

In Situ Electrical Resistance Heating (ERH) for Treatment of Solvents, Greases, Fuels, Pesticides and Fumigants

Introduction and Conceptual Approach

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September 2009

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1. ERH Background

Electrical Resistance Heating (ERH) is an aggressive in situ thermal remediation technology that was developed by the U.S. Department of Energy from the original oil production technology to enhance vapor extraction remediation technologies in low permeability soils. Soil and groundwater are heated by the passage of electrical current through saturated and unsaturated soil between electrodes, not by the electrodes themselves. It is the resistance to the flow of electrical current that results in increased subsurface temperatures, and this is typically applied to the boiling point of water. It is estimated that more than 100 ERH applications have been performed. Capacity to perform these projects has increased over the years, and as many as 15 to 20 of these applications now being performed at any given time, mainly in North America, with some European applications.

While the main focus has been to vaporize volatile organic compounds, as one would expect other semi-volatile and non-volatile organic compounds have also been encountered, resulting in observations of chemical and physical reactions that have not been normally been incorporated into environmental restoration projects that are described herein.

2. ERH Approach

Electrical resistance heating (ERH) provides in situ thermal treatment with the goal of vaporizing volatile organic compounds to remove non-aqueous phase liquids. Heating results from the resistance to the passage of electrical current through soil moisture. Heat transport from this joule heating takes place mainly through conduction and convection.

ERH was commercialized in 1998 and pioneered by DPR's Greg Smith, P.E., P.G. at the former AT&T Skokie Works in Illinois achieving IL Taco Tier II groundwater cleanup standards removing approximately 27,000 pounds of trichloroethene (TCE) expressed as DNAPL in groundwater and soils; a technology today that represents a fairly mature in situ environmental restoration treatment system, about which much is continuing to be learned. It has been applied for the cleanup of chlorinated ethenes, ethanes, and methanes, pesticides, fuels, and has been proven effective in removing heavy grease from the subsurface. It is now being used to remediate sites impacted with herbicides, pesticides, oils and greases (Figure 1) and coal and oil tars from manufactured gas plants, and creosote sites. From this experience base, much has been learned about its capabilities, such that chemical, physical and biological processes that had not been considered for hazardous waste remediation, such as hydrolysis, may now be used.

2.1 Heating

As noted above, heat is generated by the resistance to electrical current flow in the pore water. Electricity seeks the path of least resistance, flowing through the more conductive, higher total dissolved solids usually associated with more contaminated zones first, treating these in preference to the lesser contaminated zones.

As noted above, ERH was developed by the U.S. DoE in the high desert of Washington state at Hanford National Laboratories. It was proven effecting in both unsaturated and saturated zones of desert soils. An intrinsic feature of the technology is that as soil moisture is boiled away, an electrical current cannot be maintained and current flow is forced into the lesser contaminated zones.

Electrical resistivity heating (ERH) is a remediation technology that involves passing electrical current through saturated or unsaturated soil, resulting in increased subsurface temperatures, usually to the boiling point of water. ERH is generally applied using either six-phase or three-phase electrical heating. ERH has been demonstrated as an effective technology for the removal of volatile and some semi-volatile contaminants from soil and groundwater¹.

During heating, pore water increases in volume 1700-fold as it is converted to steam. This has the potential to create fissures in clayey and silty soils, facilitating vapor transport.

2.2 Biodegradation

Temperature is considered to be one of the most important physical factors controlling the distribution and abundance of organisms. Bacteria adapt to a wide variety of environments, including habitats characterized by extreme temperatures, and can be sorted into descriptive groups based on the temperatures at which optimum growth has been observed (Table 1).

