor extraction (SVE) wells.

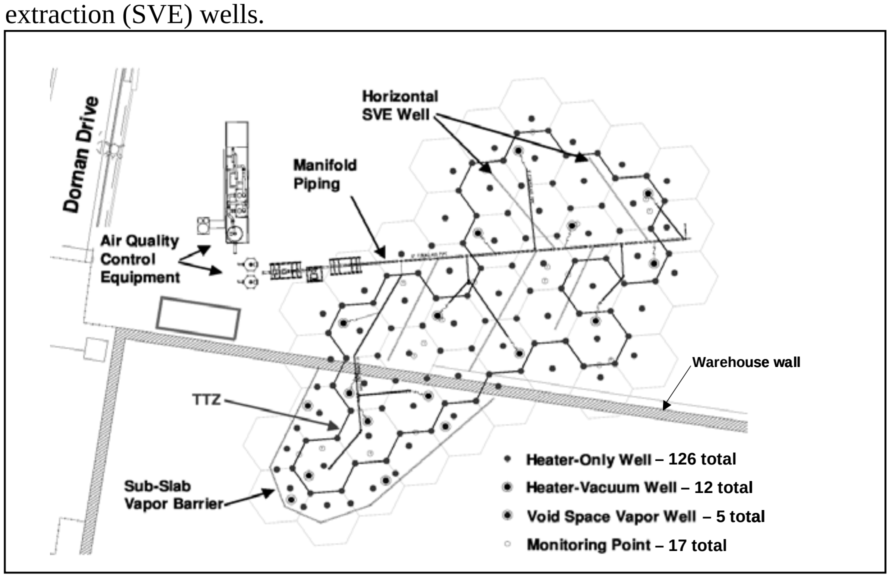

Figure 3. Plan View of Target Treatment Zone and ISTD System Layout (LaChance et al. 2006, reprinted with permission).

3.3. ISTD REMEDIAL DESIGN

TerraTherm's remedial design specified 126 vertical heater wells at 3.7-m spacing. Each heater well contained a 6.7-m long, 8.8 kW proprietary electric resistance heating element suspended within a sealed 6.35-cm diameter x 7.3-m long steel pipe. The power to the heating elements was thermostatically controlled with silicon-controlled rectifiers (SCRs) to automatically reach and maintain the desired heater operating temperature, which could be set as high as 800°C. Most of the time, the heaters operated at 70-80% of full power. To ensure attainment of the remedial goals, TerraTherm selected as the target treatment temperature the boiling point of water, 100°C, to be achieved at the coolest locations mid-way between the heaters throughout the TTZ. After installing the wells, a light aggregate concrete surface cover, 0.25-m thick was poured over the ground surface around the protruding wellheads and extending about 6 m beyond the limits of the TTZ. The surface cover: (a) provided insulation against heat loss, preventing contaminants from condensing near the land surface, which would occur if the soil were cool; (b) served as a vapor seal to increase the radius of influence of the vapor extraction screens and prevent fugitive emissions; and (c) precluded rainwater infiltration, which could lead to unwanted cooling of the treatment zone. Figure 4 shows a generalized cross-section of the subsurface conditions at the Richmond site and a conceptualization of the ISTD design.

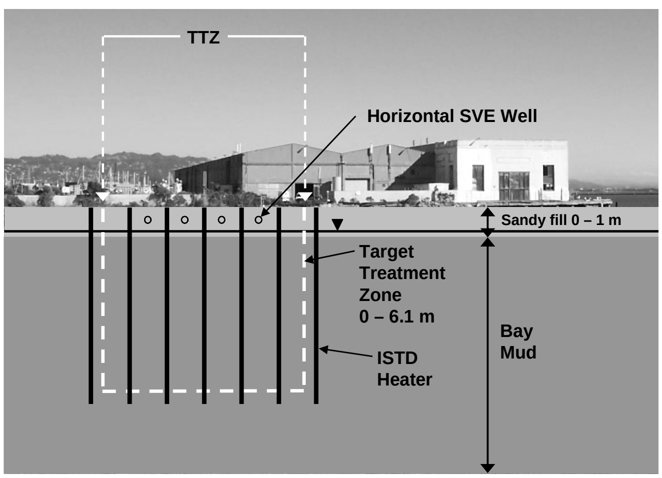

Figure 4. Cross-Section of Target Treatment Zone and Subsurface Conditions (LaChance et al. 2006, reprinted with permission).

3.3.1. *Vapor Collection*

The ISTD well field used at the Richmond site consisted of the above-described heater wells, each installed with a small sand pack between the pipe and the low permeability Bay Mud, and shallow horizontal SVE wells for the capture of steam and contaminant vapors. The sand packs around each vertical heater pipe provided a network of preferential pathways within which vapors produced during heating could move upwards along the heater wells into the overlying unsaturated high permeability layer of fill. There the vapors were readily removed by the horizontal SVE wells (Figure 4). This approach significantly reduced the cost and improved the performance of the ISTD system and minimized the potential for DNAPL banking and downward mobilization (LaChance et al. 2006).

