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In Situ Treatment Technologies for Contaminated Soil

ENGINEERING FORUM ISSUE PAPER

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1.0 Introduction

This issue paper provides summary information on a wide variety of in situ technologies for the treatment of contaminated soil in both the vadose zone and saturated and unsaturated source zones. The in situ technologies presented involve applying chemical, biological, or physical processes to the subsurface to degrade, remove, or immobilize contaminants without removing the bulk soil. Compared to excavation and ex situ treatment, the use of these technologies offers several benefits, such as addressing deep contamination and generally costing less.

The summary for each in situ technology includes a basic description of the technology, its implementation, applicability based on contaminants and site characteristics, general limitations, costs, and status of the technology's application. Information in this paper is intended to give project managers and engineers a basic understanding of the technology that will allow for further consideration of its applicability at a site. Project managers and engineers seeking guidance on the design and operation of these technologies should refer to the references listed in this paper and other material on the specific technology of interest.

The treatment technologies presented include common practices as well as innovative alternatives for treating contaminated soil and source zones in situ. The paper does not address technologies in the experimental phase, such as nanoscale iron injection, nor does it present containment technologies, such as capping, liners, and barrier walls.

Information provided in this paper comes from a number of sources. In general, every attempt has been made to use technical literature, including articles, textbooks, and U.S. Environmental Protection Agency (EPA) and other agency documents. Where appropriate and possible, Web links have been provided for additional information. This paper is not intended to serve as guidance or policy, nor does it indicate the appropriateness of using a technology at a specific site.

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November 2006
www.epa.gov/tio/tsp

2.0 Background on Issue Paper

This issue paper was developed at the request of EPA's Engineering Forum to provide information to EPA project managers on the application of in situ treatment technologies for contaminated soil. The Engineering, Federal Facilities, and Ground Water Forums, established by EPA professionals in the ten regional offices, are committed to identifying and resolving scientific, technical, and engineering issues impacting the remediation of Superfund sites and corrective action sites under the Resource Conservation and Recovery Act (RCRA). The forums are supported by and advise the Office of Solid Waste and Emergency Response's (OSWER) Technical Support Project, which established Technical Support Centers in laboratories operated by the Office of Research and Development, Office of Radiation Programs, and the Environmental Response Team. The centers work closely with the forums, providing state-of-the-science technical assistance to EPA project managers.

3.0 In Situ Treatment Technologies

For purposes of this paper, the in situ technologies are categorized into three major groups based on the primary mechanism by which treatment is achieved:

- Physical/Chemical Treatment Technologies
- Biological Treatment Technologies
- Thermal Treatment Technologies

Physical/chemical treatment includes soil vapor extraction, solidification/stabilization, soil flushing, chemical oxidation, and electrokinetic separation. Biological treatment uses microorganisms or vegetation to degrade, remove, or immobilize contamination in soil. Biological technologies include bioventing, phytoremediation, and monitored natural attenuation. Electrical resistivity heating, steam injection and extraction, conductive heating, radio-frequency heating, and vitrification are technologies summarized under thermal treatment. Table 1 provides a general summary of the effectiveness of the technologies for various contaminant classes.

The principal feature of many in situ treatment technologies is delivery and recovery of fluids or other reactants to the subsurface. The ability to control and monitor the delivery and recovery of these fluids or reactants is central to the effectiveness of in situ technologies in treating the contamination. Depending on the subsurface conditions and contaminant characteristics, each in situ technology has benefits and limitations on its ability to effectively deliver, control, and recover administered fluids and/or reactants and the contaminants. For example, soil permeability is an important factor in the delivery of a reactant for chemical oxidation or a gas for bioventing, whereas it is not as important for conductive heating. Consequently, the characterization of this parameter would generally be more critical for chemical oxidation or bioventing than for conductive heating.

The increased use in recent years of several in situ soil treatment technologies, such as chemical oxidation and thermal treatment, has shown that both technologies are a viable option for addressing source zones contaminated by nonaqueous phase liquids (NAPLs). In addition, greater emphasis is being placed on examining these technologies for their potential synergies as treatment trains to address contamination in the subsurface. This integrated approach has the potential for providing a more effective site remediation.

For information on various in situ technologies:

Harzardous Waste Cleanup Information (CLU-IN) website at: http://www.cluin.org/techfocus/

Federal Remediation Technologies Roundtable (FRTR) website at: http://www.frtr.gov/

Naval Engineering Facilities Environmental Restoration & BRAC (NAVFAC) website at: http://enviro.nfesc.navy.mil/erb

3.1 Physical/Chemical Treatment Technologies

Physical/chemical technologies, which represent the most diverse group of remediation technologies, include soil vapor extraction, solidification/stabilization, oxidation, soil flushing, and electrokinetic separation.

3.1.1 Soil Vapor Extraction

In situ soil vapor extraction (SVE) is a remediation technology in which a vacuum is applied to induce a controlled subsurface air flow to remove volatile organic compounds (VOCs) and some semivolatile organic compounds (SVOCs) from the vadose zone

Table 1. Summary of In Situ Treatment Technologies Applications for Contaminant Classes

Key: ❍ Better ◗ Average ● Worse S=Specific to chemical type	Nonhalogenated VOCs	Halogenated VOCs	Nonhalogenated SVOCs	Halogenated SVOCs	Fuels	Inorganics	Radionuclides[1]	Explosives
In Situ Physical/Chemical								
Soil Vapor Extraction	❍	❍	●	●	❍	●	●	●
Solidification/Stabilization	●	●	◗	◗	●	❍	❍	●
Chemical Oxidation	◗	◗	●	◗	●	S	●	◗
Soil Flushing	❍	❍	◗	◗	◗	❍	●	●
Electrokinetic Separation	◗	◗	◗	◗	●	❍	◗	●
In Situ Biological Treatment								
Bioremediation	❍	❍	❍	S	❍	S	S	❍
Bioventing	❍	❍	❍	●	❍	●	●	●
Phytoremediation	◗	◗	◗	S	◗	◗	●	●
In Situ Thermal								
Thermal Treatment (electrical resistivity heating, steam injection and extraction. conductive heating, radiofrequency heating, and in situ vitrification)	❍	❍	❍	❍	❍	●	●	●

Adapted from Federal Remediation Technologies Roundtable Remediation Screening Matrix, Table 3.2. http://www.frtr.gov/matrix2/section3/table3_2.html

[1]For more information on radionuclide technologies see: U.S. EPA.1996. Technology Screening Guide for Radioactively Contaminated Sites, EPA/402/R-96/017. http://www.epa.gov/superfund/resources/radiation/pdf/techguide.pdf

to the surface for treatment. The configuration of the system usually involves attaching blowers to extraction wells which are generally constructed with slotted polyvinyl chloride (PVC) to induce airflow through the soil matrix (Army Corps of Engineers [USACE] 2002). The contaminated air is brought to the surface and passed through a vapor/liquid separator to remove any moisture before the air is treated. Treatment is typically done by adsorption (activated carbon), or for more concentrated waste streams, by thermal oxidation systems (U.S. EPA 2006). The water generated by the liquid separator may also require treatment (Figure 1). When expected concentrations in the air stream are sufficiently high (1,000 to 5,000 parts per million [ppm] or more) for free product recovery for recycling, a stand alone condensation treatment system might be considered. This type of system is generally not used for mixtures of chemicals, and at some point the condenser system will need to be changed out when concentrations drop (USACE 2002).

Concrete, asphalt, geomembrane, or other low-permeability covers are often placed over the soil surface to prevent short-circuiting of air flow and to increase the radius of influence of the extraction wells. Replacement air can be introduced into the subsurface by injecting air via a blower or by allowing air to flow into passive injection wells. While vertical wells are the most widely used SVE design method, when the contamination and/or the water table is shallow, horizontal wells or trenches provide better lateral flow and superior formation access.

The SVE process is driven by the partitioning of volatile materials from condensed phases (sorbed on soil particles, dissolved in pore water, or nonaqueous liquid) into the soil gas being drawn through the subsurface. The partitioning is controlled by contaminant and soil properties. These properties include contaminant vapor pressure, Henry's law constant, solubility, soil intrinsic permeability, water content (which should be low, but very dry soils also inhibit contaminant mobilization), and organic carbon content (Air Force Center for Environmental Excellence [AFCEE] 2002). SVE is best suited in well-drained, high-permeability soil (sand and gravel) with a low organic carbon content. Low permeability soil or heterogenous soil with high carbon content are more difficult to treat with SVE and often require amendments, such as pneumatic or hydraulic fracturing.[1] Fracturing allows for high preferential flow paths, but the bulk of the contaminant load still depends upon low flow or diffusion from the competent soil matrix.

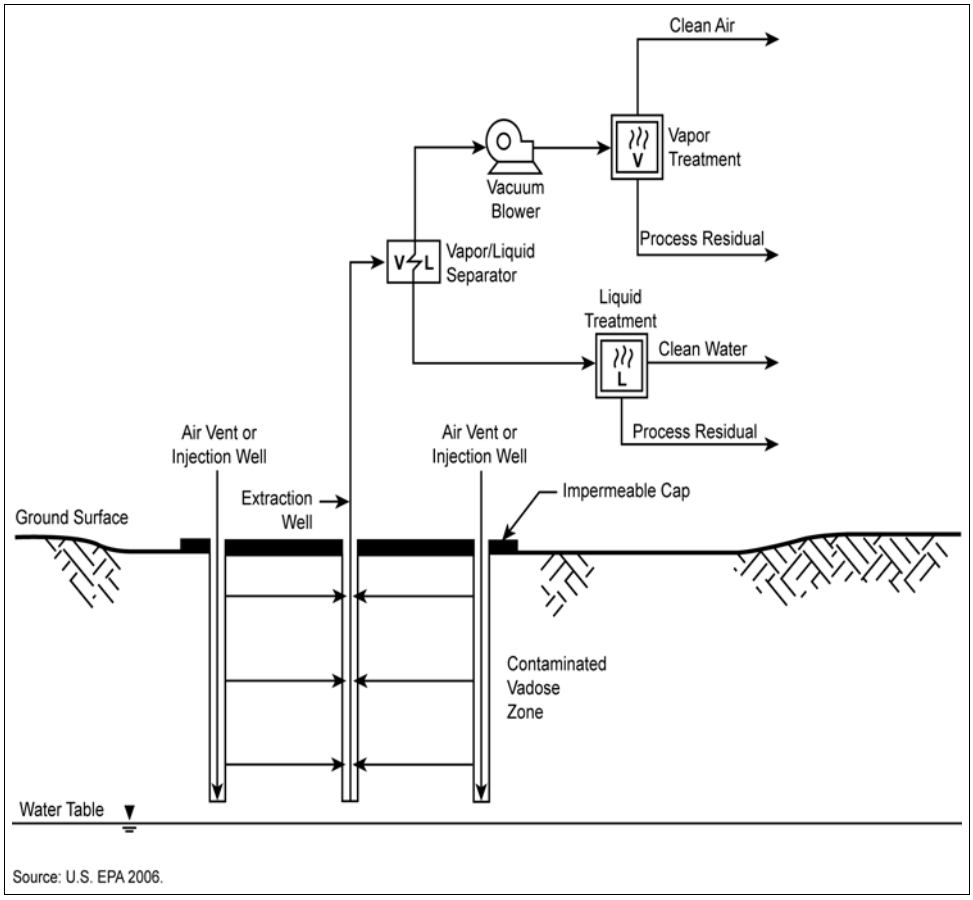

Figure 1. Typical Soil Vapor Extraction System

Like fracturing, heterogenous subsurfaces provide differential flow paths that result in efficient removal of contaminants in the permeable layers, with the less permeable layers being subject to slow diffusive forces. Rate-limited diffusion in the less permeable soils extends the time needed for remediation; therefore, it may be more efficient to approach these types of sites with a pulsed pumping strategy, in which the blowers are turned off at predetermined effluent concentrations, and the contaminants are allowed to diffuse into the "clean" permeable layers.