Table 1. Generally Recognized Optimum Growth Range for Various Groups of Microorganisms

Bacterial Classification	Optimum Growth Temperature
Psychrophiles	< 0 to < 20°C (<32 to 68°F)
Mesophiles	20 to < 45°C (<68 to <113°F)
Thermophiles	45 to 90°C (<113 to <194°F)
Extreme Thermophiles	90 to 110°C (<194 to <230°F)

In general, elevated temperatures that do not kill microbes or exceed the temperature tolerance of the microbial consortia will result in higher metabolic activity. The increased metabolic activity of enzymatic systems with temperature continues up to the temperature where the enzymes denature or lose the structural stability that enables them to function. Mesophiles are more efficient at degrading hydrocarbons at temperatures from 30 to 40°C (86 to 104°F; Bossert and Bartha, 1984²). Thermophiles actively degrade hydrocarbons and recalcitrant NAPL constituents (PAHs and high-molecular-weight hydrocarbons) at temperatures up to 70°C (158°F; Huesemann, et al., 2002)³. Even though biocatalytic reactions proceed faster at higher temperatures, the growth rate of thermophiles is often slower than mesophiles at their optimum growth temperatures. Consequently, degradation reactions at elevated temperatures found at an in situ thermal treatment site may progress more rapidly as thermophiles are capable of mediating degradation reactions at a faster pace without diverting energy to increasing biomass.

¹ USEPA, *Cost and Performance Report, Six Phase™ Heating (SPH) at a Former Manufacturing Facility, Skokie Illinois*. Office of Solid Waste and Emergency Response, Technical Innovation Office. October, 1999.

² Bossert, I. and R. Bartha. "The Fate of Petroleum in Soil Ecosystems." *Petroleum Microbiology*, R. Atlas, ed., Macmillan, New York, pp. 435-473, 1984.

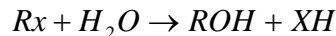
³ Huesemann, M.H., T.S. Hausmann, T.J. Fortman and M.J. Truex. "Evidence of Thermophilic Biodegradation for PAHs and Diesel in Soil." *Proceedings of the Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, May 2002.

The combination of increased metabolic activity and greater bioavailability allows for enhancing in situ biodegradation at in situ thermal remediation sites. During active thermal treatment, in situ degradation may be temporarily inhibited once subsurface temperatures increase above the tolerance range of indigenous mesophiles. Microorganisms have several mechanisms for surviving unfavorable conditions, including the formation of non-vegetative structures (i.e., spores or cysts) that are metabolically less active and allow the organism to survive until environmental conditions become more optimal. Bacterial cells in bench-scale tests of creosote-contaminated soil have demonstrated the ability to rapidly become metabolically active following steam injection (Richardson, 2000)⁴.

Cometabolic processes derive no apparent benefit from the energy derived from the reactions, and as a result, it is interpreted that there is no driving force. From a microbiological standpoint under normal groundwater temperatures, cometabolic transformations present a disadvantage because the input of reducing equivalents cost energy and toxic transformation products are formed. From an in situ thermal or electrokinetic perspective, cometabolic reactions may be considered almost serendipitous, since energy is input to heat the system to remove NAPL, the corresponding cometabolic dechlorination reactions appear as a benefit during in situ thermal treatment.

2.3 Hydrolysis

Hydrolysis involves the chemical reaction with water, without regard to redox conditions, dissolved minerals, or the presence of soil microbes. For the reaction to take place, the organic compound needs to be dissolved in water, and the reaction can be modified by pH and temperature. The general hydrolysis reaction, involves the exchange of some functional group *X* (e.g., chloride, Cl) with the hydroxide group in water.



While pH influences the rate of some hydrolysis reactions, there are few environmental situations where it can be used, resulting in temperature adjustment to be the most practical means to modify the reaction. Heating the subsurface from ambient temperatures to 80°C will increase the hydrolysis rates of most organic compounds by a factor of greater than 1,000. Heating to 100°C will increase the rate of hydrolysis by a factor of over 10,000.

