

Technology
Evaluation Report

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Technologies for Dense Nonaqueous Phase Liquid Source Zone Remediation

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FOREWORD

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1.0 SUMMARY

Dense nonaqueous phase liquids (DNAPLs) are present at numerous commercial and government sites. The presence of DNAPL poses a severe challenge for ground-water remediation technologies. Several technologies have, however, demonstrated the ability for fairly rapid removal of mass from DNAPL source zones; others have shown the ability to treat dissolved phase contamination. This report evaluates those technologies that have demonstrated a potential for remediation of DNAPL source zones. Although there is generally not sufficient data to determine the ultimate level of clean up that can be attained by a given process at a DNAPL site, the site conditions and range of contaminants for which each process is expected to be effective are identified. Those parameters that may limit performance of each technology are also discussed.

Two characteristics of common DNAPL components, low aqueous solubilities and high interfacial tensions with water, result in the persistence of a nonaqueous phase and very irregular distribution of DNAPL in the subsurface. This in turn presents significant difficulties for site characterization and remediation. Both characterization and remediation efforts also may risk mobilizing DNAPL and hence spreading contamination to previously clean regions. Assessment of the applicability of remediation technologies thus must include consideration of this risk as well as the effectiveness of the process.

The following paragraphs summarize the conclusions in this report.

Clean Up Goals: Due to the lack of carefully controlled field tests at DNAPL sites, the ultimate level of clean up attainable for most technologies has not yet been documented. Indeed, due to the difficulty in determining DNAPL distribution, the level of clean up achieved even in controlled field tests has seldom been well established.

Based on existing data, it may be expected that a combination of contaminant distribution, geologic heterogeneities and technological limitations will cause at least some DNAPL to remain after remediation by any available technology. The amount remaining will depend upon the site hydrogeology, the technology employed and the time of treatment. The implications of the residual DNAPL must be assessed before determining if source zone remediation is appropriate. Coupling of technologies may be employed to increase remediation effectiveness, but there has not been adequate testing of the treatment train approach to quantify achievable end points.

Characterization: Since an accurate characterization of the occurrence of DNAPLs is essential for design of a remediation system, and an accurate knowledge of geological heterogeneities is vital for evaluating the hydrogeological limits on remediation; a thorough site characterization is required for DNAPL sites.

Once site assessment has provided the data to evaluate the applicability of the technologies discussed in this report, and the probable limitations of remediation comparison can be made to baseline technologies such as excavation and pump and treat.

Soil Vapor Extraction (SVE): SVE is a proven technology for NAPL mass removal in the vadose zone. It can provide rapid, relatively inexpensive mass removal of volatile components of DNAPL in permeable, low water content soils. Performance is limited by low permeability, high soil water content and heterogeneities. SVE may be augmented by thermal techniques, extending its applicability to semi-volatile compounds and increasing its effectiveness for low permeability layers. It may be coupled with biodegradation to enhance remediation of hydrocarbons and other aerobically degraded compounds. SVE has excellent potential for mass removal of DNAPL in permeable, relatively homogenous soils.

Air Sparging: Air sparging has demonstrated ability to reduce concentration of dissolved phase contamination to target levels for volatile compounds. Due to the tendency of low permeability lenses to divert air flow, and the tendency of DNAPL to accumulate on such lenses, it is unlikely that an entire DNAPL source zone would be effectively sparged, although significant success has been reported in one field trial. Extended treatment times at DNAPL sites may thus be anticipated. Successful air sparging requires volatile contaminants and moderate permeability. Performance suffers in low and high permeability units and in heterogeneous sites. A thicker saturated zone is favored. Air sparging is typically coupled with SVE to treat both vadose and saturated zones.

Steam Flooding: Steam can provide rapid DNAPL mass removal in either the vadose zone or the saturated zone. It removes contaminants through a combination of thermal volatilization and mobilization, thus may be used with lower volatility compounds than SVE. Limitations include poorer performance in low permeability units and lower efficiencies due to heterogeneities. The risk of DNAPL mobilization due to condensing of vapors at the thermal front is not well defined. Steam requires several feet of overburden to provide adequate containment, otherwise some type of seal may need to be provided. Steam flooding has been coupled with electrical heating of fine-grained layers to improve performance in heterogeneous sites. Steam has the potential for rapid mass removal from DNAPL sites in both saturated and unsaturated zones where permeability is adequate and DNAPL mobilization is not a concern or can be controlled.

Cosolvent/Alcohol Flooding: Cosolvent flooding can provide rapid mass removal of DNAPL at sites with moderate to good permeability. Extraction efficiency will be lower in low permeability zones and at heterogeneous sites. High concentrations of reagents have been used in cosolvent floods, and recycling of solvents has not yet been demonstrated, hence reagent cost may be high. All cosolvents lower interfacial tension with DNAPL, raising the potential for downward mobilization. There has been no controlled DNAPL field test to

establish the ultimate clean up potential of cosolvent flooding, but it should be similar to that of surfactants (a field test is now in progress at Dover AFB). The technology has excellent potential for mass removal of DNAPL from permeable units where hydrogeology is appropriate.

Surfactants: Surfactants can provide rapid mass removal of DNAPL at sites with good to moderate permeability. Several DNAPL field tests have demonstrated surfactant's ability to remove DNAPL, including recent tests that used partitioning tracers to provide a rigorous measure of success. Recycling of surfactants has been demonstrated. Extraction will be less efficient in low permeability or heterogeneous sites. Mobility control using polymer or foam can lessen the effect of heterogeneities. Although removal of nearly all DNAPL has been accomplished in field tests, some DNAPL has remained in every case. Ultimate ground-water clean up levels have not been established. Surfactants lower the interfacial tension between water and DNAPL, thus the risk of vertical mobilization of DNAPL must be assessed at each site.

In Situ Oxidation: *In situ* oxidation can provide rapid contaminant destruction for readily oxidized contaminants. Performance may be limited by the presence of oxidation-resistant contaminants, by the large amounts of oxidizable material in the soil, by low permeability and by heterogeneities. Some oxidants also require maintenance of acid conditions and thus performance may be limited in carbonate-rich units. Field data are insufficient for determination of clean up levels or the range of conditions under which the technology is suitable, however, additional field tests are in progress.

Electrical Heating: A number of techniques for heating soils, including resistance (joule) heating, microwave heating and radio frequency heating have been shown to be capable of raising soil temperatures. Volatile compounds and, depending on the temperatures achieved, semi-volatile compounds can be volatilized. Electrical heating is most applicable to fine-grained soils. It is normally coupled with other technologies (SVE or steam) to recover the volatilized contaminant. There are no data available to determine ultimate clean up levels at DNAPL sites, but the results will depend upon site heterogeneities.

Electrokinetics: This provides mobilization of dissolved phase contamination, and possibly of DNAPL, and must be coupled to a removal or destruction technology. A LASAGNA® pilot test suggests DNAPLs can be treated, but the fraction of DNAPL remaining was not determined. Nor is the mechanism for DNAPL migration well understood. Electrokinetics is a promising technology for low permeability soils that requires more information for full evaluation. It may also be applied in the vadose zone.

In-Well Stripping: This variant of air sparging provides stripping of contaminated groundwater in treatment wells. It treats only volatile compounds and only those contaminants present as a dissolved phase, thus removal of DNAPL would occur only indirectly by dissolution as the dissolved phase was stripped. Extended treatment times would be expected.

Biodegradation: Biodegradation of most common DNAPL components (PCBs are a notable exception) has been demonstrated to be effective in treating dissolved phase contamination; however, it is not likely to be effective on DNAPL as degradation does not take place directly in the nonaqueous phase. Treatment of DNAPL will thus be indirect, by dissolution, as the dissolved phase is degraded. Biodegradation of DNAPL will thus probably require an extensive treatment time.

Reactive Barriers: Reactive barriers using zero-valent iron have proven effective for treatment of dissolved phase plumes of some chlorinated solvents, notably TCE. Other reactive units may be used to extend the technology to other compounds. Reactive barriers treat only dissolved phase contamination, thus they do not directly address DNAPL source zones. The effective life of treatment walls is still to be determined.

Containment: Low permeability barriers may be used to isolate DNAPL source zones. Although they do not address removal of the DNAPL, they may provide risk reduction and isolation of the source from the dissolved phase plume, thereby allowing treatment of the dissolved phase plume. Barriers may also allow more aggressive remediation of the source zone by other technologies.

2.0 INTRODUCTION

2.1 SCOPE OF THE REPORT

This report summarizes the capabilities and limitations of technologies for remediation of sites where DNAPL is present. The report concentrates on those technologies that can actually remove or destroy the DNAPL. Only technologies that have been deployed in the field, at least at pilot scale, are considered, as only those technologies have sufficient data available with which to make a meaningful assessment of performance.

2.2 REPORT DESIGN AND OBJECTIVES

This report is designed to provide sufficient information to help determine which, if any, technologies might be considered for a specific DNAPL site. To include most of the currently viable DNAPL technologies, without becoming cumbersome, the amount of information on each technology is kept to the minimum required to allow an initial evaluation. The discussion of each technology includes a section which lists sources of additional information on that technology.

2.3 TECHNOLOGY DEVELOPMENT/EVALUATION

Most of the technologies discussed in this report are emerging technologies that are in the early stages of development. Few well-documented pilot tests on DNAPL sites have been reported. Although technologies, including SVE and bioremediation, have had numerous pilot and full-scale applications, most of these have dealt with dissolved phase or LNAPL contamination. The critical information on the ultimate level of clean up obtainable with a process can only come from controlled field studies. Similarly, there is little meaningful information on costs associated with DNAPL remediation due to the lack of full-scale applications.

Evaluating the existing field tests of DNAPL remediation is complicated by the difficulty in assessing the extent of DNAPL removal. As discussed in the following sections, characterization of DNAPL distribution is a difficult problem and seldom is the volume of DNAPL accurately known before treatment. This makes quantification of the fraction of removal problematic. Only in cases where extensive sampling was done, evaluating both horizontal and vertical distribution of DNAPL, can the results be rigorously defended. More recently, partitioning tracers have provided additional evidence of the quantity of DNAPL present

before and after treatment.

2.4 THE DNAPL PROBLEM

Most organic compounds have a limited solubility in water. Due to their low solubilities, when released in the subsurface they often do not dissolve totally in groundwater and remain as a separate liquid, a nonaqueous phase liquid (NAPL). Those NAPLs that are denser than water (DNAPLs) tend to sink beneath the water table, while those that are lighter than water (LNAPLs) do not. Remediation of DNAPL-contaminated sites is quite different, and generally more difficult, than remediation of LNAPL-contaminated sites. The presence of DNAPL poses a serious challenge to all conventional ground-water remediation technologies (NRC, 1994; Pankow and Cherry, 1996).