After a suitable (site-specific) time, the blowers are turned back on to capture the more concentrated soil vapors (AFCEE 2002). If appropriate, this method can save money on electricity and other costs. For other examples of energy conservation, see Gill and Mahutova (2004).

When designing an SVE system, DiGiulio and Varadhan (2001) advise care in choosing standard radius of influence (ROI) methods to place extraction wells. These methods generally rely on measuring vacuum differentials with distance from the venting well. Vacuum measurements can indicate the direction of a flow gradient, but as the vacuum measured approaches ambient pressures, they may give a false indication and lead to placing wells too far apart. In addition, vacuum measurements give no information on the effective gas flow through the various subsurface materials. For example, one-dimensional measurements made on layers of sand and silty clay will yield equivalent vacuums, while the effective gas flow is through the sand, with little going through the silty clay. A more relevant approach to well layout is to achieve a pore velocity

[1] Fracturing is the creation of cracks or sand-filled fissures in low- permeability formations.

that exceeds some minimum rate everywhere within the contaminated zone (USACE 2002).

As the vapor extraction system continues to operate, effluent contaminant concentrations generally become asymptotic (steady-state removal of very low concentrations). Unless the SVE system is addressing a single contaminant species, measurements of the venting effluent should provide the total mass being removed as well as relative compound concentrations. Speciation data also help in evaluating the system's efficiency. Because the chemicals in a mixture have different chemical/physical properties, they will leave the mixture at different rates; hence, a drop in total concentration does not necessarily mean a drop in available contaminant or system efficiency, but rather exhaustion of certain species. It is also important to test each extraction well in the system individually to determine if the drop is occurring across all wells (USACE 2002). Testing of the header alone may mask wells that have low flow and high concentrations that are being diluted by other wells in the system.

Maintaining asymptotic levels over a period of many months is often interpreted as a sign that the SVE effort has been successful and should be shut down; however, as USACE (2002) states: "although the decrease of concentrations in the extracted vapor is an indication of the effectiveness of the system, it is certainly not conclusive evidence that the concentrations in the soil have decreased proportionally."

Reasons for a decrease in contaminant concentration, other than reaching cleanup goals, include:

- The system has exhausted the supply of contaminants that it can advectively reach, and their continued presence, at very low concentrations, represents a draw upon diffusion rate-limited source areas.
- The water table has risen and the source areas are no longer available to the SVE system.
- The soil has reached a dryness factor that hinders, rather than promotes, SVE.
- The measured flow represents dilution from fully flushed areas near the extraction well, while understating considerably more contaminated areas further away, near stagnation points (AFCEE 2002 and DiGiulio and Varadhan 2001).

If no rebound is found after shutting the system down for a site-specific determined time, then confirmation sampling should be done. Confirmation sampling can be accomplished with an extensive soil gas survey, continuous soil sampling on a statistically determined grid, or professional judgment with sufficient previous characterization information gained by use of direct push tools, such as the membrane interface probe or, in the presence of hydrocarbons, by laser-induced fluorescence spectroscopy.

If a site has contaminated groundwater, it should be addressed along with the vadose zone contamination. Often this can be accomplished using a multi-phase extraction (MPE) system to simultaneously remove contaminants from soil and extract contaminated groundwater. A discussion of MPE, which is not within the scope of this document, can be found in U.S. EPA (1999) and USACE (1999).

The cost of SVE is site-specific and depends in part on the hydrogeology, type and amount of contaminants, and whether the offgas requires treatment. The FRTR website estimates the cost is between $10 and $40 per cubic yard, with a typical pilot program costing between $10,000 and $40,000. The NAVFAC website provides a $20 to $60 per cubic yard estimate. USACE (2002) provides a strategy for estimating costs and a checklist for items to include in the estimate. SVE is a mature, widely used technology, and many vendors are capable of implementing the technology.

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3.1.2 Solidification/Stabilization

Solidification and stabilization (S/S) refer to closely related technologies that use chemical and/or physical processes to treat radioactive, hazardous, and mixed wastes. Solidification technologies encapsulate the waste to form a solid material. The product of solidification may be a monolithic block, a clay-like material, a granular particulate, or some other physical form commonly considered "solid."

Stabilization technologies reduce the hazard potential of a waste by converting the contaminants into less soluble, mobile, or toxic forms (e.g., Cr(VI) to Cr(III)). The physical nature and handling characteristics of the waste are not necessarily changed by stabilization.

Chemical stabilization relies on the reduction of contaminant mobility by physical or chemical reactions with the contaminant, rather than the contaminant matrix (e.g., soil or sediment), as is done with solidification. The mobility of organic and inorganic compounds can be reduced through various precipitation, complexation, and adsorption reactions. Commonly applied inorganic stabilization agents include soluble silicates, carbon, phosphates (e.g., apatite), and sulfur-based binders. Organo-clays have been used to stabilize organic chemicals that are poorly addressed by precipitation and complexation reactions (U.S. EPA 1997).

The S/S process can be accomplished using either inorganic or polymer binders. The most common inorganic binders are Portland cement, pozzolans (siliceous or aluminous materials that can react with calcium hydroxide to form compounds with cementitious properties), and cement/pozzolan mixtures. While these binders are effective for a range of inorganic cations and anions, a treatability study

should be conducted using on-site soil, contaminants, and groundwater (if applicable).

In situ chemical stabilization of inorganics using phosphorus based and other compounds was evaluated in September 1998 under EPA's Superfund Innovative Technology Evaluation Program (SITE). The Soil Rescue and Envirobond™ remediation products were applied to a small area of lead-contaminated soil at the Crooksville/Roseville Pottery site in southeastern Ohio. These products chelate the metal ions to reduce mobility. The mean Toxicity Characteristic Leaching Procedure (TCLP) lead concentrations were reduced by more than 99 percent for both products (U.S. EPA 2002 and 2003).

S/S treatment of organic contaminants with cementitious formulations is more complex than treatment of inorganic contaminants. While low levels of organic contaminants can be treated using S/S, many organics will interfere with the hydration process and impede the curing of the solid (U.S. EPA 1997). Subsurface variations in the concentrations of organics can affect both the leachability and final physical properties of the treated wastes or soil. Thorburg et al. (2005) used Portland cement to treat a sediment contaminated with coal tar-derived hydrocarbons. The results showed that the treated sediments leached polycyclic aromatic hydrocarbons (PAHs) and midrange aromatic and aliphatic hydrocarbons at concentrations well above their effective solubilities. Most cementitious processes are exothermic, and the heat generated by the curing process has the potential to volatilize VOCs.

The most significant challenge in applying S/S in situ for contaminated soils is achieving complete and uniform mixing of the binder with the contaminated matrix. Three basic approaches are used for mixing the binder with the matrix:

- Vertical auger mixing
- Shallow in-place mixing
- Injection grouting

Vertical auger mixing requires a system of augers to inject and mix binder into the soil (Figure 2). The treatment depth is limited by the torque required to turn the auger. Current testing indicates a limit of depths to less than 150 feet. The auger diameter, which determines the number of holes that need to be drilled for a given areal extent, can range from several meters for shallow mixing to much smaller diameters for deep mixing. The need for a smaller diameter auger means more holes will need to be drilled per unit area, which increases the cost for the deeper mixing. If VOCs or mercury are present at the site, the contaminant vapors should be captured and treated. The capture is usually accomplished with a hood that covers the mixing area and conveys the gases to an on-site treatment system. Auger mixing is the most commonly applied method for in situ mixing of S/S reagents with soil.

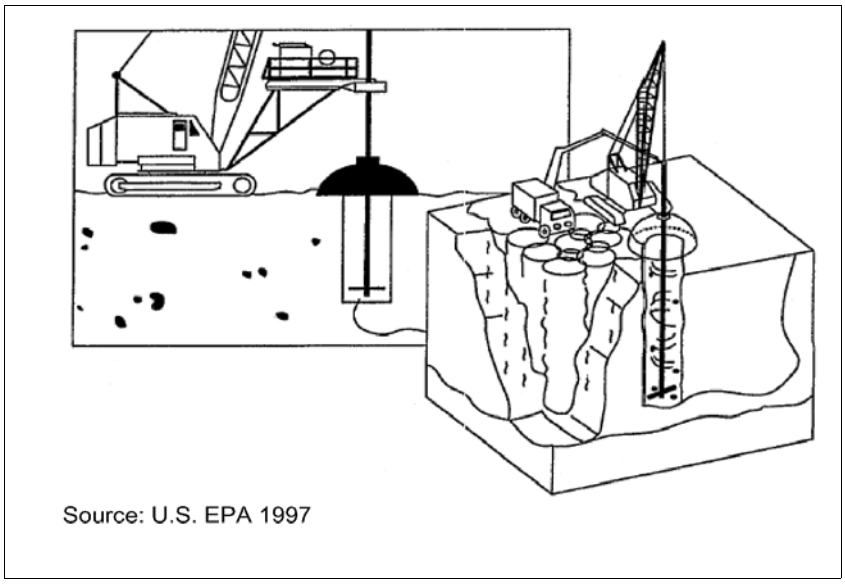

Figure 2. MecTool™ for Solidification and Stabilization of Contaminated Soils and Sludges

In-place mixing involves the spreading and mixing of binder reagents with waste by conventional earth-moving equipment, such as draglines, backhoes, or clamshell buckets. A large auger rig can also be employed for in-place mixing. The technology is applicable only to surface or shallow deposits of contamination.

A novel form of in-place waste mixing can be used for large areas of heavy-metals contaminated soil. A lime-stabilized biosolid can be plowed into the contaminated soil, yielding a mixture that reduces toxicity and bioavailability of the heavy metals

while providing a soil suitable for supporting vegetation.

Injection grouting involves forcing a binder containing dissolved or suspended treatment agents into the formation under pressure, thereby permeating the soil. Grout injection may be applied to contaminated formations lying well below the ground surface. The injected grout cures in place, producing an in situ treated mass.

Polymer binders are thermoplastic or thermosetting. Thermoplastic binders are materials that can be repeatedly melted to a flow state and will harden when cooled. Polyethylene, sulfur polymer, and bitumen are examples of theromoplastic binders. Thermosetting binders are materials that require the combination of several liquid ingredients (e.g., monomer, catalyst, promoter) that, when combined, harden to a solid that cannot be reworked (U.S. EPA 1997).

Thermoplastic binders operate in a temperature range of 120 to 180ºC, which could be an issue in soil with high moisture content. Thermosetting binders operate at ambient temperatures, but they are not amenable to high moisture content. While polymer binders are effective, they may be difficult to use in an in situ setting.

S/S has been applied to the remediation of hazardous waste sites for more than 15 years. Experience with the technology, especially the inorganic binders (Portland cement and pozzolans), is abundant.

The Army Environmental Policy Institute (1998) estimates that in situ S/S of metals using a phosphoric apatite binder costs approximately $46 per ton; using Portland cement for metals costs about $125 per ton; using ammonium modified Portland cement for organics costs about $101 per ton; and using polyethylene costs about $609 per ton. The Portland Cement Association also has costing data: http://www.cement.org/.

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3.1.3 Chemical Oxidation

Chemical oxidation typically involves reduction/oxidation (redox) reactions that chemically convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, or inert. Redox reactions involve the transfer of electrons from one chemical to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). There are several oxidants capable of degrading contaminants. Commonly used oxidants include potassium or sodium permanganate, Fenton's catalyzed hydrogen peroxide, hydrogen peroxide, ozone, and sodium persulfate. Each oxidant has advantages and limitations, and while applicable to soil contamination and some source zone contamination, they have been applied primarily toward remediating groundwater. Several key concepts in oxidant selection for site cleanup include:

- Is the oxidant capable of degrading the contaminant of concern? Is a catalyst or other additive required to increase effectiveness?

- What is the soil oxidant demand (SOD)? SOD is a measure of how the naturally occurring materials in soil will affect the performance of some of the oxidants. For non-selective oxidants, high SOD will increase the cost of cleanup, as more oxidant will be required.

- What is the naturally occurring pH of the soil/groundwater system? Some oxidants require an acidic environment to work. If the soil is basic, an acid needs to be applied in addition to the oxidant.