Thermally-enhanced hydrolysis is generally the most cost-effective remediation method for halogenated alkanes, and many fumigants and pesticides. A listing of common compounds with their hydrolysis half-lives at 100°C is shown in Table 2. In situ thermal methods have been successfully used to hydrolyze 1,1,1-trichloroethane (TCA), 1,1,2,2-tetrachloroethane (TeCA), dichloromethane (methylene chloride) and ethylene dibromide to remediate groundwater.

For compounds with relatively low volatility and non-hazardous hydrolysis progeny, it may be possible to rely on hydrolysis alone to treat the site, with potentially no vapor recovery and treatment. Examples include the fumigants dichloropropane and

⁴ Richardson, R. E. *Final Report on Post-Steam Microbial Experiments Performed at U.C. Berkeley for the Wyckoff/Eagle Harbor Superfund Site*. Submitted for publication, 2000.

trichloropropane which have the progenies propylene glycol and glycerol, respectively. Both of these progenies are relatively easy to biodegrade.

As can be seen from Table 2, the hydrolysis rates for halogenated alkenes (e.g., TCE and PCE) tend to be very slow, even at steam temperatures. However, the hydrolysis rates for halogenated alkanes (e.g., TCA and carbon tetrachloride) tend to be very fast.

Table 2. Hydrolysis half-lives at pH 7.

Compound	Half-life at 15°C (years)	Half-life at 100°C (days)	pH Effect	Hydrolysis Product	Reference
chloroform	8019	117	7.1+	mineralizes	Jeffers, et al., 1989
methylene chloride	3282	35	-	mineralizes	Mabey and Mill, 1978
bromoform	3089	43	pH++	mineralizes	Washington, 1995
dichlorofluoromethane	973	22	6.0+	mineralizes	Jeffers et al., 1996
1,1,2-TCA	479	39	pH++	DCE	Jeffers et al., 1989
1,2-DCA	386	6	-	ethylene glycol	Jeffers et al., 1989
1,1-DCA	285	3	-	acetaldehyde	Jeffers et al., 1989
carbon tetrachloride	206	1	-	mineralizes	Jeffers et al., 1989
1,2,3-trichloropropane	192	3	-	glycerol	US EPA-600/3-87-019
1,1,1,2-TeCA	178	0.3	pH++	TCE	Jeffers et al., 1989
1,2-dichloropropane	78	0.8	-	propylene glycol	Washington, 1995
Ethylene dibromide	9	0.5	-	mineralizes	Weintraub et al., 1986
1,3-dichloropropane	8	0.4	-	propylene glycol	Jeffers et al., 1989
1,1,1-TCA	6	0.03	-	1,1-DCE	Jeffers et al., 1989
1,1,2,2-TeCA	1	0.1	pH++	TCE	Jeffers et al., 1989

#.#+ = The neutral and alkaline reactions are equal at the stated pH. Higher pH accelerates hydrolysis.

pH++ = Alkaline dominant, a unit increase in pH will increase the hydrolysis rate by a factor of 10.

- = Change in pH in the range of 5 to 9 pH does not significantly change the rate of hydrolysis.

2.4 Dissolved Gases

According to Amos, et al., (2005) ebullition in saturated porous media occurs when the sum of the vapor pressures exceeds the hydrostatic and capillary pressures. For pure water, this represents a phase change from liquid to gas (i.e., boiling). Since the total vapor pressure is the sum of partial pressures of all of the components of the mixture, the boiling point of the mixture can be achieved at a lower temperature than the boiling points of any of the separate components as described by Dalton's, Raoult's, Henry's and Ideal Gas Laws (Lupis, 1983)⁵. This phenomenon has also been called co-distillation or steam distillation (Davis, 1998)⁶. The implication for in situ thermal remediation is that many contaminants can be removed as vapor at temperatures below that of the boiling point of water, or at steam temperatures where their boiling

⁵ Lupis, C.H.P. *Chemical Thermodynamics of Materials*, New York, Elsevier, 1983.