Chlorinated solvents are the most common DNAPL components and are among the most common ground-water pollutants (Table 1). Other common DNAPL components include PAHs (polycyclic aromatic hydrocarbons) and PCBs (polychlorinated biphenyls). DNAPLs are often complex mixtures of these compounds. Although there are a large number of compounds that may form DNAPL, common DNAPLs may be divided into two distinct groups; chlorinated solvent DNAPLs and PAH-dominated DNAPLs including coal tar and creosote. Chlorinated solvents generally have higher densities and lower viscosities than coal tar and creosote (Pankow and Cherry, 1996), making them much more mobile. Many sites are contaminated with both DNAPL and metals or DNAPL and radionuclides. Remediation of such mixed-waste sites are beyond the scope of this report.

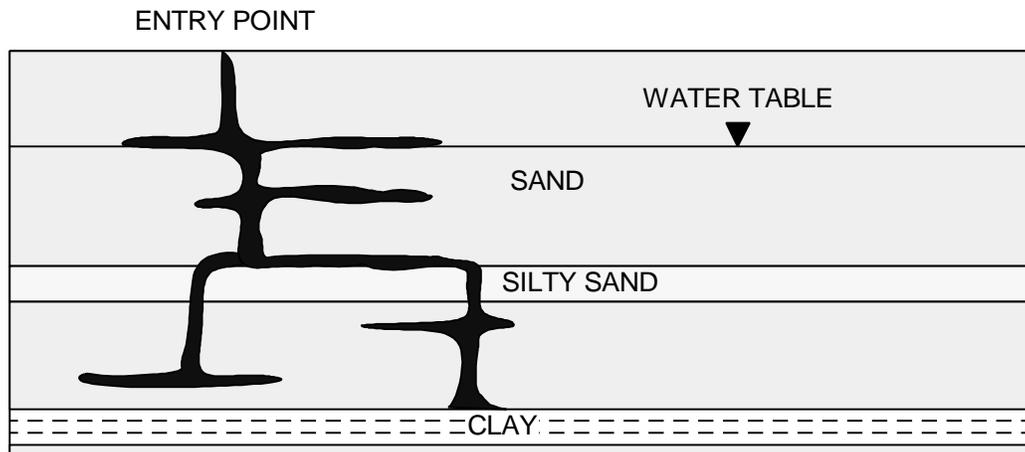
Table 1: Common DNAPL Components				
Name	Aqueous Solubility, mg/L	Density, g/cm ³	Vapor Pressure, mm	Henry's Law Constant, atm•m ³ /mol
Chlorinated Solvents				
Tetrachloroethylene (PCE)	150	1.6227	14	1.46 x 10 ⁻²
Trichloroethylene (TCE)	1100	1.4642	57.8	9.9 x 10 ⁻³
1-2 Dichloroethylene (DCE)	6260	1.2565	265	5.23 x 10 ⁻³
Vinyl Chloride (VC)	1100	0.9106	2560	5.6 x 10 ⁻²
Trichloroethane (TCA)	4500	1.4397	19	9.09 x 10 ⁻⁴
PCBs				
Aroclor 1242	0.20	1.392 (15°C)	2.5 x 10 ⁻⁴	2.8 x 10 ⁻⁴
Aroclor 1254	0.050	1.505 (15.5°C)	6 x 10 ⁻⁵	1.9 x 10 ⁻⁴

Aroclor 1260	0.144	1.566 (15.5°C)	6.3×10^{-6}	1.71×10^{-4}
Coal Tar/Creosote*				
Phenanthrene	1.10 (0.16)**	1.179 (25°C)	2.1×10^{-4}	2.35×10^{-5} (25°C)
Naphthalene	31 (3.9) **	1.162	5.4×10^{-2}	7.34×10^{-4}
Benzo(a)pyrene	3.8 mg /L (25°C)	1.351	5.6×10^{-9}	$< 2.4 \times 10^{-6}$
Phenol	93,000 ** (25°C)	1.0576	0.2	3.97×10^{-7} (25°C)
Aniline	36.65 ** (25°C)	1.02073	0.3	0.136
<p>Properties are at 20°C except where noted * Creosote/Coal Tar: Are complex mixtures with a typical composition of 85% PAHs such as Naphthalene and Phenanthrene, 10% phenolic compounds such as Phenol, and 5% heterocyclics such as Aniline. ** Due to the reduced solubility of individual components in mixtures, aqueous phase solubilities of these components from creosote or coal tar are much lower, the values in parentheses are the solubilities from a coal tar (Peters and Luthy; 1993). Sources: Mercer and Cohen (1990), Montgomery (1991), Mueller et al. (1989).</p>				

2.5 DISTRIBUTION OF DNAPL

The distribution of DNAPL in the subsurface is typically highly irregular, which makes both characterization and remediation difficult. In the vadose zone, DNAPL flows downward with relatively little spreading (Schwille,

Figure 1. Typical DNAPL Distribution



1988; Pankow and Cherry, 1996). A small quantity is retained by capillary forces in each pore (or fracture) through which the DNAPL flows. This fraction, which is not mobile under static conditions, is termed residual saturation.

Below the water table, entry of DNAPL into water-filled pores requires overcoming an entry pressure resulting from interfacial tension between DNAPL and water. The required entry pressure increases with decreasing grain size (Table 2). The downward flow of DNAPL may thus be interrupted each time a layer with a smaller grain size is encountered. DNAPL tends to flow laterally above the fine-grained layer, accumulating until there is sufficient thickness of DNAPL to overcome the entry pressure. Even very subtle variations in grain size distribution may produce significant deflection of DNAPL flow. This results in a series of horizontal lenses of DNAPL connected by narrow vertical pathways (Figure 1). As in the vadose zone, a small amount of DNAPL is retained as residual saturation in every pore through which it flows. If the DNAPL encounters a layer that has a sufficiently high entry pressure, the DNAPL will accumulate on the top of this layer, forming a "pool." Thus, DNAPL is typically found as multiple horizontal lenses, connected by sparse vertical pathways, with one or more pools above fine-grained layers. Most of the horizontal lenses and vertical pathways will be at, or below, residual saturation; only pools will have higher saturations. The distinction between residual saturation and pools is important, since only the DNAPL in pools is expected to be mobile. However, changes in the interfacial tension between water and DNAPL, which are produced either by heat (all thermal methods) or by chemicals (surfactants or cosolvents) may mobilize DNAPL at residual saturation by reducing capillary forces. The flow of DNAPL is discussed in detail in Pankow and Cherry (1996).

Clean Sand ($K= 1 \times 10^{-2}$ cm/sec)	45 cm
Silty Sand ($K= 1 \times 10^{-4}$ cm/sec)	286
Clay ($K= 1 \times 10^{-7}$ cm/sec)	4634
Fracture, 20 μ Aperture	75
Fracture, 100 μ Aperture	15
Fracture, 500 μ Aperture	3
Calculations based on TCE as the DNAPL, an interfacial tension of 34 dynes/cm, wetting angle of 0, porosity = .35. Sand and Fracture entry calculated using equations 3.17 and 11.3, respectively, from Pankow and Cherry, 1996.	

An important property of DNAPLs is that, although they are widespread, they are seldom directly detected. Their sparse distribution, and relative immobility, means that direct detection of free product is unusual (the probability of a well or core intersecting a small DNAPL pool is small, and capillary forces prevent

DNAPL from migrating to nearby wells). Further complicating the problem of recognition of DNAPL is the fact that, although water in direct contact with DNAPL will have concentrations near aqueous solubility, due to the fact that only a small fraction of an aquifer typically contains DNAPL, dilution will lower dissolved phase concentrations to only a fraction of saturation. A concentration of as little as 1% of aqueous phase concentration has been proposed to be indicative of the presence of DNAPL (Newell and Ross, 1991). A thorough discussion of the assessment of the presence of DNAPL is given in Pankow and Cherry (1996).

2.6 DNAPL AND SITE CHARACTERIZATION

The presence of DNAPL makes site characterization both more critical and more difficult. The entire volume where DNAPL occurs must be treated if remediation is to be successful; thus, the full extent of the DNAPL source zone (the volume actually occupied by DNAPL) must be determined. To minimize cost of remediation, the volume treated should be minimized; thus, accurate delineation of the DNAPL source is essential. The highly irregular distribution of DNAPL makes determination of the actual DNAPL extent difficult. No remote sensing techniques have been successful in defining DNAPL extent. Water analyses from multi-level wells or push-in samplers can provide indirect data on DNAPL distribution. Analyses of samples from cores or data from certain push-in tool sensors can provide direct evidence of the presence of DNAPL, but due to the irregular distribution of DNAPL, provide only a rough estimate of DNAPL extent. There are also substantial risks associated with drilling (or pushing) through DNAPL pools (Pankow and Cherry, 1996). Partitioning tracers (Jin et al., 1995) can quantify the amount of DNAPL present, but only provide data on that volume of aquifer swept in the tracer test. Once DNAPL is located, interfacial tracers (Annable et al., 1998) may provide an estimate of DNAPL morphology. A combination of these approaches to define the limits of the DNAPL source zone is a prerequisite to design of a successful remediation project. Since the performance of most technologies is highly affected by heterogeneities in geology and DNAPL distribution, the hydrogeology of the contaminated volume must also be carefully determined.

In addition to a careful site characterization, successful implementation of a remediation technology will also require specific information on both contaminant composition and hydrogeology. The information required is dependent upon the technology selected. For example, technologies based on vapor-phase transport require information on vapor pressures and Henry's law constants of contaminants and air flow at the site, while electrokinetics requires a knowledge of contaminant mobility under an applied electric field among other factors. Since the information required is highly technology-dependent, the relevant parameters are identified for each technology.

2.7 RISKS ASSOCIATED WITH DNAPL SITES

There are risks associated with both the characterization and remediation of DNAPLs. Any invasive technique that penetrates a DNAPL pool (drilling, push-in tools, etc.) could provide a pathway for downward migration of the DNAPL (Pankow and Cherry, 1996). Any remediation technique that alters the water table, or decreases interfacial tension between DNAPL and water may also enhance DNAPL mobility. The risks of mobilizing DNAPL are also dependent upon the hydrogeology of the site. Whether a competent confining layer is present or if there are water resources beneath the DNAPL source zone are two factors of particular importance. Thus, the risk must be evaluated for each site. Remediation may also increase the risk of DNAPL mobilization; such risks are discussed, where appropriate, for each technology.