- How will the decomposition rate of the oxidant affect application strategies? Some unreacted oxidants may remain in the subsurface for weeks to months, while others naturally decompose within hours of injection.

The type of delivery system selected depends upon the depth of the contaminants, the physical state of the oxidant (gas, liquid, solid), and its decomposition rate. Backhoes, trenchers, and augers have been used to work liquid and solid oxidants into contaminated soil and sludge. Liquids can be delivered either by gravity through wells and trenches or by injection. For vadose zones, gravity has the drawback of a relatively small area of influence. Pressurized injection of liquids or gases, either through the screen of a well or the probe of a direct push (DP) rig, will force the oxidant into the formation. The DP rig offers a cost-effective way of delivering the oxidant, and if needed, the hole can be completed as a small diameter well for later injections. Potassium permanganate and other solid phase chemical oxidants have also been added by hydraulic or pneumatic fracturing.

The site stratigraphy plays an important role in the distribution of oxidants. Fine-grained units redirect oxidants to more permeable areas and are difficult to penetrate; hence, they can be the source of rebound later on, as contaminants diffuse out. Long-lived oxidants (e.g., permanganate) have the potential to remain active as this diffusion occurs, and they can mitigate some of the potential rebound.

Chemical oxidation usually requires multiple applications. Table 2 provides a qualitative list of oxidant reactivities with contaminants commonly found at sites.

In the special case of nonaqueous phase liquids, oxidants that are in a water-based solution will only be able to react with the dissolved phase of the contaminant, since the two will not mix. This property limits their activity to the oxidant solution/NAPL interface.

Cost estimates depend on the heterogeneity of the site subsurface, soil oxidation demand, stability of the oxidant, and type and concentration of the contaminant. Care should be taken when comparing different technologies on a cubic yard basis without considering these site attributes. Cost data can be found in ITRC (2005) and Brown (2003). In situ chemical oxidation has been used at a number of sites and is available from a variety of vendors.

Sodium or Potassium Permanganate. Permanganate is a non-specific oxidizer of contaminants with low standard oxidation potential and high SOD. It can be used over a wide range of pH values and does not require a catalyst. Permanganate tends to remain in the subsurface for a long time, allowing for more contaminant contact and the potential of reducing rebound. As permanganate oxidizes organic materials, manganese oxide (MnO_2) forms as a dark brown to black precipitate. During the treatment of large bodies of NAPL with high concentrations of permanganate, this precipitate may form a coating that reduces contact between oxidant and NAPL. The extent to which this reduction negatively impacts contaminant oxidation has not been quantified. Potassium permanganate has a much lower solubility than sodium and is generally applied at lower concentrations. Commercial-grade permanganates may contain elevated concentrations of heavy metals, and they may lower the pH of the treated zone (U.S. EPA 2004). If bioremediation is planned as a polishing step, permanganate will have an adverse effect on microbial activity and may cause a change in microbe distribution. This effect is generally transitory. Also, there is some evidence that permanganates may be inhibitory to *Dehalococcoides ethenogenes*, the microbial species that completely dechlorinates tetrachloroethene (PCE) and trichloroethene (TCE) (Hrapovic et al. 2005).

Fenton's Catalyzed Hydrogen Peroxide. Fenton's reagent uses hydrogen peroxide in the presence of ferrous sulfate to generate hydroxyl radicals that are powerful oxidants. The reaction is fast, releases oxygen and heat, and can be difficult to control. Because of the fast reaction, the area of influence around the injection point is small. In conventional

Table 2. Reactivity of Oxidants with Commonly Found Contaminants[1]

Oxidant	High	Moderate	Low
Ozone	PCE, TCE, DCE, VC, MTBE, CB, PAHs, Phenols, Explosives, PCBs, Pesticides	BTEX, CH_2Cl_2,	CT, $CHCl_3$,
Hydrogen Peroxide[2]	PCE, TCE, DCE, VC, CB, BTEX, MTBE, Phenols	DCA, CH_2Cl_2, PAHs, Explosives	TCA, CT, $CHCl_3$, PCBs, Pesticides
Calcium Peroxide	PCE, TCE, DCE, VC, CB	DCA, CH_2Cl_2	CT, $CHCl_3$
Fenton's Reagent	PCE, TCE, DCE, VC, CB, BTEX, MTBE, Phenols	DCA, CH_2Cl_2, PAHs, Explosives	TCA, CT, $CHCl_3$, PCBs, Pesticides
Potassium/Sodium Permanganate	PCE, TCE, DCE, VC, TEX, PAHs, Phenols, Explosives	Pesticides	Benzene, DCA, CH_2Cl_2, TCA, CT, CB, $CHCl_3$, PCBs
Sodium Persulfate (Iron)	PCE, TCE, DCE, VC, CB, BTEX, Phenols	DCA, CH_2Cl_2, $CHCl_3$, PAHs, Explosives, Pesticides	TCA, CT, PCBs
Sodium Persulfate (Heat)	All CVOCs, BTEX, MTBE, PAHs, Phenols, Explosives, PCBs, Pesticides		

Source: ITRC 2005 and Brown 2003

[1] Contaminant names are spelled out in the abbreviations and acronyms list in Section 5.0.

[2] Peroxide without a catalyst must be applied at higher concentrations, which are inherently hazardous, and the reactions are

application, the reaction needs to take place in an acidified environment, which generally requires the injection of an acid to lower the treatment zone pH to between three and five. The reaction oxidizes the ferrous iron to ferric iron and causes it to precipitate, which can result in a loss of permeability in the soil near the injection point. Over time, the depletion of the ferrous ion can be rate limiting for the process. Chelated iron can be used to preserve the iron in its ferrous state at neutral pH, thus eliminating the acid requirement. The byproducts of the reaction are relatively benign, and the heat of the reaction may cause favorable desorption or dissolution of contaminants and their subsequent destruction. It also may cause the movement of contaminants away from the treatment zone or allow them to escape to the atmosphere. There are safety concerns with handling Fenton's reagent on the surface, and the potential exists for violent reactions in the subsurface. In many cases there may be sufficient iron or other transition metals in the subsurface to eliminate the need to add ferrous sulfate.

Hydrogen Peroxide. While catalysts can be added to increase oxidation potential, hydrogen peroxide can be used alone to oxidize contaminants. Peroxide oxidation is an exothermic reaction that can generate sufficient heat to boil water. The generation of heat can assist in making contaminants more available for degradation as well as allowing them to escape to the surface. With its high reaction and decomposition rates, hydrogen peroxide is not likely to address contaminants found in low permeability soil. Solid peroxides (e.g., calcium peroxide) in slurry form moderate the rate of dissolution and peroxide generation, thereby allowing a more uniform distribution.

Ozone. Ozone, which is one of the stronger oxidants, can be applied as a gas or dissolved in water. As a gas, ozone can directly degrade a number of chemicals in both the dissolved and pure forms, and it provides an oxygen-rich environment for contaminants that degrade under aerobic conditions. It also degrades in water to form radical species, which are highly reactive and non-specific. Ozone may require longer injection times than other oxidants, and vapor control equipment may be needed at the surface. Because of its reactivity, ozone may not be appropriate for slow diffusion into low-permeability soil.

Sodium Persulfate. Persulfate ($S_2O_8^{-2}$) is a strong oxidant with a higher oxidation potential than hydrogen peroxide and a potentially lower SOD than permanganate or peroxide. Persulfate reaction is slow unless placed in the presence of a catalyst, such as ferrous iron, or heated to produce sulfate free radicals ($\bullet SO_4^-$) that are highly reactive and capable of degrading many organic compounds. At temperatures above 40°C, persulfate becomes especially reactive and can degrade most organics (Block et al. 2004). Like Fenton's reagent, the ferrous iron catalyst (when used) will degrade with time and precipitate.

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3.1.4 Soil Flushing

Soil flushing involves flooding a zone of contamination with an appropriate solution to remove the contaminant from the soil. Water or liquid solution is injected or infiltrated into the area of contamination. The contaminants are mobilized by solubilization, formation of emulsions, or a chemical reaction with the flushing solutions. After passing through the contamination zone, the contaminant-bearing fluid is collected and brought to the surface for disposal, recirculation, or on-site treatment and reinjection. Application of soil flushing relies on the ability to deliver, control the flow, and recover the flushing fluid.

Flushing solutions may be water, acidic aqueous solutions, basic solutions, chelating or complexing agents, reducing agents, cosolvents, or surfactants. Water will extract water-soluble (hydrophilic) or water-mobile constituents. Acidic solutions may be used to remove metals or basic organic materials. Basic solutions may be used for some metals, such as zinc, tin, or lead, and some phenols. Chelating, complexing, and reducing agents may be used to recover some metals. Cosolvents are usually miscible and are effective for some organics. Surfactants can assist in the removal of hydrophobic organics (U.S. EPA 1991).

The techniques employed the most in soil flushing are surfactant and cosolvent flooding for fuels and chlorinated solvents. There are many types of surfactants (cationic, anionic, nonionic), and while adjustments can be made in the fluid composition, anionic or nonionic surfactants are generally used. This is because their negative or neutral charge reduces the possibility of their sorption to negatively charged clay particles. They also are generally less toxic than cationic surfactants.

Surfactants are commonly constructed with hydrophobic and hydrophilic chemical components, meaning that one end of the molecule is attracted to oil (or organic compounds) and the other to water. Surfactants chosen primarily to increase the contaminant (generally a NAPL) solubility are used in a solubilization flood. Surfactants chosen to produce ultra-low interfacial tensions are employed in a mobilization flood (Kueper et al. 1997). Mobilization flooding should only be considered when there is a high degree of certainty that the solution can be recovered, such as with a competent bedrock or capillary barrier underlying the treatment zone.

A typical surfactant solution also may contain additives, such as electrolytes and a cosolvent. In addition to being effective with the target contaminant, the surfactant solution also should be compatible with the site-specific soil, soil pore water, and groundwater (if applicable). A cosolvent, such as isopropanol, can be used to improve the surfactant solubility in solution and provide the surfactant/contaminant solution with an acceptable viscosity. A side effect of adding chemicals to the surfactant solution is that they need to be treated along with the contaminant at the recovery end (NAVFAC 2002).

Cosolvents, usually alcohols, are chemicals that dissolve in both water and NAPL. In an alcohol flood, the alcohol may partition into both the NAPL and water phases. Partitioning affects the viscosity, density, solubility, and interfacial tension of the NAPL (Kueper et al. 1997). The physical properties of the NAPL vary with the amount of alcohol available for interaction, and whether the alcohol preferentially dissolves into the NAPL or into the water. Complete miscibility is achievable and results in a pumpable solution that, depending upon the density of the NAPL and the proportions of alcohol and water in the solution, may be more or less dense than water.

Before implementing surfactant and/or cosolvent flushing, laboratory and bench-scale treatability testing should be done to ensure the selection of an agent(s) best suited for the contaminant and the site-specific soil and geochemical conditions. Modeling of subsurface conditions is commonly done to ensure the best delivery system. Flushing is most efficient in relatively homogeneous and permeable ($K \geq 10^{-3}$ cm/sec) soil (NAVFAC 2002). Heterogeneous soil reduces the efficiency of the flood sweep and may prevent optimum contact between the

agent(s) and the target contaminant. Flushing of relatively homogeneous but lower permeability (10^{-4} to 10^{-5} cm/sec) units is possible, but it requires a high-induced gradient to move the agent, while greatly increasing the remediation time (NAVFAC 2002). Other soil factors that may adversely affect efficiency are high cation exchange capacity, high buffering capacity, high organic soil content, and pH.

Land disposal restrictions and underground injection control regulations also may limit selection of the flushing solution. At a former drycleaner, ethanol was substituted for isopropanol because of regulatory concern about the toxicity and persistence of isopropanol. Most states allow in situ flushing of saturated or unsaturated soil, with a permit, if the aquifer in the area is already contaminated. When applying for a permit, all chemicals involved, including unreacted compounds and impurities, must be listed (NAVFAC 2002).