3.3.2. *Vapor Treatment*

The extracted vapors were collected and then cooled, causing the steam generated within the subsurface to condense. The condensate was then separated from the vapor stream and treated by passage through liquid-phase granular activated carbon (GAC) prior to discharge to the sewer system. The non-condensable vapors were reheated to lower their relative humidity to ~50%, and then treated by passage through serial vessels containing vapor-phase GAC and an additional vessel containing GAC impregnated with $KMnO_4$, which proved effective for removal of VC, prior to discharge of the polished vapors to the atmosphere.

3.4. ISTD PERFORMANCE

Over the course of the 110 days of heating, the target temperature of 100°C was generally reached throughout the TTZ, at a power consumption totaling 2,200,000 kWh. Approximately 75% of the injected energy was used to raise the temperature of the TTZ, with the balance being removed as extracted steam. Over the 110 day period, approximately 660,000 liters or 30% of the water calculated to be present within the TTZ was boiled off and recovered as condensate. This volume of water is equivalent to approximately 500 pore volumes of steam generated and removed from all parts of the TTZ, or ~5 pore volumes per day. Such a large volume of steam being generated within and being forced to sweep through each and every location within the TTZ represents a powerful and irresistible cleaning agent. Thus, even in these very low permeable soils, steam stripping is the primary contaminant removal mechanism.

Confirmatory soil sampling was performed while the soil was still hot, using a method validated during the Cape Canaveral Inter-Agency demonstration project (Gaberell et al. 2002). In accordance with this method, the soil samples were collected within steel cylinders, which were capped and chilled under crushed ice immediately after being brought to the surface. Once at ambient temperature, they were shipped to the laboratory for analysis (Table 1).

Table 1. Results of Full-Scale ISTD Treatment at the Terminal 1 Site in Richmond, CA.

		PCE	TCE	*cis*-1,2-DCE	VC
		μg/kg	μg/kg	μg/kg	μg/kg
Remedial Goal		2,000	2,000	17,000	230
Average	Avg. Pre-Treatment	34,222	1,055	6,650	932
Soil	Avg. Post-Treatment	12.4	< RL	65	4.7
Concentration	No. of Samples < RL (i.e., ND)	54	64	41	63
	% Reduction Avg. Pre- to Post-	99.96%	> 99.6%	99.02%	99.49%
Maximum	Max. Pre-Treatment	510,000	6,500	57,000	6,500
Soil	Max. Post-Treatment	44	< RL	1,500	24
Concentration	% Reduction Max. Pre- to Post-	99.99%	> 99.3%	97.37%	99.63%

RL = Reporting Limit; ND = non-detect

The results indicate very high reductions (>99%) in average contaminant concentrations. The results are based on 17 pre-treatment samples, and 64 post-treatment samples, collected in accordance with a pre-established sampling plan from centroids (i.e., coolest locations mid-way between heaters within the TTZ) at random and biased depths. Of the 64 samples, 15 or 23% were collected at a depth between 5.5 and 6.1 m, indicating that contaminants were not mobilized downward during the treatment.

During the post-treatment soil sampling effort, over 40 sacrificial soil cores were also collected from the same borings but at adjacent depths to the above samples. They were immediately opened for observation and logging. Nearly all were moist, with the clay still exhibiting its original sticky, plastic behavior. This observation is consistent with the estimate that <3% of the volume of the TTZ became desiccated during ISTD, and the above-mentioned calculation that only 30% of the volume of water within the TTZ boiled off during thermal treatment.

4. Concluding Remarks

The City of Richmond Redevelopment Agency reported that achievement of residential cleanup standards at this site enabled the City to derive ~$5,000,000 more during the sale of the property than had they opted for less-stringent industrial cleanup standards. This additional amount much more than covered the $1,961,000 ISTD cost, plus the $350,000 cost of electricity at the prevailing rate in the Bay area. The entire ISTD remediation, including construction, operation and demobilization was accomplished in 9 months. The post-redevelopment value of the property is estimated at over $300,000,000.

References

Buelt, J.L. and K.H. Oma. 1990. In-Situ Heating to Detoxify Organic Contaminated Soils US Patent #4,957,393.

Daily, W.D., A.L. Ramirez, R.L. Newmark, K.S. Udell, H.M. Buettner, and R.D. Aines. 1995. Dynamic Underground Stripping: Steam and electric heating for in situ decontamination of soils and groundwater. US Patent # 5,449,251.

Davis, E.L. 1997. How Heat Can Enhance In-Situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique. *EPA Ground Water Issue* EPA/540/S-97/502. USEPA Office of Research and Development, Office of Solid Waste and Emergency Response, Washington, DC.