2.8 DNAPL IN FRACTURED ROCK

Remediation of DNAPL in fractured rock poses considerable difficulties with respect to both characterization and remediation. Delineation of the DNAPL source zone in fractured rock is generally more difficult than in porous media. For example, in relatively homogenous porous media, “clean” water in a sample provides evidence there is no DNAPL further up-gradient. In contrast “clean” water in one well in a fractured unit provides information only on those fractures that are both up-gradient and in hydraulic contact with the well. Remediation is also more difficult in respect to both accessing the entire source zone and attaining hydraulic control. For example, in a typical porous medium, a line of wells on one side of a source zone and another line of wells on the other side provides flow throughout the entire zone. However, it is not as simple to ensure all fractures in a given volume will be swept effectively as connection among fractures cannot be assumed. Additionally, many fractures are dead-ended, potentially providing traps for DNAPLs that cannot readily be accessed. Finally, the poor connectivity of fractures in some systems and the common lack of an impermeable “bottom” in fractured media makes attaining hydraulic containment more difficult and may increase the risks of DNAPL mobilization.

Even if all DNAPL in a fractured medium was removed, much contamination might remain. Diffusion of contamination from DNAPL in fractures into the matrix produces a zone of high dissolved-phase concentration adjacent to the fractures. If the DNAPL is removed, the contamination will slowly diffuse back into the fractures (Pankow and Cherry, 1996).

2.9 DNAPL PROPERTIES

Low aqueous solubility is one characteristic of common DNAPL components that is relevant for remediation. Processes based on dissolution will be inherently inefficient unless the solubility of the DNAPL is increased.

The vapor pressure of a pure compound provides a measure of how readily a compound will volatilize (transfer to the vapor phase), and thus is important for DNAPL source zone remediation through processes such as soil vapor extraction (SVE) that are based on volatilization. The Henry's Law Constant of a compound, which is equal to a compound's vapor pressure divided by its aqueous solubility, provides a similar measure of how readily a compound will volatilize when it is dissolved in water. Table 1 shows vapor pressures and Henry's Law Constants for some common DNAPL components. Processes that involve extraction of contamination as a vapor phase will be effective only for compounds with a high vapor pressure (for direct volatilization of DNAPL) or with large Henry's Law Constants (for volatilization of the dissolved phase). It may be seen from Table 1 that most chlorinated solvents are volatile, while most PAHs and PCBs are not. Both vapor pressure and Henry's Law Constants increase with temperature, thus transfer to the vapor phase is enhanced in both thermally-enhanced SVE and steam technologies.

2.10 OVERVIEW OF REMEDIATION APPROACHES

Remediation technologies include technologies that remove the DNAPL by dissolution, displacement or volatilization and those that destroy the contamination through chemical reaction or biodegradation. Techniques for risk reduction include those that immobilize the contamination. In this section, the basic principles that govern technologies for removal or destruction of DNAPL will be briefly discussed.

Flushing: Technologies that involve flushing a liquid through the contaminated zone employ one of three approaches; dissolution, displacement or chemical destruction. The technologies that depend upon dissolution of DNAPL involve increasing contaminant solubility through the use of chemical additives (surfactants and/or cosolvents) or by increasing the temperature. The dissolved contaminant is then recovered with the groundwater, as in conventional pump and treat.

Technologies that are designed to physically displace DNAPL reduce capillary forces by reducing the interfacial tension between DNAPL and groundwater using surfactants, cosolvents or heat. The capillary forces that restrict DNAPL mobility decrease with decreasing interfacial tensions, increasing mobility. The mobilized contaminant, plus contaminated groundwater is recovered from extraction wells.

Flushing technologies that are designed to destroy DNAPL compounds involve either oxidation or reduction. Most DNAPL components, like most compounds that are stable in air, are relatively resistant to oxidation under naturally occurring conditions. Thus, technologies involving oxidation of compounds typically involve addition of strong oxidizers to the subsurface. Many DNAPL components, including most chlorinated solvents, may be more readily broken down by reduction. Reduction typically involves introduction of a reducing compound, often, but not necessarily, in solid form.

Volatilization: Technologies designed to remove DNAPL by volatilization involve inducing the flow of vapor through the contaminated zone and the transfer of the contaminants to the vapor phase. Heat can be used to increase the vapor pressure of the contaminants. DNAPL is removed by a combination of direct volatilization from the DNAPL and volatilization from the dissolved phase, leading to additional DNAPL dissolution. The contamination is recovered as vapor through vapor extraction wells.

Thermal Processes: Thermal technologies include flushing technologies (steam and hot water), volatilization processes (steam and electrical heating) and chemical destruction (*in situ* vitrification). The principles of flushing technologies and volatilization have already been discussed. *In situ* vitrification heats the soil to a temperature at which the soil melts; at these temperatures organic contaminants will thermally decompose if they have not previously volatilized.

Electrokinetics: Electrokinetics induces the migration of contaminants by applying a direct current electrical field across the contaminated zone. Groundwater and contaminants migrate, but the technology must be coupled with another technology for destruction or removal of the contaminants. The objective of the electrokinetic process is to mobilize the contaminants in low permeability soils.

Biodegradation: Biodegradation is the breaking down of contaminants by biologically-mediated reactions. A compound may be directly degraded if bacteria can obtain energy from the degradation of the compound, generally when the compound acts as an electron donor in a redox reaction. PAHs are among the many compounds that can be directly biodegraded by common bacteria (although the degradation rates of the 4 and 5 ring compounds may be very low). Chlorinated compounds generally do not act as primary electron donors or acceptors, but may be degraded by cometabolic degradation. In cometabolic degradation, enzymes produced by the degradation of some other carbon source fortuitously induce breakdown of the compound of interest. Biodegradation is generally not effective in nonaqueous phase liquid; DNAPL components may have to be dissolved in groundwater to become bioavailable.

Other Technologies: Reactive barrier walls can be used to treat the dissolved phase plume from a DNAPL source zone. Although not directly addressing the DNAPLs, reactive barrier walls are an option for DNAPL-contaminated sites. Reactive barrier walls induce a chemical reaction, typically a reductive dechlorination for chlorinated solvents, that destroys dissolved phase

contamination.

Containment, either physically with barrier walls or hydraulically by pumping (pump and treat) is also an option that, while not directly treating DNAPL, is often considered at DNAPL sites. Containment limits the spread of contamination.

3.0 FLUSHING TECHNOLOGIES

3.1 ALCOHOL OR COSOLVENT FLUSHING

3.1.1 Description

Alcohol/cosolvent flushing involves pumping a mixture of water and one or more solvents through a contaminated zone to remove DNAPL by dissolution and/or mobilization. If the solvent is added at relatively low concentration, it is termed a cosolvent. If used at high concentration, it may be termed a solvent flood; alcohols are the most common solvent used, hence the term alcohol flooding. The relative importance of dissolution and DNAPL mobilization in an alcohol/cosolvent flood is determined by the solvents and the concentrations used. If a water/cosolvent mixture is used that greatly increases the solubility of the DNAPL, and a sufficient concentration of solvent is used, the process will be based on *dissolution*. If a system is chosen that creates a very low interfacial tension between DNAPL and water, *mobilization* of the DNAPL will be the dominant displacement mechanism.

A typical system involves an array of injection wells and an array of extraction wells. Many combinations of delivery/extraction constructions may be used. If the dissolution approach is used, the DNAPL dissolves in the solvent/groundwater solution and is recovered at the extraction wells in groundwater as a dissolved phase. If a displacement approach is used, the DNAPL is physically driven to the extraction wells and is recovered as a separate phase (although some dissolution will always occur). The effluent solution containing water, solvent and contaminant must then be treated in either case.

3.1.2 Physical and Chemical Basis

Alcohol/cosolvent flooding is based upon the increase in solubility of hydrophobic organic compounds resulting from the addition of a solvent to water and the reduction of interfacial tension that accompanies the increase in solubility. The solubility of any hydrophobic organic compound in water increases as an alcohol, or other organic water-soluble solvent, is added to the water. The increase in solubility produces a parallel decrease in sorption (Rao et al., 1985). If a solvent, or mixture of solvents, is selected that is miscible with the DNAPL above some cosolvent concentration, water, DNAPL and cosolvent will form a single phase. The interfacial tension between water and DNAPL will decrease as solubility increases, going to zero for a miscible system.

The chemical basis for the use of cosolvents is well established. The ability of solvents such as short-chain alcohols (methanol, ethanol, propanol) to increase

the solubility of hydrophobic organic compounds in water has been demonstrated by numerous workers (e.g., Rao et al., 1985; Peters and Luthy, 1993; McCray and Falta, 1996; Lunn and Keuper, 1996). Although some compounds, such as the weathered hydrocarbon-based LNAPL at Hill AFB OU1 have proved to be resistant to dissolving in common cosolvents, most common DNAPL components are readily soluble in alcohol/water mixtures. Increases in solubility from a factor of a thousand to complete miscibility may be achieved, depending upon the contaminant and solvent mixture chosen.

A discussion of the chemical basis for the solubility increases in aqueous systems due to the addition of cosolvents is given by Schwartzbach et al. (1993). Phase diagrams of several relevant systems, with interpretations are provided in a technical practices manual (AATDF, 1998), which also includes an extensive reference list. A large number of alcohols and other organic solvents are available, but only a few have been tested in the field.

3.1.3 Field Trials

All field trials of solvent flooding for which results have been published involved LNAPLs. The trials have been summarized (AATDF, 1998).

1. Hill AFB, OU1 Alcohol Flood: Conducted in 1995 by the University of Florida and the U.S. EPA's R.S. Kerr Laboratory. Approximately 9 pore volumes (~10,000 gallons) of a mixture of 70% ethanol and 12% pentanol in water were pumped through a 3 x 5-meter sheet-piling cell at Hill AFB, Utah using a line drive array of injection and extraction wells. This was followed by approximately 15 pore volumes of water to remove the cosolvents. The contamination was an LNAPL consisting of a complex mixture of weathered jet fuel and other components at a depth of 4.6 to 6 meters. The sediments were poorly sorted sands and gravels. Initial LNAPL saturation averaged about 5%. Approximately 85% of the LNAPL was removed with over 99% of many NAPL constituents removed. The primary recovery mechanism was enhanced dissolution.

2. Hill AFB, OU1 Cosolvent Flood: Conducted in 1996 by Clemson University and the U.S. EPA's R.S. Kerr Laboratory. Approximately 2 pore volumes of a mixture of tertiary butanol (81%) and hexanol (16%) were followed by approximately 2.3 pore volumes of 95% tertiary butanol, then 0.3 pore volume of 47% tertiary butanol and finally 30 pore volumes of water. The test cell, sediment and contaminant were similar to those the Hill AFB OU1 Alcohol Flood just described. Between 75% and 95% of the LNAPL was recovered. The primary recovery mechanism was displacement of the LNAPL.

3. Hill AFB, OU1, Cyclodextrin Flood: Conducted in 1996 by the University of Arizona and the U.S. EPA's R.S. Kerr Laboratory. Approximately 10 pore volumes of a 10% cyclodextrin in water solution were injected. The cells, contaminant and sediments were similar to those described above for the Hill AFB OU1 Alcohol Flood. Recovery ranged from 39-93% of LNAPL originally

present. Dissolution was the primary recovery mechanism.