An example of an alcohol flood to address PCE contamination was carried out at the former Sage's Dry Cleaners in Jacksonville, FL. The depth to groundwater at the site was eight feet with the treatment zone consisting of a 24-ft by 9-ft elliptical source area at 26 to 31 ft below ground surface (bgs). About 9,000 gallons of a 95 percent ethanol/5 percent water solution were injected into the target zone. Approximately 160,000 gallons of a ternary mixture of PCE/ethanol/water were treated on site to remove the PCE. The ethanol/water solution was disposed of offsite. Forty-two liters of PCE were recovered, which represented approximately 63 percent of the estimated volume (Florida Department of Environmental Protection 1998). Ethanol had an advantage in that it could be left in the ground at elevated levels while other alcohols, such as isopropanol, would have had to be contained due to their toxicity. The residual ethanol formed an organic substrate that promoted subsequent microbial reductive dechlorination of the remaining PCE. The authors of the study noted that overall cost could have been lowered had they recovered the ethanol and recycled it (Florida Department of Environmental Protection 1998).

Due to its use in oil field applications, soil flushing is considered a mature technology; however, it has found limited application in the environmental arena. ITRC (2003) estimates the cost of surfactant/cosolvent flushing of a DNAPL source zone to range between $65 and $200 per cubic yard. Cost estimates of $100 to $300 per cubic yard for flushing are given on the NAVFAC website. The variability stems from the waste type and the quantity to be treated. The NAVFAC figures do not include design and engineering costs, which can be considerable. Cost per cubic yard can be misleading, and the cost per gallon recovered or destroyed should also be evaluated.

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3.1.5 Electrokinetic Separation

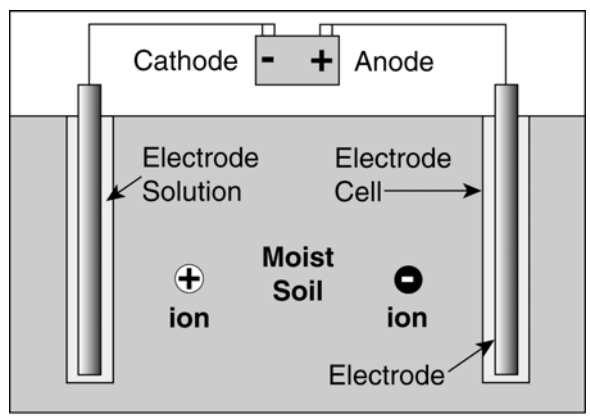
Electrokinetic separation is an emerging technology that relies on the application of a low-intensity, direct current through the soil to separate and extract heavy metals, radionuclides, and organic contaminants from unsaturated soil, sludge, and sediment. The current is applied across electrode pairs that have been implanted in the ground on each side of the contaminated soil mass. During electromigration, positively charged chemical species, such as metals, ammonium ions, and some organic compounds, move toward the cathode, and negatively charged chemicals, such as chloride, cyanide, fluoride, nitrate, and negatively-charged organic species, migrate toward the anode (Figure 3). Electromigration does not require advective flow of pore water for the chemical species to move. In fine-grained soil, the electric current also causes electroosmosis, which is an electrically induced hydraulic flow of ground or soil pore water between the electrodes. This flow can carry neutrally charged species with it. Suspended, charged colloids and miscelles can also move by electrokinetics through the process of electrophoresis. Electrophoresis, in this instance, is similar to electromigration except that the species moving are not single molecules.

Electrolysis reactions (conversion of electrical energy into chemical potential energy) create H_2 and OH^- at the cathode and O_2 and H^+ at the anode. These reactions create an acid front near the anode and a base front near the cathode that migrate towards each other. The acid front aids in increasing the mobility of cationic species, but in some soils, it can retard electroosmois (Saichek and Reddy 2005). The hydroxide front needs to be controlled to avoid the premature precipitation of some target metal ions.

This technology can be applied to contaminant concentration ranges from a few ppm to greater than 10,000 ppm, but may not be effective for treating multiple contaminants that have significantly different concentrations. The target compounds are either extracted to a recovery system or deposited at the electrode. Surfactants and complexing agents may be used to increase solubility and assist in the movement of the contaminant, although care should be taken when choosing between charged (anionic/cationic) and neutral surfactants. When electroosmotic flow is from the anode to the cathode, the flow will assist cationic species and retard anionic ones (Saichek and Reddy 2005).

For the electrokinetics to work, the soil moisture must be conductive and sufficient to allow electromigration but, optimally, not saturated. Removal efficiencies are directly related to the solubility of the target contaminant (which can be amended with surfactants), its electrical charge, and its concentration relative to other ions or contaminant species (Van Cauwenberghe 1997).

Unfavorable conditions at a site include soil with a high cation exchange capacity, high buffering capacity, high naturally occurring organic content, salinity, and very low moisture content. The presence of subsurface metal structures or utilities can also adversely affect performance.



Source: NAVFAC 2000.

Figure 3. Simple Electrokinetic Separation System

Electrokinetic separation has been demonstrated at several sites with mixed results. An independent evaluation was performed at the Department of Energy (DOE) Sandia National Laboratories in Albuquerque, New Mexico for their patented process with Cr(VI) as the target contaminant (U.S. EPA 1999). Also, a field test was conducted by the Navy at Point Mugu with one conclusion being that there was a large discrepancy between what was expected from the bench study, which showed the technology would be very effective, versus what was actually obtained in the field, where the technology performed poorly (ESTCP 2000).

A system that uses in situ treatment combined with electrokinetic separation is the Lasagna™ technique. In this system electrode arrays and treatment zones (e.g., crushed limestone, zero valent iron) are interlayered. The applied current causes the contaminants to move through the treatment zones where they are either destroyed or immobilized. Lasagna™ was applied with some success to treat a TCE contaminated clay soil at the DOE gaseous diffusion plant in Paducah, Kentucky (U.S. DOE 2002).

Because of the limited application of electrokinetic separation, reliable cost data for full-scale applications are scarce. Costs will vary significantly depending upon the concentration of the target contaminant, presence of non-target ions, and soil characteristics and moisture content. Estimates from three vendors were collected by Van Cauwenberghe (1997) and ranged from $20 to $100 per cubic yard for one vendor to $60 to $225 per cubic yard for the high vendor estimate.

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3.2 Biological Treatment Technologies

Biological treatment involves the use of microorganisms or vegetation (phytoremediation). Many naturally occurring microorganisms (typically, bacteria and fungi) can transform hazardous chemicals to substances that may be less hazardous than the original compounds. Microrganisms also have been used to alter the valence of some hazardous metals (e.g., Cr(VI)), thereby making them less hazardous and less mobile. Several plant species have the ability to bioaccumulate heavy metals found in the soil, and some tree species can sequester, destroy, and/or evapotranspire various organic compounds.

Microbial bioremediation occurs under both aerobic and anaerobic conditions and at contaminated sites as either intrinsic and/or enhanced biodegradation. Intrinsic bioremediation depends on indigenous microorganisms to degrade contaminants without any amendments. Monitored natural attenuation (MNA) often relies on intrinsic bioremediation as an important removal mechanism. During enhanced bioremediation, biodegradation is facilitated by manipulating the microbial environment. Typically, the environment is manipulated by supplying amendments, such as air, organic substrates, nutrients, and other compounds, whose absence limit

treatment. In some cases, bioremediation has been enhanced by adding microbial cultures (bioaugmentation).

3.2.1 Bioventing

Bioventing involves the injection of a gas into the subsurface to enhance the biodegradation of a contaminant. The gas can be used to keep the subsurface aerobic or anaerobic, or to provide a substrate that enables cometabolic degradation to occur.

Aerobic Bioventing

Aerobic bioventing has a robust track record in treating aerobically degradable contaminants, such as fuels. Bioventing involves supplying oxygen to contaminated unsaturated soils with low oxygen concentrations to facilitate aerobic microbial biodegradation. Using the supplied oxygen, the microbes oxidize the contaminants to gain energy and carbon for growth. Oxygen is typically introduced by air injection wells that push air into the subsurface.

Aerobically degradable contaminants may be treated by bioventing, but fuels have received the most attention. The U.S. Air Force Bioventing Initiative and the U.S. EPA Bioremediation Field Initiative evaluated bioventing at 125 sites contaminated by petroleum hydrocarbons. At sites where initial studies were positive, pilot-scale bioventing was installed and operated for one year. The experience from bioventing demonstrations at these sites was condensed into a manual (U.S. EPA 1995a & 1995b). The manual contains information on bioventing principles; site characterization; field treatability testing; system design, operation, and installation; site closure; and techniques to demonstrate the extent and mechanism for contaminant removal. Based on this research, bioventing proved to be an economical and effective method to treat unsaturated soil contaminated by petroleum products. Regulatory acceptance of this technology has occurred in 30 states and in all 10 EPA regions. The use of this technology in the private sector has increased following the U.S. Air Force Bioventing Initiative and the U.S. EPA Bioremediation Field Initiative. Estimated costs range from $10 to $60 per cubic yard (U.S. EPA 1995b).

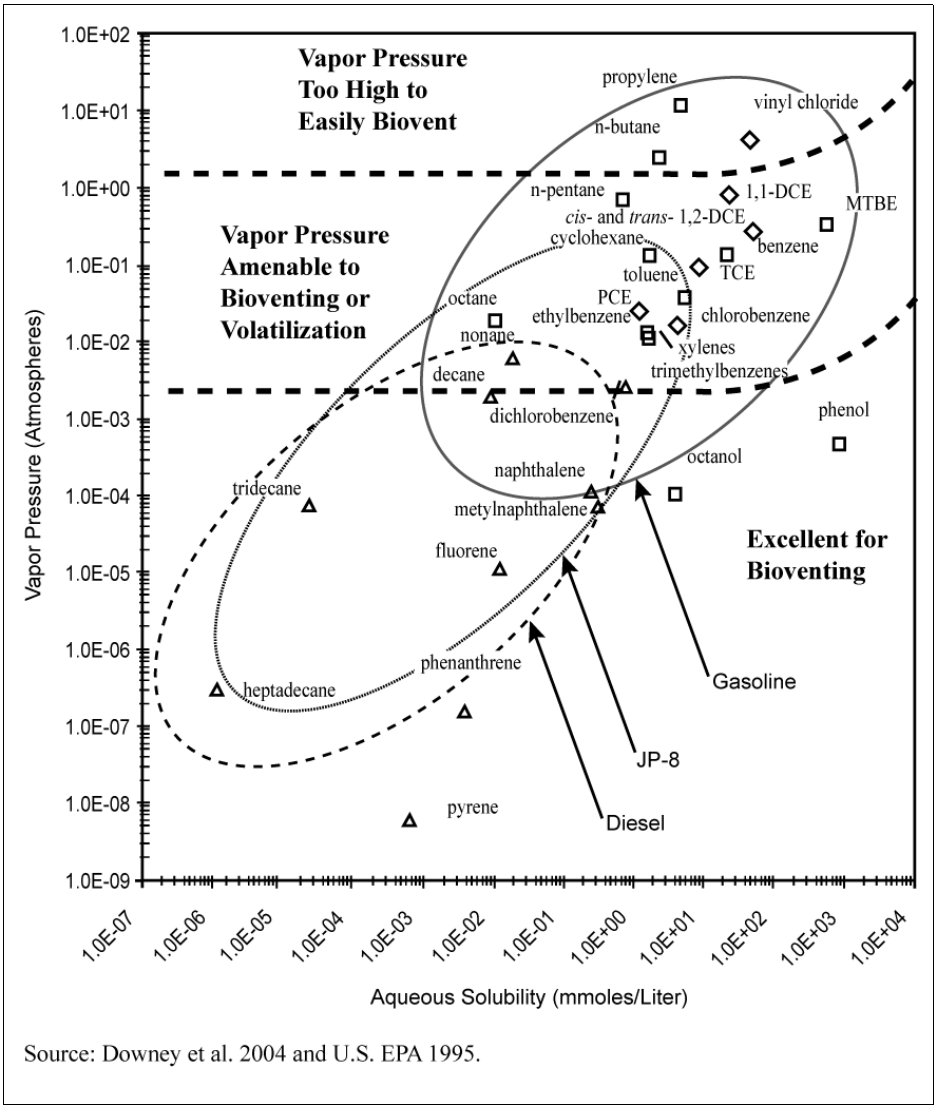
In addition to fuels, aerobic bioventing has treated a variety of other contaminants, including nonhalogenated solvents, such as benzene, acetone, toluene, and phenol; lightly halogenated solvents, such as 1,2-dichloroethane, dichloromethane, and chlorobenzene; and SVOCs, such as some PAHs (Figure 4). The principles outlined in the manual are also applicable for aerobically degradable non-fuel contaminants, but since the experience with these other types of contaminants is more limited, more information may be needed. For example, laboratory and pilot-scale studies may be needed to evaluate effectiveness, design the bioventing system, estimate treatment times, and demonstrate that biodegradation is the primary mechanism of removal. In evaluating the feasibility of treating other contaminants, the key is to understand the volatility relative to the biodegradability.