Davis, E.L. 2006 "Does Field Data Show Downward Mobilization of DNAPL during Thermal Remediation?" Abstract F-39, in: Bruce M. Sass (Conference Chair), *Remediation of Chlorinated and Recalcitrant Compounds—2006*. Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2006). ISBN 1-57477-157-4, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

De Rouffignac, E.P., G.L. Stegemeier and H.J. Vinegar. 2005. Thermally Enhanced Soil Decontamination. EPC Patent #1467826; other European patents issued.

Francis, J. and J. Wolf. 2004. "In Situ Remediation of Chlorinated VOCs and BTEX Using Electrical Resistance Heating." Paper 2B-19, in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds —2004*. Battelle Press, Columbus, OH.

Gaberell, M., A. Gavaskar, E. Drescher, J. Sminchak, L. Cumming, W.-S. Yoon, and S. De Silva. 2002. "Soil Core Characterization Strategy at DNAPL Sites Subjected to Strong Thermal or Chemical Remediation." in: A.R. Gavaskar and A.S.C. Chen (Eds.), *Remediation of Chlorinated and Recalcitrant Compounds—2002*. Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2002). ISBN 1-57477-132-9. Battelle Press, Columbus, OH.

Heron, G., M. van Zutphen, M.; T.H. Christensen, and C.G. Enfield. 1998. Soil heating for enhanced remediation of chlorinated solvents: A laboratory study on resistive heating and vapor extraction in a silty, low-permeable soil contaminated with trichloroethylene. *Environmental Science and Technology*, 32 (10), 1474-1481.

Heron, G. S. Carroll, and S.G.D. Nielsen. 2005. Full-Scale Removal of DNAPL Constituents using Steam Enhanced Extraction and Electrical Resistance Heating. *Ground Water Monitoring and Remediation*, 25 (4), Winter 2005, pp. 92-107.

Heron, G, R.S. Baker., J.M. Bierschenk and J.C. LaChance. 2006. "Heat It All the Way - Mechanisms and Results Achieved Using In-Situ Thermal Remediation." Paper F-13, in: Bruce M. Sass (Conference Chair), *Remediation of Chlorinated and Recalcitrant Compounds—2006*. Proceedings of the Fifth International Conference on Remediation of

Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2006). ISBN 1-57477-157-4, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

LaChance, J., G. Heron and R. Baker. 2006. "Verification of an Improved Approach for Implementing In-Situ Thermal Desorption for the Remediation of Chlorinated Solvents." Paper F-32, in: Bruce M. Sass (Conference Chair), *Remediation of Chlorinated and Recalcitrant Compounds—2006*. Proceedings of the Fifth International Conference on Remediation of Chlorinated and Recalcitrant Compounds (Monterey, CA; May 2006). ISBN 1-57477-157-4, published by Battelle Press, Columbus, OH, www.battelle.org/bookstore.

McGee, B.C.W. 2003. Electro-Thermal Dynamic Stripping Process for in situ remediation under an occupied apartment building. *Remediation*, Summer: 67-79.

Newmark, R.L. (ed.) 1994. Demonstration of Dynamic Underground Stripping at the LLNL Gasoline Spill Site. Final Report UCRL-ID-116964, Vol. 1-4. Lawrence Livermore National Laboratory, Livermore, California.

Pritchett, W.C. 1976. Method and apparatus for producing fluid by varying current flow through subterranean source formation. US Patent #3,948,319.

Stegemeier, G.L., and Vinegar, H.J. 2001. Thermal Conduction Heating for In-Situ Thermal Desorption of Soils. Ch. 4.6, pp. 1-37. In Chang H. Oh (ed.), *Hazardous and Radioactive Waste Treatment Technol. Handbook*, CRC Press, Boca Raton, FL.

Udell, K.S., N. Sitar, J.R. Hunt, and L.D. Stewart. 1991. Process for In Situ Decontamination of Subsurface Soil and Groundwater. US Patent # 5,018,576.

Udell, K.S. 1996. Heat and mass transfer in clean-up of underground toxic wastes. In *Annual Reviews of Heat Transfer*, Vol. 7, Chang-Lin Tien, Ed.; Begell House, Inc.: New York, Wallingford, UK, pp. 333-405.

USEPA. 2004. *In-Situ Thermal Treatment of Chlorinated Solvents: Fundamentals and Field Applications*. EPA 542-R-04-010. Office of Solid Waste and Emergency Responses, Washington, DC.

Vinegar, H.J., G.L. Stegemeier, E. P. De Rouffignac, and C.C. Chou. 1993. Vacuum Method for Removing Soil Contaminants Utilizing Thermal Conduction Heating. US Patent #5,190,405.

Vinegar, H.J., G.L. Stegemeier, E. P. De Rouffignac, and C.C. Chou. 1994. Vacuum Method for Removing Soil Contaminants Utilizing Thermal Conduction Heating. US Patent #5,318,116.