3.1.4 Capabilities and Limitations

Each cosolvent or alcohol flood showed the ability to remove NAPL mass by dissolution and/or mobilization. None achieved full recovery, although it should be noted that the Hill AFB LNAPL is very difficult to dissolve, even in the laboratory. It is likely that these technologies would be more effective for easily dissolved DNAPLs such as chlorinated solvents.

The performance of a solvent flood is dependent upon the ability of the chosen mixture to dissolve the target NAPL. Not all compounds are highly soluble in common cosolvents, however, the solubility of a specific DNAPL can be readily verified in the laboratory. The extent of dissolution and the extent of removal (desorption) from weathered soils can also be evaluated with soil samples in the laboratory. Thus the chemical effectiveness of a proposed solvent flood should be predictable from laboratory testing.

For any flooding technique to be effective, the entire contaminated volume of soil must be effectively flushed with treatment solution; thus, there also are hydraulic limitations for any flooding technology. Alcohols are generally less dense than water. High concentration alcohol floods may be less dense than groundwater, and problems with density overriding may occur. Gradient injection of the cosolvent flood and water can minimize the density override problem (Rao et al., 1997). Heterogeneities in the aquifer will also decrease extraction efficiency as they will for all flushing technologies (Mackay and Cherry, 1989). As heterogeneity increases, some areas become relatively poorly swept, requiring a longer treatment time and a larger treatment volume than for a homogenous system.

The lowering of interfacial tension (IFT) that is produced by the addition of solvents poses a risk of mobilization of the DNAPL. If the DNAPL is perched on an impermeable layer and kept out of the layer by high entry pressure, lowering of IFT, which reduces the capillary forces and hence the entry pressure, may allow the DNAPL to penetrate the aquitard and move down into previously clean zones. The reduction of IFT depends upon the system used, and the risk involved depends upon the hydrogeology of the site, particularly the integrity of the aquitard. This risk must be evaluated for each site. The ultimate level to which DNAPLs may be reduced by cosolvent flooding is unknown since no field trials have been reported for solvent flushing of DNAPLs. Two trials are currently underway, however, one at Dover AFB and one in Jacksonville, Florida. In principle, results should be similar to that of surfactant flooding.

3.1.5 Further Information

The AATDF Technology Practices Manual for Surfactants and Cosolvents (AATDF, 1998) contains an extensive discussion of the physical and chemical basis for solvent flooding, including phase diagrams of some sample systems. It also includes case studies of cosolvent field trials. Finally it contains references to an extensive literature on the technology. The more concise GWRTAC Technology Evaluation Report "Surfactants/Cosolvents" (Jafvert, 1996) also contains a discussion of the physical and chemical principles of alcohol/cosolvent flooding as well as descriptions of field trials and a bibliography.

AATDF (1998). Surfactants and Cosolvents for NAPL Remediation," Technology Practices Manual for Surfactants and Cosolvents, Ann Arbor Press

Jafvert, C. T. (1996). "Surfactants/Cosolvents." Technology Evaluation Report #TE-96-02, Ground-Water Remediation Technologies Analysis Center (GWRTAC), Pittsburgh, PA. [gwrtac.org].

Rao P.S.C., Annable, M.D., Sillan, R.K., Dai, D., Hatfield, K. and Graham, W.D. (1997). Field-scale evaluation of in situ cosolvent flushing for enhanced aquifer remediation. *Water Resources Research*. 33:2673-2686.

3.2 SURFACTANT FLUSHING

3.2.1 Description

Remediation of DNAPL-contaminated sites by surfactant flushing involves injection of a solution of water plus surfactant into the source zone and removal of the DNAPL through a combination of dissolution and displacement. The relative importance of dissolution compared to displacement can be controlled by formulation of the surfactant solution. The surfactant mixture may be composed of more than one surfactant and may include an alcohol and/or a salt (typically sodium chloride) added to optimize phase behavior. A polymer or foam may be used for mobility control. The extracted solution of water, surfactant, contaminants, plus other additives must be treated; the surfactants may be recycled. A typical system involves an array of injection wells and an array of extraction wells. As with cosolvent flushing, any combination of delivery/extraction systems may be used.

3.2.2 Physical and Chemical Basis

The term surfactant is a contraction for surface active agent. Surfactants are the active ingredients in soaps and detergents and are common commercial chemicals. Two properties of surfactants are central to remediation technologies; the ability to lower interfacial tension and the ability to increase solubility of hydrophobic organic compounds. Both properties arise from the fact that surfactant molecules have a hydrophobic portion and a hydrophilic portion. As a result, when water containing surfactant and DNAPL come into contact, surfactant molecules will concentrate along the interface, with their polar ends in the water and their nonpolar ends in the DNAPL; this lowers the interfacial tension between the two immiscible fluids. When present in sufficient concentration (the critical micellar concentration), surfactant molecules form oriented aggregates, termed micelles. In water, the molecules in a micelle are arranged with their polar ends outwards and their nonpolar ends inwards, forming a nonpolar interior to the micelle. Micelles can incorporate hydrophobic molecules in their interior, producing an apparent increase in solubility. The process of dissolving by incorporation into micelles is termed solubilization. Once solubilized, a compound is transported as if it were a typical dissolved phase. Micellar solutions may either be a single phase system in which micelles containing solubilized contaminant are transported as a dissolved phase in the groundwater, or a separate phase, termed a middle phase microemulsion, in which a separate phase containing approximately equal volumes of surfactant and contaminant is formed.

The extent of increase of solubility (solubilization) produced depends upon the contaminant, the surfactant, the salinity and the surfactant concentration. Increases in solubility of more than five orders of magnitude and solubilities in the hundreds of thousands of mg/L have been reported for common DNAPL components (Baran et al, 1994). Early surfactant field trials used surfactants that produced modest increases in solubility (one or two orders of magnitude) and extracted the DNAPL through slow dissolution. This approach required multiple pore volumes (more than 10) (Fountain et al, 1996). More recent work has emphasized higher performance systems that produce solubilizations above 100,000 mg/L (Brown et al., 1997).

Selection of the appropriate surfactant requires consideration of performance, toxicity, biodegradability and surfactant sorption. Published work has identified surfactant systems with appropriate properties that produce high solubilization of a wide range of compounds of environmental interest. Although high solubilization of contaminants may be produced by a variety of types of surfactants, recent work has focused on anionic surfactants. Anionic surfactants have a negatively charged functional group; common examples include sulfate and sulfonate. The negative charge results in very low adsorption, while those surfactants with a positive functional group (cationic surfactants) are characterized by high sorption and even those without charged groups (nonionic

surfactants) have high enough sorption to cause problems in the presence of clay (Shiau et al., 1995).

Anionic surfactants typically require the addition of cations or the use of cosurfactants to produce the desired solubilization. It is known from enhanced oil recovery research that the addition of cations (typically sodium from adding NaCl) decreases the solubility of the surfactant in water, driving it into the NAPL (Lake, 1989). As salinity is increased, partitioning into the NAPL increases and solubilization of the NAPL in water increases. At the point at which the partitioning is equal between NAPL and water phases, solubilization is a maximum. Near this point, termed the optimal salinity, a third phase may form. This new phase is termed the middle phase, or middle phase microemulsion as it is intermediate in density between DNAPL and water and hence occurs between the liquids in experiments. A nonionic surfactant may be used to induce the same effect, and alcohols may be added to optimize the phase behavior and control the appearance of unwanted viscous phases (Lake, 1989; Pope and Wade, 1995).

The interfacial tension between NAPL and water decreases as solubilization increases. The interfacial tension may decrease by up to four orders of magnitude at optimal salinity. Since capillary forces are reduced with decreasing interfacial tension, surfactant systems may induce DNAPL mobility (Abriola et al., 1995). This aids in recovery of the NAPL by increasing DNAPL flow to the extraction wells, but may pose risks of spreading of DNAPL contamination if the reduced IFT allows the DNAPL to invade underlying layers previously uninvaded due to high displacement pressure (displacement pressure scales directly with interfacial tension).

After extraction, surfactants may be separated from the contaminants and reused. Air stripping has been successfully used in three field trials (PCE, carbon tetrachloride and TCE were the contaminants stripped), and a permeable membrane system using solvent extraction has been developed that could be used for non-volatile compounds (Harwell, cited in AATDF, 1998). Due to the enhanced solubility produced by the surfactants, the extraction processes are less efficient and more costly than separation from surfactant-free water.

A modification to surfactant flooding to improve performance in heterogeneous media is the use of mobility control agents. In enhanced oil recovery, polymers are routinely added to surfactant floods to increase sweep efficiency (Lake, 1989). Polymers (xanthan gum, a food-grade additive is among the most commonly used polymers) are added in low concentrations (a few hundred mg/L) and produce a non-Newtonian fluid, a fluid whose viscosity changes with flow conditions. In high permeability units, the polymer causes the fluid to have an increased viscosity, slowing the flow. In contrast, in low permeability layers, the high shear conditions produce a lower viscosity. Thus, the relative flow rates in low and high permeability zones are more nearly equal. Foam may also be used to reduce the effect of heterogeneity and requires only the injection of air (AATDF, 1998).

3.2.3 Field Trials

There have been more than a dozen field trials using surfactants, including several sites with DNAPLs. Recent representative trials are summarized here. For a full listing of trials see the AATDF manual (AATDF, 1998) and the GWRTAC report (Jafvert, 1996).

1. Hill AFB OU2 Surfactant Flood: Conducted in 1996 by Intera, Radian, and the University of Texas. Approximately 2.5 pore volumes of a solution of 8% surfactant, 4% isopropanol and sodium chloride were pumped through a poorly sorted sandy unit contaminated with a DNAPL primarily composed of TCE. A line drive system was used without confining walls. DNAPL was originally present at approximately 4%. The fraction of DNAPL removed has been reported to exceed 99% (Brown et al., 1997) although there was some uncertainty in the estimate. Concentrations in groundwater were approximately 10 mg/L at the end of the test.

2. Hill AFB, OU1 Surfactant Mobilization Flood: Conducted in 1996 by the University of Oklahoma with the U.S. EPA's R.S. Kerr Laboratory. Approximately 6.5 pore volumes of a mixture of 4.3% surfactant in water were pumped through a 3 x 5-meter sheet-piling cell at Hill AFB, Utah using a line drive array of injection and extraction wells. The contamination was an LNAPL consisting of a complex mixture of weathered jet fuel and other components. The sediments were poorly sorted sands and gravels above a clay layer at a depth of about 8 m. An estimated 90% of the LNAPL, which was initially present at approximately 8.5% saturation, was removed. The surfactant system used a mixture of two surfactant to produce a middle phase system with ultralow interfacial tensions. The primary recovery mechanism was mobilization.