Bioventing is typically operated in air injection mode to alleviate low oxygen levels in the subsurface. The injection system should be designed considering soil gas permeability, contaminant diffusion and distribution, and environmental factors, such as moisture content, pH, temperature, and electron acceptor conditions. When building foundations or similar structures are close to the site, vacuum extraction wells, which draw air through the subsurface, may be used to avoid the buildup of contaminated, and possibly explosive, vapors in the building basements.

Extracted gases require treatment since volatile compounds may be removed from the ground. In cases of remote locations without electric power, passive air delivery systems may be used. These systems use one-way valves and changes in barometric pressure to deliver air to the subsurface; however, passive systems may have longer treatment times depending on the quantities of air supplied to the subsurface. Compared to soil vapor extraction, all bioventing delivery systems employ lower air flow rates that provide only the amount of oxygen required to enhance removal. When operated properly, the low flow rates of air injection do not result in the release of the contaminants into the atmosphere through volatilization.

To determine if bioventing is appropriate at a specific site, existing site data should be evaluated and, if needed, additional data collected. For example, information about the types, quantities, and three-dimensional distribution of contaminants is needed. This includes the presence and location of free product and whether there is a chance of

continuing contamination from leaking pipes or tanks. Bioventing alone is not sufficient to remediate sites with large quantities of free product or ongoing releases. Information about the historical water table levels and soil characteristics, such as gas permeability, is also needed. A soil gas survey can provide useful information, especially at sites with relatively shallow contamination (depths typically less than 20 ft). The soil gas survey is useful to determine whether oxygen-limited conditions exist. Low oxygen levels (less than five percent) are a good indicator that existing bacteria are capable of degrading the contaminants of concern, because soil gas in uncontaminated soil generally exhibits oxygen concentrations similar to ambient air. In addition, the soil gas survey can be useful in delineating the extent of contamination and identifying locations for vent wells and monitoring points. If this preliminary information looks promising, more specific information should be gathered, such as soil contaminant concentrations and distribution and soil characterization. Respiration rate, soil gas permeability, and oxygen radius of influence will be needed to properly design the system.



Source: Downey et al. 2004 and U.S. EPA 1995.

Figure 4. Amenability of Common Contaminants to Bioventing Technologies (aerobic, anaerobic, and cometabolic)

Performance monitoring, after a bioventing system has been installed, typically includes soil gas monitoring to ensure that the site is well oxygenated, in situ respiration testing to monitor the progress of remediation, and operation and maintenance of the bioventing system. At some sites, surface emissions sampling may be needed. At sites using extractive bioventing, the degree of volatilization versus biodegradation may be determined by measuring offgas concentrations. Injection-based systems may be briefly reconfigured to gain similar information. Measurements of the rate and amount of contaminant removed, oxygen supply, and carbon dioxide generation, as well as mass balances relating the three amounts, may be useful in establishing bioremediation as the primary mechanism of removal. For sites where non-fuel contaminants are to be treated by bioventing, other factors may be considered in establishing biological activity as the primary mechanism of removal. Finally, measurement of stable isotope ratios may be useful in qualitatively validating biodegradation as the mechanism of contaminant removal. This measurement is not required, but it is available to resolve regulatory concerns.

Aerobic bioventing has proven to be a useful cleanup technology at many sites under a variety of

conditions, but like all technologies, bioventing has some limitations. One limitation revolves around the ability to deliver oxygen to the contaminated soil. For example, soil with an extremely high moisture content may be difficult to biovent due to reduced soil gas permeability. Similarly, low permeability soils limit the ability to distribute air through the subsurface; however, in both cases, the design of the bioventing system may compensate for low permeability. Sites with shallow contamination also pose a problem to bioventing because designing the system to minimize environmental release and achieve sufficient aeration, may be difficult. In this situation, operating in extraction mode may be needed.

Another limitation is that aerobic bioventing will not stimulate contaminant removal if the contaminated zone is aerobic. If a soil gas survey measures soil oxygen levels consistently above five percent, then the soil is sufficiently aerated for biodegradation to occur, and oxygen is not limiting degradation. Bioventing will not enhance removal in this situation. This situation is unusual, and if encountered, may indicate that some other species, such as metals, is inhibiting degradation.

While relatively inexpensive, aerobic bioventing can take a few years to clean up a site, depending on the contaminant concentrations and site-specific removal rates. For petroleum hydrocarbon sites, the heavier the product being treated, the longer the remediation time. If a quicker cleanup is needed, other technologies may be more appropriate.

Anaerobic Bioventing

While aerobic bioventing is useful for degrading many hydrocarbons, some chlorinated compounds are not effectively treated aerobically. Microbes may degrade these contaminants directly via anaerobic reductive dechlorination or through anaerobic cometabolic pathways. Anaerobic reductive dechlorination is a biological mechanism, typically marked by sequential removal of chlorine ions from a molecule. Microbes possessing this pathway gain energy from this process. In some situations, microorganisms fortuitously degrade contaminants, while gaining energy and carbon from other compounds (cometabolites). These organisms usually do not obtain any benefit from contaminant degradation, and the removal process is called cometabolism. Anaerobic bioventing may involve both anaerobic reductive dechlorination and anaerobic cometabolism to destroy the contaminants of concern.

Anaerobic bioventing uses the same type of gas delivery system as aerobic bioventing, but instead of injecting air, nitrogen and electron donors (e.g., hydrogen and carbon dioxide) are used. The nitrogen displaces the soil oxygen, and the electron donor gas facilitates microbial dechlorination. Volatile and semivolatile organic compounds may be produced during anaerobic bioventing that are not anaerobically degradable. Volatile compounds may be aerobically degraded in the soil surrounding the treatment zone. Semivolatile compounds may be treated by following anaerobic bioventing with aerobic bioventing. Since aerobic and anaerobic bioventing share similar gas delivery systems, the switch can be made by simply changing the injected gas.

Anaerobic bioventing is an emerging technology that may be useful in treating highly chlorinated compounds, such as PCE, TCE, pentachlorophenol (PCP), some polychlorinated biphenyls (PCBs), and pesticides, such as lindane and dichlorodiphenyltrichloroethane (DDT). Due to the limited experience with this technique, laboratory, pilot, and field demonstrations are recommended to apply this technology with confidence to remediate a site.

Particular attention should be paid to the formation of degradation products and whether contaminants are converted to non-toxic compounds. For example, sites contaminated by PCE and TCE may not show complete dechlorination, rather dechlorination stalls at cis-1,2-dichloroethene (cis-DCE) or vinyl chloride (VC). Since VC is more toxic than the original contaminants, incomplete dechlorination would not be acceptable. The cis-DCE or VC stall may be due to the availability of an electron donor or the indigenous microbial community. If the electron donor is limited, additional donor should be added. If the indigenous culture is not able to completely dechlorinate the solvents, the site could be switched to another type of bioventing (e.g., cis-DCE is aerobically degradable through cometabolism, and VC is aerobically degradable). Laboratory testing can demonstrate whether complete dechlorination occurs at a site, provide information about suitable electron donors and the quantities required, estimate removal rates, and demonstrate whether hazardous byproducts are formed.

As with the other bioventing technologies, the ability to deliver gases to the subsurface is important. Soil with a high moisture content or low gas permeability may require careful design to deliver appropriate levels of nitrogen and electron donor. Sites with shallow contamination or nearby buildings are also a problem, since this technology is operated by injecting gases. In addition, anaerobic bioventing can take a few years to clean up a site depending on the contaminant concentrations and site-specific removal rates. If a quicker cleanup is needed, other technologies may be more appropriate. Finally, no rigorous cost models have been developed for anaerobic bioventing; however, the costs should be similar to aerobic bioventing with the following additional costs: laboratory treatability test and field testing; nitrogen and electron donor additions; and additional soil and gas analyses.

Cometabolic Bioventing

Cometabolic bioventing involves injecting air into the subsurface along with a suitable gaseous substrate to promote cometabolic reactions with the target compound. As with anaerobic cometabolism, some microorganisms fortuitously degrade contaminants while oxidizing other compounds (cometabolites) for energy and carbon. The organisms usually do not obtain any benefit from contaminant degradation. A suitable substrate should be determined in the laboratory but may include methane, ethane, propane, butane, and pentane. The delivery system is similar to other bioventing technologies and subject to many of the same limitations. Cometabolic bioventing is applicable to contaminants, such as TCE, trichloroethane (TCA), ethylene dibromide, and dichloroethene (DCE), that resist direct aerobic degradation. This technology is not applicable to PCE.

The Bioremediation Consortium under the Remediation Technology Development Forum (RTDF) conducted cometabolic bioventing demonstrations at Dover and Hill Air Force Bases (AFB). At Dover AFB, a field demonstration of cometabolic bioventing was done at Building 719. The site was contaminated with fuel and solvents during engine inspection and maintenance operations. The targeted contaminants of the demonstration were TCE, as high as 250 mg/kg; TCA, 10 to 1,000 mg/kg; and DCE, 1 to 20 mg/kg. Laboratory tests were used to select propane as the cometabolic substrate and predict that a substrate acclimation period would be needed. The test plot was acclimated to propane addition through pulsed propane/air injections for three months, and then the test plot was operated for 14 months with continuous propane injection. Concentrations of TCE, TCA, and DCE were reduced to less than 0.25, 0.5 and 0.25 mg/kg, respectively. Soil chloride accumulation confirmed biodegradation as the mechanism of removal (U.S. EPA 2000).

Because experience with cometabolic bioventing is limited, laboratory and pilot-scale studies are recommended to evaluate effectiveness, select a cometabolite, identify needs for acclimation periods, design the system, and estimate treatment times. Operational costs should be similar to those of aerobic bioventing except for the addition of the substrate gas and additional monitoring of soil and soil gas.

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3.2.2 Phytoremediation

Phytoremediation uses plants to extract, degrade, contain, or immobilize contaminants in soil, groundwater, and other contaminated media. The phytoremediation mechanisms used to treat contaminated soil in situ are phytoextraction, rhizodegradation, phytodegradation, phytovolatilization, and phytostabilization.

Phytoremediation is best used to treat large areas of shallow contamination. Because high levels of contaminants may be toxic to plants and inhibit their growth, phytoremediation is best applied to low and moderate levels of contamination, used in conjunction with other treatment methods, or used as a final polishing step in site remediation.

The various mechanisms of phytoremediation can treat a wide range of contaminants, including metals, VOCs, PAHs, petroleum hydrocarbons, radionuclides, and munitions, although not all mechanisms are applicable to all contaminants. Phytoremediation may take longer than other technologies to treat a site, but it has the potential to be less expensive than excavating and treating large volumes of soil ex situ.

There are a number of limitations to the technology that must be considered before it can be implemented at a site. The depth of the contamination requiring treatment must be within the range of depth of plant root growth; thus, treatment of contaminated soil typically focuses on the upper 8 to10 inches of the soil horizon, although the roots of hybrid poplar trees, a species commonly used in phytoremediation, can grow to depths of about 15 feet. Contaminants must be in contact with the root zone to be treated; therefore, a denser root mass is preferred to help contact more of the contamination. Because treatment depends on this contact with the root zone, phytoremediation is limited by the rate of root growth. Slower growth rates increase the time required to treat a site, and winter months may shut down the treatment system completely while plants are dormant.