⁶ Davis, E.L. *Steam Injection for Soil and Aquifer Remediation*. EPA/540/S-97/505, January 1998.

temperatures are greater than 100°C. Figure 1 shows the removal of heavy grease from the subsurface at Ft. Lewis, achieved through gas bubble floatation.



Figure 1: Heavy grease recovered through gas bubble floatation mechanism, Ft. Lewis, WA

2.4.1 Carbon Dioxide

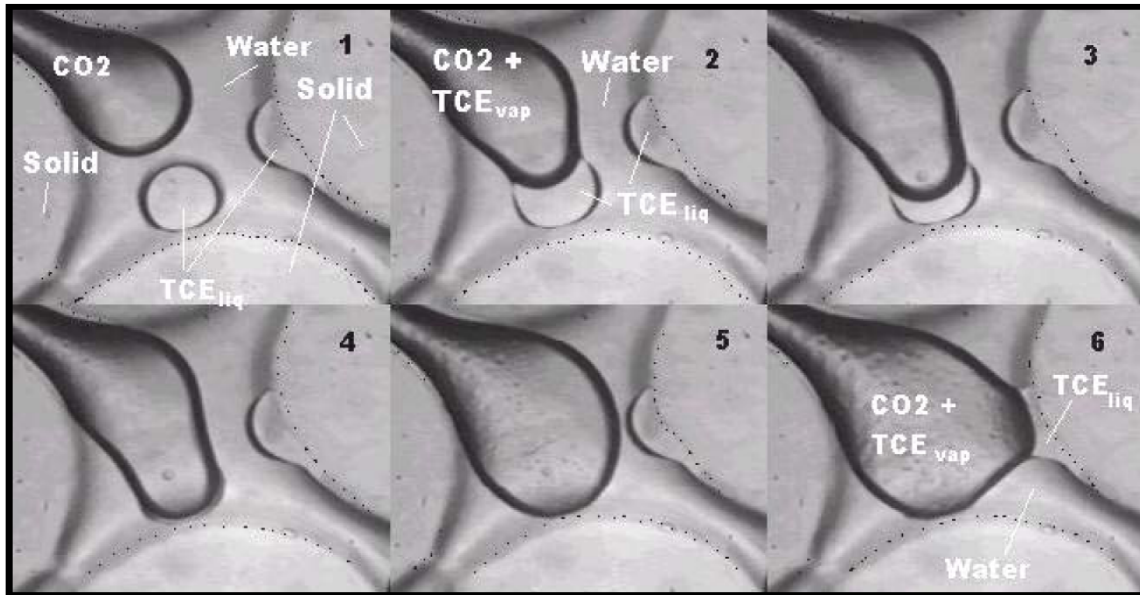
Groundwater contains many dissolved gases, with one of the most significant being carbon dioxide (CO₂), which is at saturation in natural groundwater (Stumm and Morgan, 1981)⁷. Heating natural groundwater results in creating super-saturated conditions with respect to carbon dioxide, creating bubbles and potentially ebullition if the vapor pressures exceed the hydrostatic and capillary pressures (as mentioned above). Carbon dioxide results from the dissolution of carbonate minerals into groundwater.

Figure 1 presents photomicrographs of carbon dioxide bubble growth in saturated porous media. Globules of trichloroethene (TCE) as dense non-aqueous phase liquid (DNAPL) are also present. In photomicrograph 1, we can see the saturated porous media and the TCE globules. Where carbon dioxide is at supersaturation in groundwater, bubbles form and grow. Carbon dioxide is a non-polar and organic gas, which facilitates its ability to dissolve organic liquids and gases. Carbon dioxide being an organic gas, and since like-dissolves-like, provides for the dissolution of organic compounds into this gas in preference to water or steam. In photomicrograph 2, we see the CO₂ bubble grow and come into contact with the TCE DNAPL globule. Note that the contact between the TCE globule and the CO₂ bubble are maximized; this facilitates dissolution of TCE into

⁷ Stumm, W. and J.J. Morgan (1981). *Aquatic Chemistry, An introduction Emphasizing Chemical Equilibria in Natural Waters, 2nd Edition*. John Wiley and Sons, New York, NY.