3. Hill AFB, OU1 Single-Phase Microemulsion Flood: Conducted in 1996 by the University of Florida at Hill AFB in a 3 x 5-meter sheet-piling cell of similar design to the OU1 mobilization flood described in the previous paragraph. Nine pore volumes of a mixture of 3% surfactant and 2.5% pentanol were injected, followed by one pore volume of 3% surfactant and then 6.5 pore volumes of water using a line drive array of injection and extraction wells. Removal of the contamination, an LNAPL consisting of a complex mixture of weathered jet fuel and other components, was estimated from partitioning tracers and soil core data. The core data suggested NAPL removal of over 90%, the partitioning tracer data suggested 72% removal (Jawitz et al., 1998). Removal was by single-phase microemulsion; the surfactant system used was designed to solubilize, not mobilize the LNAPL.

4. Corpus Christi Surfactant Flood: Conducted in 1991-1993 by the University of Buffalo and DuPont. A total of 12.5 pore volumes of 1% surfactant in water were injected using six injection wells around the treatment zone and two extraction wells near the center. The contamination was a DNAPL composed primarily of carbon tetrachloride. The contaminated unit was a sand

lens within a thick clay. Removal was by solubilization without mobilization. Effluent was treated by air stripping and the surfactant solution was recycled continuously. Cores taken at the conclusion of the test found no residual DNAPL in a core located directly between an injection and an extraction well. A core taken from the outer portion of the treated area revealed DNAPL remaining in the fine-grained portion of the core, but no DNAPL in the higher permeability sections. This test showed that heterogeneities limit the rate of DNAPL removal.

3.2.4 Capabilities and Limitations

The field trials have demonstrated that surfactants can rapidly remove contaminant mass from DNAPL sites. Removal of more than 90%, and perhaps as much as 99% of DNAPL was achieved in a short time in the Hill AFB OU2 test. High removals were achieved in a number of other tests. No surfactant field tests have been continued long enough to determine the ultimate level of clean up attainable.

Low permeability units, heterogeneities and insoluble contaminants may impose limitations. Heterogeneities result in some portions of the treated zone receiving more solution than others, requiring a longer treatment time and larger treatment volumes than for homogenous media. The effect of heterogeneities can be minimized by the use of mobility control (polymers or foam). Low permeability may result in very long treatment times. It may not be practical to circulate the required volume of surfactant solution through very low permeability units (clays, and clay-rich units with a hydraulic conductivity below 1×10^{-4} cm/sec). The time required for treatment can be estimated from standard hydrological characterization. It has also been shown that numerical modeling is capable of predicting the general performance of surfactant flooding (Freeze et al., 1994).

The use of surfactants reduces the interfacial tension between NAPL and water, thus reducing capillary forces and posing the potential for mobilization of the DNAPL. While mobilization can be an effective technique for rapid removal of DNAPL, it also raises the risk of downward mobilization of the DNAPL. The resulting risk must be evaluated at each site based on the integrity of confining layers (aquitards) and the presence of water supplies at greater depth that could be impacted by mobilized DNAPL. Research currently in progress is evaluating neutral-density surfactant systems that can minimize the risk of downward mobilization by creating a neutral buoyancy solution.

None of the field trials at DNAPL sites have continued long enough to establish the ultimate clean up level attainable. The persistence of some NAPL in every test conducted suggests that heterogeneities will inevitably result in some residual contamination, although the level may be minimal.

3.2.5 Further Information

An extensive manual on surfactant and cosolvent flooding has been developed by the AATDF (1998). This manual contains a review of basic surfactant chemistry, a guide to the design of surfactant systems, a review of all field trials and cost estimation data. An extensive bibliography is also included. A GWRTAC report (Jafvert, 1996) provides a more concise summary of the technology, including a summary of field trials and a bibliography.

A Citizen's Guide to *In situ* Soil Flushing: EPA 542-F-96-006 [clu-in.com]

In situ Remediation Technology Status Report: Surfactant Enhancements: EPA 542-K-94-003. Describes field demonstrations or full-scale applications of *in situ* abiotic technologies for nonaqueous phase liquids and ground-water treatment. [clu-in.com]

Jafvert, C. T. (1996). "Surfactants/Cosolvents." Technology Evaluation Report #TE-96-02, Ground-Water Remediation Technologies Analysis Center (GWRTAC), Pittsburgh, PA. [gwrtac.org].

Roote, D. S. (July, 1997). Report: *In situ* Flushing - Technology Overview, Source: Ground-Water Remediation Technologies Analysis Center, Document Number: TO-97-02. [gwrtac.org]

In situ Remediation Technology Status Report: Cosolvents: EPA 542-K-94-006, Describes field demonstrations or full-scale applications of *in situ* abiotic technologies for nonaqueous phase liquids and ground-water treatment. [clu-in.com]

AATDF. (1998). Surfactants and Cosolvents for NAPL Remediation. Technology Practices Manual for Surfactants and Cosolvents. Ann Arbor Press.

Fiorenza, S. and Annable, M. (1997) NAPL Solubilization Through Single-Phase Microemulsions and Cosolvents, Ground Water Currents, EPA 542-N-97-004.

Jawitz, J.W., Annable, M.D., Rao, P.S.C., and Rhue, R.D., 1998, Field Implementation of a Winsor Type I Surfactant/Alcohol Mixture for *in situ* Solubilization of a Complex LNAPL as a Single-Phase Microemulsion. *Environmental Science and Technology*, 32:523-530.

3.3 IN SITU OXIDATION

3.3.1 Description

In situ oxidation involves injection of an oxidizing compound into a DNAPL source zone. DNAPL is destroyed through chemical reaction with the oxidizer. Excess oxidizer is extracted by flushing water through the treatment zone.

Potassium permanganate and hydrogen peroxide are the oxidizers that have been field tested.

3.3.2. Physical and Chemical Basis

The process is based on the ability of a strong oxidizer to destroy organic compounds. Virtually all organic contaminants can be oxidized to carbon dioxide and water under sufficiently strongly oxidizing conditions. The ability of a given reagent, such as potassium permanganate or hydrogen peroxide, to oxidize a specific DNAPL can readily be demonstrated in the laboratory (e.g., Gates and Siegrist, 1995; Miller et al., 1996; Schnarr et al., 1998). Oxidation is a non-specific process, thus all compounds in the system that can be oxidized by a given reagent will react.

Solid organic matter in the soil may react with an oxidizer (Miller et al., 1996) thus increasing the volume of reagent required. Redox reactions are often also affected by the pH of the solution, requiring acid conditions for effective oxidation in some cases. This is significant for the system of hydrogen peroxide and ferrous iron (Fenton's reagent); the reaction is optimum at low pHs (2-4) and is less effective at higher pH (Miller et al., 1996). Hydrogen peroxide spontaneously decomposes to water with a half-life on the order of hours (Pardiek et al., 1992).

For application, a reagent, potassium permanganate or hydrogen peroxide (with or without ferrous iron as a catalyst), is injected into the source zone. Reaction with the DNAPL yields carbon dioxide and water, plus chloride and other byproducts. The extent of the reaction and the end products are determined by a combination of the reagents used, the DNAPL components and time. Potassium permanganate, or any other persistent reagent, would be washed from the treated zone by water flooding after oxidation is complete. Hydrogen peroxide can be allowed to decompose in place.

3.3.3 Field Trials

1. Base Borden Permanganate Tests: Two field trials were conducted by the Solvents in Ground-water Program of the University of Waterloo at Canadian Forces Base Borden in a 3m x 1m x 2.5 m-deep test cell. In the first test, the unconsolidated sand aquifer was contaminated with 1.64 kg of PCE that was mechanically mixed with soil and emplaced in the cell. The cell was flooded with a 10 g/L solution of potassium permanganate by injecting on one side of the cell and withdrawing on the other, initially at 100 L/day, later at 50 L/day. After 120 days of flooding, followed by 60 days of water flooding, it was estimated 1.49 kg of PCE had been destroyed, based on observed chloride concentrations. Analysis of cores, however, found no residual PCE.

In the second test, 6.19 kg of both PCE and TCE were introduced into the cell through a pipe in the center of the cell, inserted to a depth below the water table. A 10 g/L permanganate solution was injected at a rate of 50 L/day for 290 days. It was estimated from chloride content that 62% of the original mass of contaminant was oxidized. The primary conclusion of the tests was that distribution of the DNAPL controlled the effectiveness of oxidation (Schnarr et al., 1998).

2. Savannah River Site, Department of Energy Fenton's Reagent Test: Forty two hundred gallons of hydrogen peroxide with ferrous sulfate (to generate Fenton's chemistry) were injected to a depth of 140 ft (42.7 m) into a saturated zone contaminated with a DNAPL consisting primarily of PCE and TCE. It was estimated that 94% of the DNAPL was destroyed in a zone approximately 50 ft (15.2 m) by 50 ft (15.2 m) (Jerome, 1997).

3. Portsmouth DOE Plant Permanganate Test: Potassium permanganate was injected into a zone contaminated with TCE in a test conducted in 1997 by DOE. Existing horizontal wells were used to inject groundwater, augmented with potassium permanganate, into a sand and gravel zone in the X-701B area known to be contaminated with TCE. The solution was injected in one well, recovered in the other and recirculated (although permanganate never broke through during the test). A total of 206,000 gallons of solution were injected in a volume approximately 220 x 90 x 5 ft (67 x 27.4 x 1.5 m). The volume injected corresponds to approximately 0.77 pore volumes. The results, based on numerous analyses of TCE from cores taken before and after the test, indicate significant reductions in TCE in all locations where permanganate reached. Concentrations, originally as high as several hundred thousand $\mu\text{g/L}$, were reduced to nondetect in numerous monitoring wells immediately after the test, and rebounded to low levels (tens to hundreds of $\mu\text{g/L}$) after two weeks. Reduction in concentration was not uniform. Apparently heterogeneities in the flow field produced uneven flow of the oxidizing solution and hence uneven TCE reduction. Permanganate did not break through to the extraction wells during the test, thus recycling of permanganate solution was not attempted (Jerome et al., 1997)

3.3.4 Capabilities and Limitations

The initial results from Base Borden suggest that potassium permanganate has considerable potential for effective destruction of PCE and TCE. Laboratory data indicate it is not effective in destruction of chlorinated compounds without double bonds (Pankow and Cherry, 1996). Strong oxidizers will react with any oxidizable compound, thus organic rich soils may increase the amount of reagent required and may even react violently with strong oxidizers. The use of hydrogen peroxide, as part of Fenton's reagent (hydrogen peroxide and iron (II) ions), requires acidic conditions. Calcium carbonate or other acid-soluble compounds

may make maintenance of appropriate pH difficult. Precipitation may result from reaction induced by oxidation and/or pH changes, potentially causing plugging of the aquifer. In addition, hydrogen peroxide has a limited life time, thus it can treat only a volume that can be reached within a few hours. The range of conditions under which the technology will be effective has not been determined nor has the ultimate level of clean up.