Another limitation of phytoremediation is possible bioconcentration of contaminants up the food chain. Several phytoremediation mechanisms work by incorporating the contaminant into the plant or holding it within the root zone. The contaminated vegetation and root zone may impact plant-eating

animals and soil organisms. This is particularly a concern with metals and radionuclide contamination that accumulate in plants and the root zone. Most plants do not accumulate significant levels of organic contaminants (U.S. EPA 2000); thus, bioconcentration is of less concern. The potential for plant-eating animals to be exposed is greatest when these contaminants accumulate in fruits, seeds, and leaves, so monitoring the fate of contaminants within the plants is important. To avoid bioconcentration in the food chain, contaminated plants can be harvested for disposal, destruction, or the extraction of metals for reuse ("phytomining"). In these cases, perimeter fencing and overhead netting can be installed to prevent animals from consuming contaminated plant matter.

Finally, it is important to ensure that unwanted transfer of contaminants from soil to other media, such as the volatilization of organic compounds to the atmosphere through plant uptake and transpiration, does not occur or that the transfer results in the destruction of the contaminants. Evaluating the limitations of phytoremediation in its various applications, as well as assessing its potential effectiveness at contaminated sites, can be done in laboratory and field studies prior to implementation. Samples of site soil containing the target contaminants in a range of concentrations should be tested using the specific plants under consideration. Ultimately, sites undergoing phytoremediation must be monitored to assess the fate of contaminants.

In general, phytoremediation has been implemented at a number of sites at full-scale (U.S. EPA 2006). Also, a wide range of site conditions, plants, and contaminants have been studied under laboratory or field testing. As of this publication, phytoemediation technologies have been selected 18 times by the Superfund program.

Phytoextraction

Phytoextraction involves the uptake of contaminants by plant roots, with subsequent accumulation in plant tissue, which may require that the plant be harvested and properly disposed of. This mechanism is typically used to treat inorganic contaminants, such as metals, metalloids, and radionuclides. Organic contaminants are more likely to be transformed, rather than accumulated, within the plant tissue. Successful field applications of phytoextraction to up take metals have been limited; however, there is some promising research for using phytoextraction on mercury and persistent organic pollutants.

Plants used in phytoextraction include Indian mustard, pennycress, and alyssum sunflowers. They are typically effective only in the top one foot of soil because of their shallow root systems and generally slow growth. Baňuelos et al. (2005) has shown that Indian mustard can be genetically modified to grow in contaminated soil with greater biomass to hyper-accumulate selenium in a shorter time than unmodified Indian mustard. In other genetic research, Meagher (undated) is modifying various plant species to survive in mercury-contaminated soil and to transform organic mercury into ionic and/or metallic mercury. The mercury is either sequestered in the plant or transpired.

Persistent organic pollutants, many of which are pesticides, resist biodegradation and may remain in the environment for decades. White (2001) and Mattina (2000) have shown that a number of plants are capable of extracting chemicals, such as chlordane and 2,2-bis(p-chlorophenyl) 1,1-dichloroethene (p.p'-DDE), and storing them in their roots, leaves, and fruits.

Rhizodegradation

Rhizodegradation is essentially "plant-assisted bioremediation" in that the root zone enhances microbial activity, thus increasing the breakdown of organic contaminants (such as petroleum hydrocarbons, PAHs, pesticides, BTEX, chlorinated solvents, PCP, PCBs, and surfactants) in the soil. The term comes from "rhizosphere," which is the zone of soil influenced by plant roots. This zone extends only about 1 mm from each root.

The presence of plant roots increases soil aeration and moderates soil moisture, making conditions more favorable to bioremediation. Bioremediation is enhanced by the production of root exudates, such as sugars, amino acids, and other compounds, that can stimulate the population growth and activity of native microbes. Root exudates may also serve as food for the microbes, which can result in cometabolism of contaminants as degradation of exudates occurs. Because the microbes consume nutrients, the plants in a rhizodegradation plot often require additional fertilization.

The advantage of rhizodegradation is the actual breakdown of contaminants, rather than their translocation; thus, harvesting is not necessary. In some instances, complete mineralization of the contaminant can occur. Success, however, is site-specific, and laboratory microcosms may not reflect the microbial conditions encountered in the field. Petroleum hydrocarbons have been shown to be successfully degraded in the rhizosphere; however, degradation of aged hydrocarbons has been demonstrated to be more problematic.

Phytodegradation

Like phytoextraction, phytodegradation involves the uptake of contaminants; however, the contaminants are subsequently broken down through metabolic processes within the plant. Phytodegradation also comprises the breakdown of contaminants in the soil through the effects of enzymes and other compounds produced by the plant tissues (other than the roots).

Phytodegradation is applicable to organic contaminants. Their uptake is affected by their hydrophobicity, solubility, and polarity. Moderately hydrophobic and polar compounds are more likely to be taken up after sorbing to plant roots (Schnoor et al. 1995 and Bell 1992). Contaminants with the potential for phytodegradation include chlorinated solvents, herbicides, insecticides, PCP, PCBs, and munitions.

Phytovolatilization

Phytovolatilization is the uptake of a contaminant into a plant and its subsequent transpiration to the atmosphere, or the transformation or phytodegradation of the contaminant with subsequent transpiration of the transformation or degradation product(s) to the atmosphere. Phytovolatilization is more commonly applied to groundwater, but can also be applied to soluble soil contaminants.

Phytovolatilization involving transformation or degradation of the contaminant has the advantage of potentially creating a less toxic product that is transpired; however, this also poses a potential drawback in that degradation of some contaminants, like TCE, may produce even more toxic products (e.g., vinyl chloride). This possibility has to be assessed on a site-specific basis, and measurement of transpired compounds can be difficult. Once in the atmosphere, these products may be more effectively degraded by sunlight (photodegradation) than they would be by the plant (phytodegradation).

Both organic and inorganic contaminants have been treated by phytovolatilization. Inorganic contaminants include selenium, mercury, and arsenic; however, simply volatilizing a contaminant may not be an acceptable alternative.

Phytostabilization

Phytostabilization is a mechanism that immobilizes contaminants—mainly metals—within the root zone, limiting their migration. The contaminants are immobilized by adsorption of metals to plant roots, precipitation of metal ions (e.g., due to a change in pH), formation of metal complexes, or a change to a less toxic redox state. Phytostabilization can occur when plants alter the chemical and microbial makeup of the soil (e.g., through the production of exudates or carbon dioxide), which affects the fate and transport of the soil metals. Phytostabilization also encompasses the use of plants to prevent migration of soil contaminants with wind and water erosion, leaching, and soil dispersion.

Since contaminants are retained in the soil, phytostabilization does not require the harvesting and disposal of plants. A phytostabilization system must be evaluated, however, to ensure that translocation of contaminants into the plant tissue is not occurring. Since contaminants remain in the root zone, the health of the plants must be maintained to prevent future release of contaminants when the plants die or are inadvertently destroyed. Maintenance may include the addition of fertilizers or soil amendments.

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3.2.3 Monitored Natural Attenuation

Monitored natural attenuation (MNA) encompasses the dilution, dispersion, chemical and biological degradation, sorption/precipitation, and/or radioactive decay of contaminants in soil and groundwater (U.S. EPA 1999). It has been applied mainly to groundwater contamination, but the same principles apply to soil. Because MNA is a passive process in which the reduction in contaminant concentration is due solely to natural mechanisms, continuous sources of significant contamination should be addressed before implementing MNA. If MNA is implemented, reaching remediation goals may take longer than other remedies.

Site contaminants most amenable to MNA include petroleum hydrocarbons, low-molecular weight alcohols, ketones, esters, ethers, and iron and manganese. Under a narrow range of conditions, MNA may be applicable to halogenated solvents, lightly halogenated aromatics, polychlorinated biphenyls, nitroaromatics, some pesticides, and chromium, copper, cadmium, lead, zinc, and nickel (NRC 2000).

A full characterization of subsurface conditions at the site, including a delineation of the extent of contamination and the development of a site conceptual model, are necessary before MNA can be

considered. As part of the characterization, the microbial species present (more important for chlorinated compounds), redox potential, pH conditions, mineralogy, and geochemistry should be evaluated. If the evaluation concludes that the conditions may exist to support natural attenuation, the next step is to determine if it is occurring. This is accomplished by looking at such parameters as microbial respiration products, chemical reaction products, prevalent metal species, degradation products, and declining concentrations of target compounds/species over time. For a more complete list and discussion, see Kram and Goetz 1999. If a large amount of historical data is not available to confirm that the contaminant mass is stabilized or contracting, it probably will be necessary to model the fate and transport of the contaminants to show that migration is unlikely to occur.

Performance monitoring is an integral part of any MNA effort (Pope et al. 2004 and Wiedemeier, Lucas, and Haas 2000). The monitoring system should be tailored to site conditions to enable detection of any changes in the assumptions used to select MNA. Key parameters, such as degradation products or an increase in target metal concentration that would indicate mobilization, should be chosen along with an appropriate frequency. The frequency of sample collection is related to the uncertainties inherent in the site conceptual model and the consequences of failure. As a precaution, a preapproved site remedial contingency plan should be created that can be implemented if monitoring indicates MNA is not meeting the project's performance goals.

The Naval Facilities Engineering Command provides an estimate for implementing MNA of between $50,000 and $200,000 per acre. This cost does not include site characterization, which may be higher than that for a site not being considered for MNA. These cost estimates were developed for a groundwater scenario.

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3.3 Thermal Treatment Technologies

Five technologies are grouped under the in situ thermal treatment classification: electrical resistance heating, steam injection and extraction, conductive heating, radio-frequency heating, and vitrification. With the exception of vitrification, all of these treatment technologies rely on the addition of heat to the soil to increase the removal efficiency of volatile and semivolatile contaminants. Vapor extraction is an integral part of these remediation systems to ensure the removal and treatment of mobilized contaminants. Liquid extraction is also used during steam injection, and sometimes with other thermal technologies when groundwater flow rates are high and/or when the contaminant being recovered is semivolatile.

In situ vitrification is unique among the thermal technologies in that the temperatures used will vitrify soil. The stable glass that is formed by vitrification will immobilize any nonvolatile contaminants that are present, including metals and radioactive materials.

Davis (1997) provides a general discussion of the effects of heat on chemical and physical properties of organic contaminants. Vaporization is the main mechanism used in these technologies to enhance the recovery of VOCs. Vapor pressures of organic compounds increase exponentially with temperature, causing significant redistribution to the vapor phase as the subsurface is heated. When a NAPL is present, the combined vapor pressure of the NAPL and water determine the boiling temperature, and co-boiling of the two liquids occurs at temperatures less than the boiling point of water. Thus, by raising the temperature of the subsurface above the co-boiling temperature, NAPL can be removed. Continued heating of the subsurface recovers contaminants from the dissolved and adsorbed phases as well.

Increasing the temperature also decreases viscosity, increases solubility, and decreases adsorption, all of which aid in the recovery of VOCs and SVOCs. For some SVOC NAPLs, such as creosote, viscosity reduction may be an important mechanism for increased contaminant recovery (Davis 1997). Hydrolysis may play a role in the destruction of some contaminants (e.g., chlorinated methanes and ethanes) as the soil temperature approaches 100ºC; however, the breakdown products may be more recalcitrant than the original contaminants (Washington 1995).

Care should be taken in designing the systems to ensure that all plumbing, including monitoring wells, are capable of withstanding high heat. In the presence of clay, vadose zone heating by resistivity, conductance, or radio frequency may result in some settlement of the treatment area due to the drying of the clay.

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3.3.1 Electrical Resistance Heating

Electrical resistance heating (ERH) involves passing electrical current through moisture in the soil between an array of electrodes. As the current flows through the moisture in soil pores, the resistance of the soil produces heat. Originally, ERH for remediation purposes was developed by DOE and Battelle using six-phase electricity and hexagonal electrode arrays, however, expansion of a six-phase hexagonal array may result in the creation of cold and hot spots within the target subsurface area. Three-phase power and triangular electrode arrays are generally more applicable to irregularly shaped cleanup areas for full-scale treatment and are commonly used today (Beyke and Fleming 2005).