CO₂. In photomicrographs 3 and 4, the CO₂ bubble remains relatively static in size, yet the TCE globule is reduced, showing that the TCE is being dissolved into the CO₂ bubble. In photomicrograph 5, we see the CO₂ bubble continue to grow, as would occur during heating and in photomicrograph 6 come into contact with another TCE globule, again with the contact between the two organic materials maximized.

FIGURE 2: Photomicrograph of Carbon Dioxide Bubble Growth in Saturated Porous Media. (Courtesy of Dr. Marios Ioannidis)



2.4.2 Other Gases

Groundwater contains many dissolved gases besides CO₂, including nitrogen and trace amounts of argon (Amos, et al., 2005)⁸. With the release of organic compounds to the subsurface additional gases are generated, including nitrogen and ammonia from the reduction of nitrates and nitrites in groundwater, hydrogen sulfide from the reduction of sulfate in groundwater and methane from the reduction of water and bicarbonate.

Quantification of various processes that produce these gases, including the rate of methane production, consumption, and transport in the saturated and unsaturated zones, as well as mass transfer between the zones, is difficult (Amos et al., 2005). Methane production from below the water table may be significant where highly reducing conditions are found, and because methane is fairly insoluble, formation of gas bubbles and ebullition may be possible (Reeburgh, 1972⁹; Kipphut and Martens, 1982¹⁰; van Breukelen et al., 2003¹¹). Methane may also be produced in the vadose zone, but may be

⁸ Amos, R.T., U. Mayer, B.A. Belkins, G.N. Delin and R.C. Williams (2005). Use of dissolved and vapor phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface. *Water Resources Research* Vol 41.

⁹ Reeburgh, W. S. (1972), Processes affecting gas distribution in estuarine sediments, in Mem. Geol. Soc. Am., 133, 383– 389.

¹⁰ Kipphut, G. W., and C. S. Martens (1982), Biogeochemical cycling in an organic-rich coastal marine basin, part 3: Dissolved gas transport in methane-saturated sediments, *Geochim. Cosmochim. Acta*, 46, 2049 – 2060.

¹¹ van Breukelen, B. M., W. F. M. Roling, J. Groen, J. Griffioen, and H. W. van Verseveld (2003), Biogeochemistry and isotope geochemistry of a landfill leachate plume, *J. Contam. Hydrol.*, 65, 245– 268.

oxidized by the flux of atmospheric oxygen from the ground surface as part of the normal flow of air and percolation of water (Hers et al., 2000¹²; Chaplin et al., 2002¹³).

3 ERH System Layout

The ERH system consists of a series of electrodes. Most commonly, electrodes are constructed using steel pipe, but other configurations have also been used, such as sheet pile. Typical spacing is 17 to 25 ft, with 17 to 19 ft being the most typical to strike a balance between material and drilling costs and time to achieve the target temperature.

The components required to implement ERH include:

- Electrodes.
- Vapor recovery wells (which are often co-located in the same boreholes as the electrodes).
- A steam and vapor collection system, including piping, blower, and condenser.
- A vapor treatment system.
- An ERH power control unit to condition power for application to the subsurface.
- Data acquisition systems.
- A computer control system with modem for continuous remote monitoring and control of power.

The ERH electrodes conduct electrical energy into the subsurface and can be designed to allow independent control of the energy input to discrete depth intervals. Electrodes are typically constructed using either galvanized steel pipe, copper plate or sheet pile as illustrate in Figure 3 to treat distinct zones in the subsurface, such that multiple electrodes can be installed within the same boring. Electrodes constructed using steel pipe are installed in the subsurface in a way similar to the methods for installing groundwater monitoring wells. In the electrically conductive intervals, the surrounding borehole annulus is packed with a conductive material, such as graphite and/or steel shot, to increase the effective diameter of the electrode. In those portions of the subsurface where electrical resistivity heating is not desired, the electrode construction materials are insulated and the surrounding annulus is filled with relatively non-electrically conductive materials such as sand, bentonite, or cement.