The technology requires delivery of the reagent to the entire DNAPL source zone; low permeability zones and heterogeneities may limit performance as they do for flushing technologies. Specifically, since the distance a reagent penetrates from an injection well is a function of the hydraulic conductivity, in source zones with a range of conductivities, a large volume of reagent might have to be injected before it reaches the lower permeability areas within the zone. If the low permeability zones contain organic matter, solid or liquid, that reacts with the reagent, then additional amounts of reagent will be required. Destruction of large volumes of DNAPL may be limited by the volume of reagent delivered to the DNAPL pool and by mass transfer limitations.

3.3.5 Further Information

Jerome, K. (1997). "In situ Oxidation Destruction of DNAPL" In: EPA Ground Water Currents, Developments in innovative ground-water treatment, EPA 542-N-97-004.

Jerome, K. M., Riha, B., and Looney, B.B., 1997, Final Report for Demonstration of In Situ Oxidation of DNAPL using the Geo-Clense® Technology. Westinghouse Savannah River Company, WSRC-TR-97-0028.

Schnarr, M. J., Truax, C. T., Farquhar, G. J., Hood, E. D., Gonullu, T., and Stickney, B. (1998). "Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media". *Journal of Contaminant Hydrology*, 29:205-224.

Pankow, J. F., and Cherry, J. A. (1996). *Dense Chlorinated Solvents and other DNAPLs in Ground-water*, Waterloo Press., Portland.

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4.0 VOLATILIZATION TECHNOLOGIES

4.1 SOIL VAPOR EXTRACTION AND DERIVATIVES

4.1.1 Description

Soil vapor extraction (SVE) involves pumping of air from the subsurface by using vacuum pumps to withdraw air from wells. Air may, or may not, be injected in other wells. Either horizontal or vertical wells may be used. The process is applied in the vadose zone; the water table may be lowered by pumping to increase the depth of applicability. The combined pumping of groundwater and air is termed Multi-Phase Extraction (MPE). Air sparging is a related process in which the air is injected below the water table. A variant of air sparging involves circulation of air within a well. Air sparging may be combined with SVE to treat both saturated and unsaturated zones. SVE may be enhanced by heating the soil to increase the volatility of the contaminants. Aerobic biodegradation may be stimulated by the circulation of oxygen and by elevated temperatures, thus biodegradation may occur during SVE or air sparging. Injection of air or oxygen to stimulate such biodegradation may be employed. Each of these variations is discussed below. Off-gas from a SVE system typically must be treated to remove/destroy the volatilized contaminants.

4.1.2 Physical and Chemical Basis

SVE is based on the volatilization of contaminants either directly from a DNAPL or from water when dealing with the dissolved phase. The quantity of contaminant that will volatilize under equilibrium conditions may be calculated from vapor pressure (for equilibrium between a pure organic liquid and air), or from the Henry's Law Constant (for equilibrium between a contaminant dissolved in water and air). The mass transfer to a vapor phase may be kinetically limited, thus actual mass removal may be somewhat slower than calculated from equilibrium models (see Staudinger et al., 1997 for a review of the more than 30 models for SVE).

Performance of SVE systems is a function of both the volatility of the contaminants and of vapor flow. The volume of air that can be drawn through a given zone is a function of the soil permeability, water saturation and heterogeneity of the site. In low permeability soils it may be difficult to achieve adequate vapor flow rates. Similarly, in soils with a high water content, permeability to air is low and SVE is less effective. Heterogeneities can cause problems both from the lower flow rates achieved through low permeability zones and diversion of flow by impermeable layers. Horizontal wells, or trenches may

provide better flow in some cases than vertical wells. Numerical models coupled with careful site characterization may be used to evaluate the effects of site heterogeneities and determine optimum well spacing or injection/extraction configuration. Pilot-scale field tests are generally required to provide the information on air flow necessary to design an SVE system (Johnson et al., 1993), particularly in heterogeneous systems (Widdowson et al., 1997).

4.1.3 SVE with Thermal Enhancement

The addition of heat can increase the effectiveness of SVE by two mechanisms; increasing the vapor pressure of contaminants and increased vapor transport by vaporizing (boiling) the soil-water. The vapor pressure of all compounds increases with increasing temperature, thus the transfer of contaminants to the vapor phase is increased with increasing temperature. SVE may be extended to semi-volatile compounds through the use of heat. The benefits of increased vapor pressure can be achieved by any means of heating the soil including joule (resistance) heating, radio frequency heating or steam heating.

A second benefit of thermal enhancement is derived from the mass transport provided by vaporizing the water in the soil. Air flow through low permeability soils (silts and clays) may normally be too low for effective remediation by SVE. If the low permeability units are heated until the soil water vaporizes, the resultant flow of hot vapors out of the fine-grained units may increase contaminant mobility. Finally, if the temperature is raised sufficiently to volatilize the DNAPL, the vapors of the contaminants themselves may be driven out of the soil. The various types of thermal enhancement are discussed in the thermal enhancement section; each may be coupled to SVE.

4.1.4 SVE with Biodegradation

Oxygen is one of the prime electron acceptors for biodegradation; thus, SVE, or any process that increases the oxygen flow through contaminated soil, has the potential for increasing the rate or extent of aerobic biodegradation. It has been found that biodegradation is often a significant factor in remediation by SVE of petroleum hydrocarbon (BTEX) sites. A number of variations of SVE have been developed to enhance such biodegradation. Bioventing is a widely used technology in which air flow is primarily provided to stimulate biodegradation, not to remove contaminants as a volatile phase. The volumes of air and flow rate required are much less than with SVE. The benefits of this approach are that the off-gas does not have to be collected and treated.

Highly halogenated DNAPL components are generally not readily degraded under aerobic conditions (Pankow and Cherry, 1996); thus, it would not be expected that significant biodegradation would accompany the unaugmented

SVE of halogenated DNAPLs. In addition, the DNAPL components are generally not bioavailable while in the NAPL; they typically must be in the dissolved state before they can be degraded by microorganisms. Combined injection of oxygen and an organic compound that serves as an electron donor (including methane, phenol and toluene) has shown potential for chlorinated compound degradation. The forms of biodegradation that may be effective at DNAPL remediation are discussed in the biodegradation section.

4.1.5 Field Trials

SVE has been widely implemented, and numerous remediation case studies have now been documented. A report summarizing 37 case studies is available from NTIS (NTIS, PB95). A list of over 100 sites where SVE has been applied is provided in a recent EPA document (EPA Engineering Forum Issue Paper, 1996). A few illustrative examples where halogenated compounds were present are cited here:

1. Canadian Forces Base Borden SVE Test: Conducted by the University of Waterloo, this test took place in a 9m x 9m sheet-piling cell at Canadian Forces Base Borden, Ontario. Approximately 600 kg of PCE was present in the surficial sand aquifer in the cell. Approximately 230 kg of PCE was removed in the first 25 days of SVE operation, and after 450 days, approximately 63% of the mass was removed. Changing well configuration, pulsed pumping and use of short-screened drive points to localize flow did not increase mass removal performance. Eight soil cores removed after 250 days revealed high levels of PCE remained in areas of high soil moisture. The conclusions of this test were that heterogeneities in the system limited DNAPL removal effectiveness (Neil Thompson and David Flynn, written communication).

2. Verona Well Field Superfund Site, Battle Creek Michigan: Conducted from 1988-1992, soil consisting mostly of fine to medium sand with low water content (5%) was treated by installing 23 extraction wells. Contaminants included chlorinated compounds, primarily PCE and 1-1-1 TCA, as well as an LNAPL. Off-gas was treated by catalytic oxidation when concentrations were high and carbon adsorption at low concentrations. Over 45,000 pounds of VOCs were removed. Clean up standards were met for all compounds in all samples except PCE, which had a few high values. The average concentration of PCE was within clean up standards.

3. SMS Instruments Superfund Site, Deer Park, NY: Conducted from May 1992-October 1993. The site consisted of well sorted sands to a depth of 16 feet (4.9 m), and then silty sands and fine gravels to a depth of 26 feet (7.9 m). Contamination included both volatile and semivolatile compounds; various chlorinated benzene derivatives were the primary contaminants. No NAPL was observed. Contamination initially was over 1000 µg/Kg. Extraction used two horizontal wells in 75-foot (22.9-m) long trenches. Off-gas was treated by

catalytic oxidation. All clean up standards were met for all 9 volatile and all 9 semi-volatile compounds.

4. Savannah River Site Horizontal Well Demonstration Site: Conducted at the M Area, Savannah River Site, Aiken, SC. in 1990. Sediments in the vadose zone are heterogeneous composed sand and gravel with discontinuous clay layers. A more continuous clay layer was encountered at a depth of about 160 feet (48.8 m). The water table was at a depth of 120 feet (36.6 m). Contamination was mostly PCE with other chlorinated solvents present; DNAPL had been found at the site. Air was injected in a horizontal well below the water table and extracted through a second horizontal well in the vadose zone. The injection well was screened over a 310-foot (94.5-m) length and reached a maximum depth of 176 feet (53.6 m). The extraction well was emplaced at a maximum depth of 75 feet (22.9 m) and was screened over a 205-foot (62.5-m) section. Approximately 16,000 lbs. (7258 kg) of VOCs were removed in 139 days. Final concentrations of TCE in groundwater showed considerable scatter, with both large decreases and some apparent increases being found; PCE showed similar results. VOC extraction was continuing at a high rate when the test was stopped. Thus, the test achieved significant mass removal but did not determine the clean up levels attainable.

4.1.6 Capabilities and Limitations

SVE has been demonstrated to be effective at rapid and relatively inexpensive removal of mass from volatile contaminants in the vadose zone. SVE is considered applicable for those compounds with vapor pressures above 0.5 mm and dimensionless Henry's Law Constants above 0.01 (EPA SVE Engineering Forum Issue Paper, 1996). Performance decreases when soil permeability is low or soil moisture is high. Heterogeneities may result in slower clean up. Care must be taken in heterogeneous soils to ensure that the entire source zone will be adequately swept. The use of heating, by electrical, electromagnetic or steam, may increase vapor pressures and extend the technology to compounds with lower volatilities (Davis, 1997). If the heating is sufficient, chlorinated solvent DNAPLs could be volatilized totally and extracted by SVE.