Electrodes can be thought of as wells that are equipped to deliver electric power at selected depths and also act as vapor recovery wells. When groundwater flow rates are high and/or a semivolatile NAPL is to be recovered, liquids can also be extracted (Beyke and Fleming 2002). Electrodes may be installed using conventional drilling rigs. Installation can also be done using horizontal or angular drilling techniques. Care should be taken to ensure that the potential for stray currents is accounted for in the design.

ERH systems can be deployed to any depth and used in both the vadose and saturated zone. If the system is deployed only in the vadose zone, water should be added at the electrodes to maintain the moisture content and thus, the flow of electricity (U.S. EPA 2004).

The horizontal spacing between electrodes is usually between 14 and 24 feet (Beyke and Fleming 2005). The trade-off in distance is between the cost of installing more electrodes and heating the soil more quickly or installing fewer electrodes and heating the soil over a longer time.

While heating all soil, ERH preferentially heats the more conductive silt and clay first. Temperatures over 100ºC can be generated in the saturated zone, and these temperatures produce steam and steam stripping, which is especially beneficial for the silts and clays as contaminant movement in them is usually diffusion limited.

Volatilization and steam stripping with SVE-capture are the predominant removal mechanisms for most contaminants using this technology. (Beyke and Fleming 2005). Soil with a high natural organic carbon content will slow or prevent the recovery of some organic contaminants.

U.S. EPA (2004) provides remediation cost estimates of $32 and $73 per cubic yard at two full-scale ERH sites. Beyke and Fleming (2005) estimate that ERH costs $200,000, plus $40 to $70 per cubic yard. The technology is proven and has been used at a number of sites. The number of vendors offering the technology are limited.

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3.3.2 Steam Injection and Extraction

Steam injection and extraction (also known as steam enhanced extraction [SEE]) involves injection of

steam into injection wells and the recovery of mobilized groundwater, contaminants, and vapor from the recovery wells. Initially, when steam is injected into the subsurface, it gives up its latent heat of vaporization to the soil. As the steam loses heat, it condenses into a hot water phase that moves radially into the soil and displaces air and water in front of it. Continued input of steam eventually causes the soil near the well to reach steam temperatures, creating a steam front that begins to propagate away from the well. This process creates a moving front consisting of ambient temperature water/air that is pushed by a variable temperature zone of warm to very hot water. The water in turn is pushed out by the pressure of the steam moving into the steam temperature zone. The movement of the ambient-temperature water may displace NAPLs, a process that is aided by viscosity reduction when the hot water reaches the NAPL. The arrival of the steam phase vaporizes compounds remaining as residual saturation or adsorbed to the soil. These vapors are transported to the leading edge of the steam zone where they condense, forming a contaminant condensate bank. The condensate bank may have a tendency to sink, and it is important in the design of the system to ensure its capture. Schmidt et al. (2002) and Kaslusky and Udell (2002) have found that co-injection of air with the steam helps prevent downward contaminant migration.

Thus, contaminant removal occurs by several mechanisms. Which one is most important in a given situation depends on the volatility of the contaminant. For VOCs, vaporization and co-boiling are the most important recovery mechanisms, while for SVOCs, displacement as a NAPL and viscosity reduction may be more important. Recovery wells are used to capture both liquids and gases and transport them to a surface facility for treatment.

The applicability of steam injection to a particular site is determined by the permeability of the soil, the depth at which the contaminants reside, and the type and degree of heterogeneity, as well as the contaminant type. The permeability of the soil must be high enough to allow sufficient steam to be injected to heat the entire source zone. Higher injection rates can be achieved by increasing the injection pressure; however, in general, pressures should not be higher than 1.65 pounds per square inch per meter of depth, or the overburden pressure will be exceeded, and fracturing to the surface can be expected (Davis, 1998). Thus, shallow treatment areas are difficult to heat with steam, and collection of all the vapors generated may be challenging. An impermeable surface cover may help in this regard.

Heterogeneity of the Subsurface and Soil Type

The soil type affects the ability of the steam to remove contaminants in two ways. The permeability determines how fast a steam front can move into and through the soil. Low permeability soil may not allow steam to move through it at an economical rate or may require unsupportable pressures to do so. The other aspect of soil that affects contaminant removal is its reactivity with contaminants. Silica based sands are not particularly reactive, and contaminants can be removed easily. Smectite clays and soil rich in organic matter both have the ability to bind some organic compounds and prevent their full removal at steam temperatures.

When there is heterogeneity, steam tends to channel to the more permeable layer, or in the case of discontinuous layers, by-pass the less permeable one. If this happens, heating in the less permeable soil usually is done by conductive methods. To fully heat low permeability zones by conduction, steam should be injected on both sides of the low permeability zone, and the zone should be less than about 10 feet in thickness.

Injection and Extraction Well Placement and Operation

The most effective design of steam injection and extraction systems is to surround the contaminated zone with four to six injection wells and to extract the contaminants from the center. If the area to be treated is large, repeating patterns of injection and extraction wells may be used to cover the entire area (Davis 1998). The propagation of the steam front is a balance between the injection well's ability to add heat and the surrounding soil's ability to absorb it. When the rate of heat loss to the soil surrounding the front equals the system's ability to input it, the steam front will stop growing. The extraction well needs to be closer to the injection well than this point of equilibrium. Distances between wells have been reported as close as 1.5 meters and as far apart as 18 meters.

The wells and couplings handle very hot streams of vapors and their construction is a concern. Plastics, such as PVC, are generally not appropriate, and steel

is typically used. Since the injection wells are both very hot and pressurized, couplings should be carefully designed and an appropriate sealant for the annulus should be chosen. Cement grouts used in conventional water well completion may not withstand the pressure, heat, and expansion/contraction of the well casing itself and could crack, causing the release of steam to the surface.

A characteristic of steam treatment in a source zone under saturated conditions that needs to be considered is override. Override occurs when there is a difference in density between two fluids (such as that between steam and ambient temperature water). The resulting interface tends to move the steam out and up, causing the top of the steam front to be considerably further from the injection well than the bottom. This situation can lead to untreated spots near the bottom of the injection well. Override cannot be completely eliminated, but it can be minimized within the constraints of the site hydrogeology by using high injection rates.

Pressure cycling of the steam injection is generally utilized as part of the system operation. Cycling is the process where, after breakthrough of steam at the extraction wells, the steam injection system is shut down while allowing the extraction process to continue. The loss of pressure thermodynamically destabilizes the system, forcing the temperature to drop to restore stability. The system loses heat by evaporation of residual moisture and the contaminants that are collected by the extraction wells. Davis (1998) and Davis et al. (2005) report on several studies where repeated cycling has resulted in increased contaminant concentrations in the extracted vapors.

Steam is a well documented technology for addressing NAPL source zones in unconsolidated subsurfaces (Davis 1998). For example, over 150,000 gallons of creosote were destroyed or removed by steam at the Southern California Edison Company pole yard in Visalia, California. Several small scale, short duration demonstrations of steam injection in fractured rock have shown the potential for this technology to be effective in fractured rock settings (e.g., Loring Air Force Base, Davis et al. 2005), but additional research and field demonstrations are needed to fully determine its effectiveness. Because of the sensitivity of steam flow to heterogeneous subsurface conditions, more site characterization efforts may be required than for other heating technologies.

Another steam delivery system combines steam injection with an in situ auger mixing system. In this application, steam is applied through specially designed augers while the soil is being mixed. The steam strips the volatile contaminants from the moving soil and brings them to the surface, where they are captured in a shroud or bell device and transported to a treatment system. Moos (1998) describes the use of an auger system at Argonne National Laboratory to treat primarily chlorinated solvent contaminated clays. The system applied steam and hot air injection to bring 70 to 80 percent of the contaminants to the surface for treatment. Following the steam application, zero-valent iron was mixed into the soil by the augers as a polishing step. A similar steam system was used at the DOE Pinellas site for remediating chlorinated hydrocarbon hotspots. It successfully removed a large amount of the contamination, but it was hampered by an undersized offgas treatment system that probably prevented it from reaching site cleanup goals (Davis 1998).

Cost data for steam injection and extraction are limited. U.S. DOE (2000) reported cleanup at approximately $39 per cubic yard, but their system also employed electrical heating. The technology is mature and well established; however, few vendors use it for environmental remediation.

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3.3.3 Conductive Heating

Conductive heating uses either an array of vertical heater/vacuum wells or, when the treatment area is within about six inches of the ground surface, surface heater blankets. While it is feasible to deploy all the wells in a heater/vacuum mode, the typical deployment is to place six heater-only wells in a hexagonal shape with a heater vacuum well occupying the center of each hexagon.

The wells can be installed using conventional drilling techniques or direct push. Heater wells are constructed of steel pipe with the base sealed. A resistive heating unit is lowered into the well and current is supplied. The heating element typically operates at temperatures between 540° and 815°C (Baker and Heron 2004). The steel pipe is heated by radiant energy and the soil surrounding it by thermal conductance.

The vacuum well contains the same steel pipe and heating element components as a standard heater well, but it is placed within a larger screened well to which a vacuum can be applied. Heat propagates in a cylindrical fashion from the well outward. The heating is fairly even through all dry textures of soil. The hottest soil (typically 590°C) is in the immediate vicinity of the wells, while the coolest soil is at the midpoint between wells. When the vacuum is applied to the center well, volatilized organics are pulled through the high-temperature soil, where some of the contaminants may be degraded (Baker and Heron 2004). The extracted vapors are transported to the surface for treatment.

Well spacing is chosen based on contaminant type and depth, soil moisture content, the minimum required temperature between wells, and the time desired to reach that temperature (U.S. EPA 2004). SVOCs, including high boiling components, such as PAHs or PCBs, generally need a soil temperature of 325°C for adequate desorption, while VOCs require less heat (usually 100°C) (Baker and Heron 2004). The ability to treat high-boiling contaminants at temperatures well below their boiling points is largely due to the significant increase in vapor pressures at the temperatures present and the relatively long residence time in a very hot

subsurface (Biershenk et al. 2004).The temperature requirements typically lead to well placement distances of 6 to 7.5 feet for the SVOCs and 12 to 20 feet for the VOCs. As with electrical resistance heating, the closer the wells, the faster the desired temperatures are reached.

Conductive heating operates best in unsaturated soil; however, it does find application in saturated soil with low hydraulic conductivity. As the temperature around the heater wells increases, the water evaporates and a "dry" zone is created that expands outward. At the leading edge of this cylindrical zone, steam is created, which further expands the zone. In low permeability soil, any replacement water that attempts to flow into the "dry" zone is quickly boiled off. In soil with high hydraulic conductivities, the influx of water to replace that boiling off may be sufficient to prevent the soil from exceeding the boiling point of water, and target temperatures may not be met. If the treatment area contains saturated high hydraulic conductivity soil, then a dewatering system should be considered, or Baker and Heron (2004) suggest using a steam system to control water influx, as well as sweeping the permeable areas. Drying soils, especially fine-grained silt and clay, at high temperatures can result in shrinkage and cracking that will promote the removal of organics contained within them (U.S. EPA 2004).

If concentrated halogenated organics are the contaminants of concern, the system—both piping and treatment—must be designed to withstand highly corrosive conditions.

Thermal conductance systems also can consume large quantities of power. At a site in Alhambra, California, the remediation had to be carried out in phases to avoid exceeding the capacity of the local power supplier (Biershenk et al. 2004).

Vendor cost estimates cited range from $100 to $250 per ton (NAVFAC 1999). TerraTherm has an exclusive license in the United States to offer this technology for remediation.