Vapor recovery (VR) is accomplished using conventional vapor extraction techniques utilizing shallow wells installed either vertically or horizontally. The wells may extend into the water table, depending upon site conditions. Once steam and volatile contaminants have been collected by the VR system, the steam is condensed and the vapor is cooled to ambient temperatures. Conventional vapor treatment techniques are used to adsorb or destroy the vapors. However, owing to temperatures resulting from application of ERH, the materials for the construction of the wells and headers must be able to withstand temperatures in the order of 100°C.

¹² Hers, I., J. Atwater, L. Li, and R. Zapf-Gilje (2000), Evaluation of vadose zone biodegradation of BTX vapors, J. Contam. Hydrol., 46, 233– 264.

¹³ Chaplin, B. P., G. N. Delin, R. J. Baker, and M. K. Lahvis (2002), Long term evolution of biodegradation and volatilization rates in a crude oil contaminated aquifer, Bioremediation J., 6, 237–255.



Figure 3: Layout of ERH treatment area, Ft. Lewis, WA

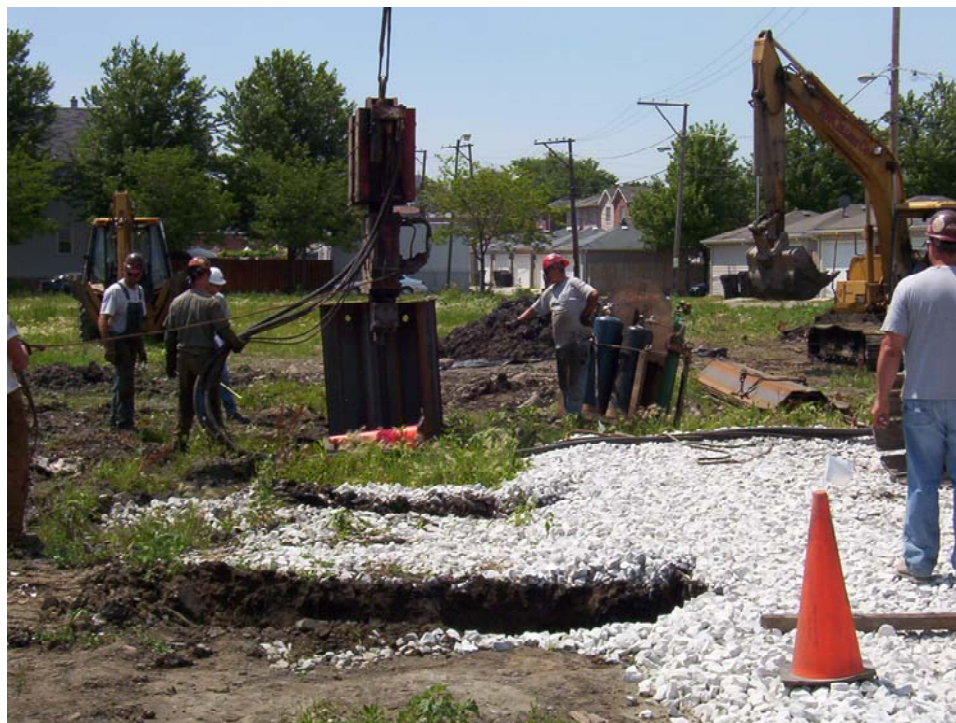


Figure 4: Installation of sheet pile for use as electrodes

An ERH power control unit (PCU) is used to control and distribute standard three-phase electrical power and to adjust the utility voltage to the appropriate level for subsurface heating. The PCU includes isolation transformers that force ERH current to flow between the electrodes only, preventing ERH current from flowing to a distant

electrical sink. Because there is no electrical path through the isolation transformer, electricity cannot leave the ERH field and move away from the site—the current cannot find a return path to complete the circuit.