SVE is applied in the vadose zone. The water table may be lowered locally by pumping to increase the depth to which SVE can be applied. Lowering the water table may induce a risk of DNAPL mobilization. If the entry pressure required for a DNAPL to enter a water-saturated layer is exceeded by the capillary pressure, the DNAPL will invade the layer. The capillary pressure is equal to the difference between the water pressure at a given point and the pressure on the DNAPL. This difference is generally equal to the height of a DNAPL pool times the difference in density between DNAPL and water; if the water pressure is lowered by pumping, the resulting increase in capillary pressure may allow a DNAPL to migrate (Pankow and Cherry, 1996). Both the distribution of the DNAPL and the

site hydrogeology must be considered before lowering the water table.

Heterogeneities, which restrict air flow through fine grain regions and may channelize flow may govern the ultimate clean up levels and treatment time (Webb and Phenlan, 1997).

4.1.7 Further Information

A Citizen's Guide to Soil Vapor Extraction and Air Sparging: EPA 542-F-96-008 [clu-in.com]

Remediation Case Studies: Soil Vapor Extraction. PB95-182937. Documents project design, operation, performance, cost, and lessons learned. The reports should be useful to those evaluating the feasibility or design of these technologies at similar sites. [clu-in.com]

Innovative Site Remediation Technology, Vacuum Vapor Extraction (1995). EPA, OSWER Technology Innovation Office, EPA/542-B-94-002, 222p. A monograph providing expert guidance on application of SVE.

Soil Vapor Extraction Treatment Technology Resource Guide, September 1994, EPA542-B-94-007. A bibliography of publications and other sources of information about SVE, air sparging and other innovative treatment technologies.

Davis, E. L. (1997). "How Heat Can Enhance In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique." *EPA Ground Water Issue*, EPA/540/S-97/502, 18.

Staudinger, J., Roberts, P. V. and Hartley, J. D. (1997). "A Simplified Approach for Preliminary Design and Process Performance Modeling of Soil Vapor Extraction Systems." *Environmental Progress*, 16(3), 215-227.

EPA (April 1996). "Engineering Forum Issue Paper: Soil Vapor Extraction Implementation Experiences." *EPA 540/F-95/030*, US EPA Office of Solid Waste and Emergency Response.

EPA (1997) Presumptive Remedy: Supplemental Bulletin Multi-Phase Extraction (MPE) Technology for VOCs in Soil and Ground-water." EPA 540-F-97-004.

4.2 AIR SPARGING

4.2.1 Description

Air is injected below the water table using vertical or horizontal wells. The air flows upwards through the contaminated groundwater, extracting the contaminants as they volatilize into the flowing air. The air may be captured with

a SVE system in the overlying unsaturated zone for treatment. Wells must be placed close enough so that their radius of influence, the radius in which they induce air flow, overlap. The size of the radius of influence depends upon the media permeability and the thickness of the saturated zone (Lundegard and LaBrecque, 1995; McCray and Falta, 1996). Low permeability units may not allow adequate air flow. Very permeable units may have very small radii of influences. Heterogeneities may cause channeling of air flow (Johnson et al., 1993). Mounding of the water table may occur around the injection wells, potentially causing flow of contaminated groundwater either horizontally away from the wells or vertically downward below the treatment zone. The addition of oxygen may stimulate aerobic biodegradation (biosparging).

4.2.2 Physical and Chemical Basis

The physical process for mass transport in air sparging is volatilization of the contaminant from a dissolved phase in the groundwater to the air sparged through the zone. If DNAPL is directly contacted by the sparged air, the transfer may be direct volatilization from the DNAPL to the air. As with SVE, the process is governed by the Henry's Law Constant of a compound for the dissolved phase and vapor pressure for direct sparging of DNAPL. Only volatile compounds will be readily sparged. The mechanism of air transport through saturated porous media is not completely understood. In highly permeable media, actual bubbles of air may flow through the unit, while in finer grained material, air transport as bubbles is less likely (e.g., Lundegard and LaBrecque, 1995).

4.2.3 Field Trials

1. Burlington, NJ: A large-scale combined SVE and air sparging system is being used to remediate a site contaminated with TCE, TCA and other chlorinated VOCs; DNAPL was present in one portion of the site. Depth to the water table ranges from 1 to 9 feet (0.3-2.74 m), the principal zone of contamination for the air sparging system is at 10 feet (3.05 m). The aquifer is sand and gravelly sand, underlain by a clay layer that limits vertical flow. 134 air sparge wells and 58 SVE wells on a 2.7-acre (1.09-ha) site were started in June 1995 and had operated 450 days at the time of the report (Gordon, 1998). Mounding of approximately 3 feet (0.9 m) was observed at the injection wells, but monitor wells outside the contaminated zone remained clean, indicating contamination was not spread horizontally. Wells downgradient from the source zone dropped rapidly to non-detect in most cases; concentrations were lower by a factor of 30 to 500. Concentrations within the source zone showed no regular trend with time. Apparently source zone remediation is still continuing. Approximately 0.1 to 0.5 lbs/hr (0.05-0.23 kg/hr) of VOCs have been removed by the system. A six-year operating cycle is projected.

2. Service Station Pilot Study: A service station site, contaminated by petroleum hydrocarbons to a depth of approximately 10 meters was used for an evaluation of air sparging (Johnson et al., 1995; 1997). The site was composed of sands, with discontinuous silty layers. A three-well air sparge test was conducted for 110 days to evaluate the performance of air sparging. Extensive monitoring was done to evaluate the system. A flow rate of 0.3 cubic meters per minute was maintained in each well. BTEX concentrations dropped, and dissolved oxygen rose in monitoring wells soon after injection began and stayed constant. After the test was completed, BTEX concentrations rebounded to the original levels in one month. The conclusions from this test were that the heterogeneities at the site controlled air flow, limiting air sparging performance.

4.2.4 Capabilities and Limitations

Air sparging has been shown to be effective at reducing dissolved phase contaminant concentrations within the radius of influence of sparging wells. A recent test at the Canadian Forces Base Borden test site, for which results have not yet been published, suggests under optimum conditions air sparging may be effective at DNAPL removal. Data are too sparse to define the conditions under which complete removal may be expected. Performance will be affected by permeability. Low permeable units may not allow adequate air flow, while vapor flow may become highly localized in high permeability units resulting in a very small radius of influence for each well. The process is more efficient in thick saturated zones; the radius of influence of a well may be small if the saturated thickness is small. Finally, sparging is limited to those compounds with adequate Henry's Law Constants.

If DNAPL is directly contacted by sparged air, direct remediation of the nonaqueous phase will occur (volatilization from the DNAPL into the vapor phase). However, if not all DNAPL is directly contacted by the sparged air, the portion of the DNAPL not contacted will be removed only indirectly by the dissolution of DNAPL into the groundwater as the dissolved phase contamination is removed by sparging. In this case remediation will be slow. Since DNAPL tends to be concentrated above lower permeable units, and sparging of such zones is difficult, pools and lenses on low permeability layers may be expected to be resistant to rapid treatment by air sparging (Unger et al., 1995). Careful site characterization is essential in evaluating the likely cleanup scenario.

4.2.5 Further Information

A Citizen's Guide to Soil Vapor Extraction and Air Sparging: EPA 542-F-96-008 [clu-in.com]

Miller, R. (October, 1996). Report: Air Sparging - Technology Overview Source:

Ground-Water Remediation Technologies Analysis Center, Document Number: TO-96-04. [GWRTAC.org]

Technology Assessment of Soil Vapor Extraction and Air Sparging, (September 1992) EPA 600-R-92-173.

Hinchee, R.H., Miller, R.N., and Johnson, P.C (1995). In Situ Aeration, Air Sparging, Bioventing and Related Processes. Batelle Press, Columbus OH.

Johnson, P.C., Johnson, R.L., Neaville, C., Hansen, E.E., Stearns, S.M. and Dortch, I.J. (1995). Do Conventional Monitoring Practices Indicate In-Situ Air Sparging Performance. In: Hinchee et al, 1995, In Situ Aeration, Air Sparging, Bioventing and Related Processes. Batelle Press, Columbus OH. P. 1-20.

Johnson P.C., Johnson, R.L., Neaville, C., Hansen, E.E., Stearns, S.M. and Dortch, I.J., 1997, An Assessment of Conventional In Situ Air Sparging Pilot Tests. *Ground Water* 35, 765-774.

Unger A. Sudicky E. and Forsyth P. (1995). Mechanisms Controlling Vacuum Extraction Coupled With Air Sparging For Remediation Of Heterogeneous Formations Contaminated By Dense Nonaqueous Phase Liquids. *Water Resources Research*. 31(8):1913-1925.

4.3 IN-WELL STRIPPING

4.3.1 Description

In-well stripping involves pumping of water from the contaminated zone into a well, sparging the water within the well by pumping air from the surface, removing the contaminants by volatilization within the well casing, then finally pumping the water back out of the well through separate screens higher in the well. There are several commercial variants on the basic design.

4.3.2 Physical and Chemical Basis

The technology is basically air sparging within a well. The contaminants are removed by volatilization into the sparged air. As with air sparging, the process is limited to volatile contaminants. Application to DNAPLs is indirect as contaminants are introduced to the well as dissolved phase, thus DNAPL will be removed only by dissolving slowly into the clean groundwater returned from the treatment well. Advantages of the technique over air sparging include easier control of the off-gas and possible elimination of the necessity of air discharge permits.

4.3.3 Field Trials

The technology has proved effective at a number of sites with chlorinated solvents in a dissolved phase plume. One example:

1. **March AFB, CA:** An EPA SITE Demonstration of the UVB vacuum vaporizing well system was demonstrated at March AFB from 1993-1994. A permeable alluvial aquifer contaminated with TCE with minor other VOCs was treated from 43 to 75 feet (13.1-22.9 m). TCE averaged 56 µg/L before treatment and 3 µg/L after treatment. Concentrations were below 5 µg/L in 9 of the 10 monitoring periods. Dye tracer studies indicated a radius of influence of 40 feet (12.2 m). Treatment effectiveness and circulation pattern were governed by anisotropies and heterogeneities at the site. The upper and central portion of the treatment zone was effectively treated. Limited data on the lower zone suggested treatment was not as complete (EPA 540 R 9550A).

4.3.4 Capabilities and Limitations

In-well stripping, like all volatilization technologies that do not use heating, is limited to those contaminants with adequate vapor pressure. Most chlorinated solvents are sufficiently volatile, however, PCBs and most PAHs are insufficiently volatile to be treated by this approach. Even for volatile compounds, only the dissolved phase contaminants are addressed. Thus, a DNAPL source zone would be treated only by sparging the dissolved phase plume, resulting in slow dissolution of the DNAPL into the clean water. Such a process is likely to be time-consuming and require circulation of very large volumes of water. The technology has shown significant potential for treating dissolved phase contamination. Careful hydrogeologic characterization is required to ensure the induced circulation cells include all contamination and provide the required recirculation pattern. It is essential to verify that the circulation pattern established for the wells reaches the entire volume that it is designed to treat and that the flow path provides adequate capture of expelled liquids. Heterogeneities may limit both the volume treated for each well and the extent of recirculation achieved.