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3.3.4 Radio-Frequency Heating

Radio-frequency heating (RFH) uses a high frequency alternating electric field for in situ heating of soils. The technique depends on the presence of dielectric materials with unevenly distributed electrical charges. The application of an electric field produces movement of the "polar" molecules, and this vibration creates mechanical heat. A spread of radio frequencies (e.g., 6.78 MHz, 13.56 MHz, 27.12 MHz, and 40.68 MHz along with seven higher frequencies) regulated and assigned by the Federal Communications Commission (FCC) can be used in industrial, scientific, or medical applications. Under 47 CFR18.301 (FCC 2006) an equipment designer or operator can use these frequencies without obtaining a license from the FCC. Higher frequencies increase the rate of heating but reduce the depth of penetration (Halliburton NUS Environmental 1995).

A radio-frequency heating system usually consists of:

- A three-phase power supply.
- A radio-frequency source with an oscillator that generates a low-power current at the desired radio frequency, several serial amplifiers that increase the strength of the oscillator current, and a final amplifier that delivers the current at the prescribed output level.
- An applicator system consisting of electrodes or antennae.
- A monitoring control system.
- A grounded metal shield over the treatment area.
- A vapor collection and treatment system (Haliburton NUS Environmental 1995).

Depending upon the vendor, a row or rows of applicator electrodes are placed in the ground to the depth of the treatment zone. The electrodes can be placed with conventional drilling equipment or direct push. In some designs, the electrodes themselves are used to recover soil gas and heated vapors. In other designs, wells are placed specifically for soil vapor extraction and to act as electromagnetic sinks to prevent heating beyond the treatment zone (Figure 5). Heating is both radiative and conductive, with soil near the applicator electrodes heating fastest (the radio frequency wave gets weaker the further from the electrode due to energy absorption).

At the oscillation frequencies of the applied electromagnetic field, water generally acquires the largest dipole moment of any of the soil constituents before the polarity of the field reverses. As the water content falls, the heating relies on other polar parts of the soil. Careful consideration should be given to purely sandy soils as to whether RFH is applicable. Silica sand is non-polar, and heating in sand must rely on impurities present (Iben, Edelstein, and Roemer 1996). Also, the drier a soil becomes the more difficult it is to move organic gas through it. Conversely, too much water becomes a heat sink. In saturated conditions, RFH boils the water in the immediate vicinity of the applicator electrode and does not heat the treatment zone to a useful temperature. If the water table is shallow, dewatering techniques may need to be applied (Edelstein et al. 1996 and Davis 1997).

The antenna method places vapor recovery wells around the treatment area. Drilled or pushed applicator boreholes on site-specific spacing are lined with a fiberglass casing or other nonconductive non-polar material that will withstand the temperatures expected. The antenna are lowered into the applicator holes to an appropriate depth, and the heating is begun. The antenna can be lowered or raised as desired.

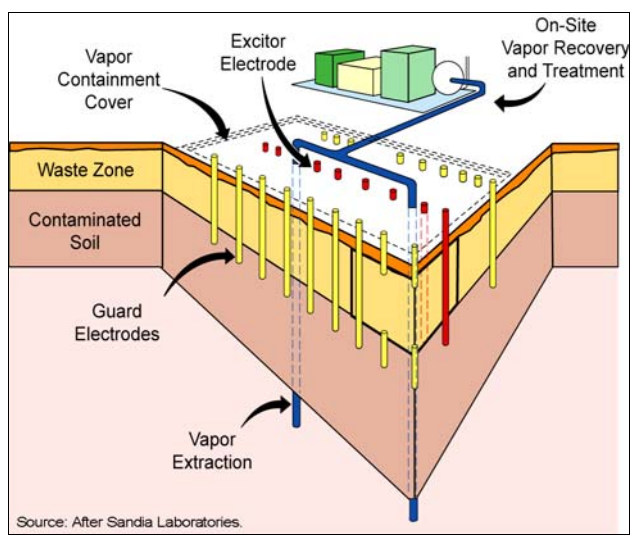

Figure 5. Radio-Frequency Heating with Electrodes

Both antenna and electrode systems monitor the heat distribution in the subsurface (usually with thermocouples, but other devices can be used) to ensure target temperatures are obtained throughout the treatment area. Depending upon the chemicals of concern, RFH can obtain temperatures over 250°C with some vendors claiming temperatures to 400°C (Davis 1997 and U.S. EPA 1997). These tempera-

tures allow the system to treat both VOCs and many SVOCs. Also monitored is the impedance of the applicator system and the impedance of the subsurface soil. As the soil is heated, its impedance changes. If the applicator system impedance is not adjusted to match it, energy reflects back at the system, resulting in heating and potential failure.

The vapor extraction system consists of conventional vapor extraction wells. Also, for safety and prevention of potential interference with local radio transmissions, a grounded metal shield is usually employed over, and just beyond, the treatment area. Metal structures are very efficient at absorbing RF energy and preventing it from escaping the treatment zone. For this reason, RFH is not applicable for treatment zones that contain metal or other conductive objects. Both antenna and electrode technologies were demonstrated by the EPA SITE program in 1994 (U.S. EPA 1995a & 1995b and Haliburton NUS Environmental 1995).

Only the antenna system is currently offered, and that by one vendor.

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3.3.5 In Situ Vitrification

In situ vitrification (ISV) is a thermal treatment process that converts contaminated soil to stable glass and crystalline solids. There are two methods for producing heat for melting the contaminated soil. The older method uses electrodes and electrical resistance to vitrify materials, while the emerging technique uses plasma arc technology.

In the electrical resistance method, high voltage is applied to electrodes (typically four) placed in the soil. Starter frit (generally graphite) is placed on the soil surface and electrical current heats the soil from the top down to temperatures between 1,400 and

2,000°C. Typical melt sizes range from 200 to 1,200 tons, with a processing rate of four to six tons per hour (U.S. EPA 1995). Maximum treatment depth is approximately 20 feet in a single setup. The process depends upon the presence of 1.4 to 15 percent alkali metal oxides in the material to be treated to ensure a proper balance between electrical conductivity and melting temperature. Too much alkali metal content increases the conductivity to a point where insufficient heating occurs.

If the silica content of the soil is sufficiently high, contaminated soil can be converted into glass. Heating vaporizes or pyrolyzes organic contaminants. Most inorganic contaminants are encased in the glass-like monolith that results when the soil cools after treatment. The system requires a vapor hood that traps offgases and channels them to a treatment train that generally consists of a quencher to cool the 100° to 400°C gases and, depending upon what is being treated, a scrubber, activated carbon unit, or thermal oxidizer (U.S. EPA 1997a). The scrubber and quench water may require secondary treatment.

The conventional ISV process can destroy or remove organics and immobilize most inorganics in contaminated soil, sludge, or other earthen materials The process has been used on a broad range of VOCs and SVOCs, other organics including dioxins and PCBs, and on most priority pollutant metals and radionuclides (http://www.frtr.gov/). Mercury is not captured in the vitrified soil and therefore must be treated by the above ground treatment system. The majority (70 to 99.9 percent by weight) of heavy metals, such as arsenic, lead, cadmium, and chromium, and radionuclides are entrained in the melt mass (Thompson, Bates and Hansen 1992). SVOCs and VOCs can be treated with this process, with about 97 percent of the VOCs destroyed and the remainder captured by the offgas treatment system (U.S. EPA 1997a). ISV is applicable to sites with high clay and moisture content, although treatment costs increase with increasing moisture content. Treatment of materials in a permeable aquifer may require dewatering, and if the treatment area is expected to contain large voids, dynamic compaction is recommended (U.S. EPA 1997a).

ISV, using the electrical resistance method, has been tested in the field several times, including a SITE Program demonstration (U.S. EPA 1995), a demonstration at the DOE Hanford Nuclear Reservation (http://www.frtr.gov/) and Superfund cleanups at the Wasatch Chemical Company, Lot 6 site (U.S. EPA 1997b) and General Electric Spokane Shop (U.S. EPA 2005). Costs are estimated at $400/ton (U.S. EPA 1997a). The technology is licensed to only one vendor.

Planar melting is a modification of the conventional ISV method. It differs in that the starter material is injected in a vertical plane between electrodes at depth. Generally, two electrode pairs are used with a starter plane between each pair. As the melt proceeds, it grows vertically and horizontally away from the starter planes. Because the melts are initially separated and only merge late in the process, the potential for driving gases down into the formation is greatly reduced as compared with conventional ISV (Figure 6). The maximum established treatment depth is 26 feet, but deeper melts are theoretically possible. The cost of the process is estimated at between $355 and $460 per ton (Thompson 2002). A successful field demonstration of the planar technique was carried out at the Los Alamos National Laboratory in 2000 (Coel-Roback et al. 2003).

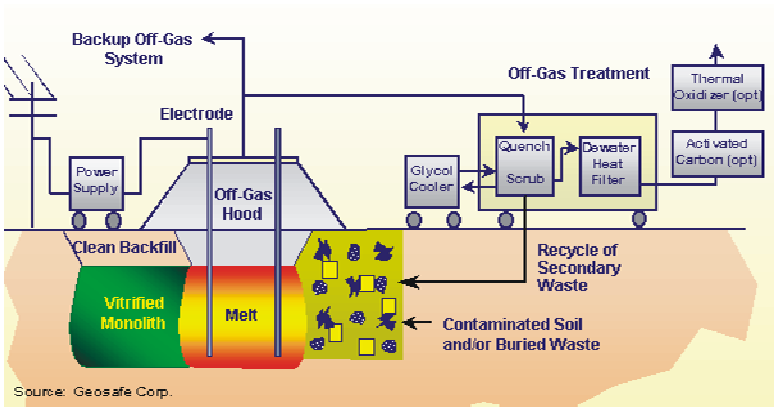

Figure 6. Planar Vitrification—Melting from the Bottom

In situ vitrification using plasma arc technology has been demonstrated at the DOE Savannah River Complex (Blundy and Zionkowski 1997) but has yet to reach commercialization. The process consists of lowering a plasma arc torch into a cased hole and initiating a columnar melt from the bottom up.

Offgases are collected in a hood and treated by a system similar to the electrode method. The torch can achieve temperatures exceeding 7,000ºC, and theoretically, it can operate at any depth. Melts can be initiated below the contaminated area to ensure all contamination is addressed. Since a full-scale demonstration has yet to be done, cost data are unavailable.

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4.0 Notice, Disclaimer, and Acknowledgments

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5.0 Abbreviations and Acronyms

AFCEE	Air Force Center for Environmental Excellence
BTEX	benzene, toluene, ethyl benzene, xylene
C	centigrade
CB	chlorobenzenes
CH_2Cl_2	dichloromethane or methylene chloride
$CHCl_3$	trichloromethane or chloroform
Cr	chromium
CT	carbon tetrachloride
CVOC	chlorinated volatile organic compound
DCA	dichloroethane
DCE	dichloroethene
DDT	dichlorodiphenyltrichloroethane
DNAPL	dense nonaqueous phase liquid
DP	direct push
ERH	electrical resistance heating
FCC	Federal Communications Commission
FRTR	Federal Remediation Technologies Roundtable
H_2	hydrogen gas
ISV	in situ vitrification
MNA	monitored natural attenuation
MPE	multi-phase extraction
MTBE	methyl tert-butyl ether
NAPL	nonaqueous phase liquid
NAS	National Academy of Sciences
NAVFAC	Naval Facilities Engineering Command
NPL	National Priority List
OAR	Office of Air and Radiation
OH^-	hydroxide
ORD	Office of Research and Development
OSWER	Office of Solid Waste and Emergency Response
PAHs	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyl
PCE	perchloroethene or tetrachloroethene
PCP	pentachlorophenol
ppm	parts per million
PVC	polyvinyl chloride
RFH	radio-frequency heating
SCM	site conceptual model
SEAR	surfactant-enhanced aquifer remediation
SEE	steam enhanced extraction
SITE	Superfund Innovative Technology Evaluation
SOD	soil oxidant demand
S/S	solidification/stabilization
SVOCs	semivolatile organic compounds
SVE	soil vapor extraction
TCA	trichloroethane
TCE	trichloroethene
TCLP	Toxicity Characteristic Leaching Procedure
USACE	United States Army Corps of Engineers
U.S. DoD	United States Department of Defense
U.S. DOE	United States Department of Energy
U.S. EPA	United States Environmental Protection Agency
VC	vinyl chloride
VOCs	volatile organic compounds