The ERH process is typically automated, with an onsite computer equipped with a modem and appropriate software for remote access and monitoring. Multiple applications can be monitored and controlled remote from the remediation site or sites, connected via dial-up modem. Site visits are required for periodic checks of the equipment, maintenance of mechanical equipment, monitoring, manual adjustments to the electrode configurations, and troubleshooting equipment malfunctions.

The only additive normally required for ERH is a drip source of potable water that is applied to soil immediately surrounding the operational electrodes. This water addition, normally incorporated in low permeability environments, prevents the soil adjacent to the electrodes from drying out and becoming nonconductive. Most aquifers contain sufficient recharge capacity to keep the electrodes moist and conductive throughout the heating process and water addition to the deeper sections of the electrodes is typically not required.

The process of in situ steam generation converts groundwater to steam and then vapor recovery removes the steam from the subsurface. This has the same effect as groundwater pumping. The net result is a slight drawdown of the water table and some measure of hydraulic control. Within the vadose zone, some decrease of soil moisture may occur if the site is covered (preventing rainfall percolation); however, the reduction of moisture observed under ERH applications has not significantly enhanced the vapor permeability of the soil and to date has not been observed to adversely affect soil geotechnical characteristics.

After the initial heat up to steam temperature, contaminant concentrations in the recovered soil vapors decrease. In a remedial cleanup, when these concentrations decrease by approximately 80% from peak concentrations, electrical resistivity heating typically is stopped and interim groundwater or soil sampling is performed. The analytical results are then evaluated to determine if additional treatment is required. Natural attenuation processes (most importantly intrinsic biodegradation) are also commonly assessed at this time to determine if remediation goals can be attained under post-thermal treatment conditions. Based upon the results of interim sampling, heating can be continued or post-remedial sampling can be conducted to document that the remedial action objectives for soil and groundwater have been met.

Above ground treatment typically involves treating vapors, condensate, and entrained water. Vapor treatment involves reducing the moisture content, typically through conventional “knock-out” pot arrangements, followed by appropriate treatment (e.g., granular activated carbon, combustion, thermal oxidation, etc.) prior to atmospheric discharge. Treatment of condensate and entrained water involves condensation and cooling through a cooling tower. The cooling tower is analogous to an air stripper, with the vapor fed to the vapor stream treatment equipment. Typically, the condensate and entrained water makes multiple passes through the cooling tower, significantly reducing concentrations of volatile constituents. The treated water is then disposed as appropriate for the site (e.g., offsite treatment and disposal, discharge to the local POTW, NPDES-permitted discharge, etc.).

4 Estimated Treatment Costs

Treatment costs are dependent on the nature of the compounds being treated, the cleanup goals, the depth of treatment, and the volume and geometry of the soil volume being treated. The lower the chemical's boiling point, the less energy is required to vaporize it. A more spherical shaped soil volume has less surface area for heat loss than a flat shaped geometry, resulting in lower costs. In general, costs range from \$85 to \$150 per cubic yard. However, costs as low as \$35 per cubic yard has been achieved.

5 Health, Safety and Community Acceptance

ERH has been applied in residential areas and factory settings, with electrodes located adjacent to and beneath homes and beneath operating factories. As noted above, isolation transformers prevent stray currents from migrating from the treatment zone. Grounding checks are preformed to ensure that metallic objects (e.g., chain link fence, plumbing, hydraulic lifts, rebar, roof drains, etc.) are not charged by this process.

The technology is well accepted by the public because of its rapid cleanup and minimal disruption to communities. In many cases, electrode completion can be below grade, with the equipment contained behind chain link fence.



Figure 5: ERH system in operation behind a dry cleaner in a strip mall in suburban Chicago. ERH is keeping alley clear of snow and equipment is hidden behind chain link fence.