4.3.5 Further Information

Miller, R. (1996). Report: In-well Vapor Stripping - Technology Overview
Source: Ground-Water Remediation Technologies Analysis Center, Document
Number: TO-97-01. [gwrtac.org]

SITE Technology Capsule: UVB Vacuum Vaporizing Well, EPA 540 R95 550A
[EPA.gov/cincl/]

5.0 THERMAL PROCESSES

5.1 STEAM INJECTION

5.1.1 Description

Steam injection involves injection of steam into a contaminated unit. The steam volatilizes and mobilizes contaminants present, including DNAPLs. Condensed steam plus contaminant is recovered at extraction wells. Steam is injected in injection wells at the boiling point of water under the depth being treated, optimally bringing the entire treated volume to the boiling point of water (at the local pressure). The technology has been widely applied in enhanced oil recovery with considerable success (Lake, 1989). The recovered fluids, hot water plus contaminants, must be treated on the surface. Steam generators and steam handling equipment are readily available commercially. A variant of steam injection uses hot water with the objective to mobilize the contaminant through reduction of viscosity and in a commercial application termed Contained Recovery of Oily Wastes (CROW®), to reduce downward migration through reduction of DNAPL density.

5.1.2 Physical and Chemical Basis

Steam injection promotes contaminant recovery through several mechanisms. Those components that have boiling points lower than that of the steam will be volatilized. Components that have higher boiling points than the steam will have their vapor pressures greatly increased by the increased temperature, which also promotes volatilization. Finally, the increased temperatures will lower the viscosity of DNAPLs, promoting displacement of the fluids (Hunt et al., 1988).

The actual process of DNAPL recovery is complex. Volatile components will enter the vapor phase and migrate away from the injection wells toward the cooler regions (Hunt et al., 1988). Condensation will occur at the thermal front, creating a bank of contaminant in front of the advancing steam. DNAPL mobilization may also occur as a result of the lowered interfacial tensions and lowered velocities accompanying increase in temperature. The relative contribution of volatilization, condensation and displacement will be dependent upon the specific contaminants, site conditions and operating parameters (Udell, 1996)

A variant of the process combines steam injection with direct electrical heating of fine-grained units. Since steam requires a sufficient fluid flow to supply enough energy to heat the entire unit, it is less effective in fine-grained units. Electrical heating may be applied to the fine-grained units to drive the contaminants to the

steamed zones. The use of electrical heating and combined steam and electrical heating, demonstrated in the dynamic underground stripping demonstration, are described in the next section.

5.1.3 Field Trials

1. Dynamic Underground Stripping Demonstration, Lawrence Livermore National Laboratory: Conducted at Lawrence Livermore National Laboratory by LLNL and the University of California, Berkeley in 1992-1993. The site consisted of a sequence of sands and gravels interbedded with silty and clayey units. Contamination was primarily gasoline as LNAPL. It was estimated there were 6500 gallons (24,602 liters) of gasoline in the treatment zone prior to the start of the test. The test was conducted at and above the water table at the site. The water table was about 100-120 feet; (30.5-36.6 m) steam was injected in two zones one at 80-100 feet (24.4-30.5 m) and one at 110-120 feet (33.5-36.6 m) depth through 6 injection wells arranged in a circle on the outside of the treatment zone. Air was recovered through a central extraction well. Four electrodes were emplaced in the treatment zone and electrical resistive heating was used to heat the fine-grained layers. The treatment zone was heated to boiling, (200 °F (93.2 °C) at applied vacuum). More gasoline was recovered (7000 gallons; 26,495 liters) than was thought to be present (6500 gallons; 24,602 liters). Subsequently the site was found to have met clean up standards and has been closed (DOE, 1995).

2. Visalia Pole Yard: A site contaminated with large volumes of creosote DNAPL is undergoing remediation with steam. An area of 4.3 acres (1.74 ha) has been treated to a depth of 100 feet (30.5 m), including a volume of 0.5 million cubic yards (0.38 million cubic meters). In the first six weeks of operation 200,000 lbs. (90,720 kg) of NAPL was recovered, 29,000 lbs. (13,154 kg) were extracted in the vapor phase and burned, 17,500 lbs. (7,938 kg) was captured on activated carbon and an estimated 45,500 lbs. (20,639 kg) was destroyed by *in situ* decomposition. At this time, the outer portions of the site are clean and operations are continuing in the central portion of the site (Aines, 1998)

3. Manufactured Gas Plant, Stroudsburg, PA: A coal-tar DNAPL site at Stroudsburg, PA was treated in 1994-1995 using the commercial hot-water injection process CROW (contained recovery of oily wastes). After pumping recovered over 30,000 liters of free phase coal tar in 1982-1983, one area of the site, the RCC area, which was believed to contain an additional 22,700 liters of coal tar was treated by hot water flushing. The hot water reduced the viscosity of the coal tar and lowered its density. Overlying groundwater acted as a cold-cap reducing volatilization. Water was injected in six wells outside the treatment zone and extracted from two within it. Extracted water and product were treated; treatment included pH control, oxidation and filtering. The treatment allowed separation of coal tar and water and reinjection of the water. A total of 29 pore

volumes of water was injected and a total of 5400 liters of coal tar recovered. The process thus served to enhance DNAPL-extraction, but did not approach complete restoration. The test is described in more detail in Leuschner et al., 1997.

5.1.4 Capabilities and Limitations

Steam has demonstrated the ability to effectively remove petroleum hydrocarbons; large amounts of mass have been removed relatively quickly. Fine-grained zones may require electrical heating. Limited information on DNAPL treatment is available, but the technology should be directly applicable to DNAPLs in permeable media. A risk inherent in steam flooding of DNAPL sites is that the condensed solvent front at the leading edge of the steam bank may be more mobile than the original DNAPL. Low permeability and heterogeneities will reduce the effectiveness of the process.

5.1.5 Further Information

Aines, R. (1998) Dynamic Stripping/Hydrous Pyrolysis Oxidation *in*: Proceedings, Advances in Innovative Groundwater Remediation Technologies, GWRTAC and EPA, San Francisco.

Davis, E. L. (1997) How Heat Can Enhance In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique. EPA Ground Water Issue Paper EPA/540/S-97/502.

Davis, E.L. (1998) Steam Injection for Soil and Aquifer Remediation. EPA Ground Water Issue. EPA/540/S-97/505.

U.S. DOE Office of Technology Development, Innovative Technology Summary Report (1995). Dynamic Underground Stripping, demonstrated at Lawrence Livermore National Laboratory Gasoline Spill Site: GSA, Livermore, CA. [DOE.gov]

In situ Remediation Technology Status Report: Thermal Enhancements, (1995) EPA 542-K-94-009.

Leuschner A.P., Moeller, M.W., Gerrishe, J.A. and Johnson L.A. (1997) MGP Site Remediation Using Enhanced DNAPL Recovery, Soil and Groundwater Cleanup, October, 1997, p 6-13. Additional Information on CROW can be found at: <http://wri.uwyo.edu/Projects/Crow>.

5.2 ELECTRICAL HEATING

5.2.1 Description

Soil may be heated by a variety of processes based on electrical heating. Resistance (joule) heating, microwave heating and radio-frequency heating have all been applied in remediation. In each case, electrical energy is applied to heat the soil. Heat increases the volatility of contaminants and may induce groundwater to boil, forming steam. The contaminants are driven out of the source zone by a combination of volatilization and thermally induced vapor phase transport. Electrical heating is usually coupled with SVE or steam injection to recover the volatilized contaminants. DNAPL will be volatilized if the soil is heated to near the DNAPL boiling point; DNAPL may be mobilized through a reduction of viscosity as it is heated.

5.2.2 Electrical Resistance Heating (Joule Heating)

Electrical resistance heating involves inserting electrodes in the ground and passing an alternating current through the water and soil between the electrodes heating the soil. The degree of heating depends upon the current and the resistance of the unit. Soils and rocks are generally non-conductive, thus most current flows through soil moisture or groundwater. Current decreases as the soil dries, decreasing conductivity. The technique is thus well suited to fine-grained units, which typically have a high soil moisture content.

5.2.3 Six-Phase Soil Heating

Six-phase soil heating is a variant of electrical resistance heating, differing in how the AC current is applied. The reported advantages of six-phase heating are the more even distribution of heat due to splitting of the electrical energy into six phases and the ability to use conventional 3-phase AC current as the power source (DOE, 1995).

5.2.4 Radio-Frequency Heating

Radio-frequency heating utilizes an electrical field created by inserting antennas into the treatment zone and exciting the soil at approved frequencies (6.68 – 40.68 Megahertz). The technology has proven capable of heating low permeability soils to over 150 °C. (Edelstein et al., 1994; EPA, *In Situ*

5.2.5 Field Trials

1. Six Phase Soil Heating Demonstration, M Area, Savannah River Site, NC: Conducted in 1993 by U.S. DOE. The target area was a 10-foot (3.04-m) thick clay layer at a depth of 40 feet (12.2 m). Contamination was primarily PCE and TCE, found at maximum concentrations of 181 and 4529 µg/kg, respectively (dissolved phase, not DNAPL). Six electrodes were placed in a circle with a diameter of 30 feet (9.14 m). An extraction well for SVE was placed in the center of the array. Temperatures were raised to 100 °C in the target zone and maintained at 100 °C for 17 days. Over 99% of the contamination was removed (DOE, 1995)

2. Radio-Frequency Heating- Rocky Mountain Arsenal Basin F: Conducted by IIT Research Institute, 1992. Fifty cubic yards (38.2 cubic meters) of clayey soils were heated to over 250 °C with radio frequency heating. Organochlorine pesticide concentrations were reduced by 97-99% from initial concentrations up to 5,000 mg/kg (EPA, *In Situ* Remediation Technology Status Report, Thermal Enhancements, 1995).

3. Radio-Frequency Heating, Schenectady, NY: Conducted by General Electric, this test targeted a volume of 2 m x 3 m x 2 m deep. After a 25-day heating run, the upper and middle portions of the soil reached 140 °C at 2 m depth, the temperature exceeded 100 °C (Edelstein et al., 1994).

4. Radio-Frequency Heating/SVE, Kirtland AFB: In this field test, a 10-foot (3.04-m) cube of soil contaminated with petroleum hydrocarbons was heated for 42 days. Initial treatment by SVE alone found that gasoline-range organics (< C₁₂) could be removed, but the less volatile heavier fraction could not; the target for the RF heating test was the heavier diesel range organics (C₁₂-C₂₀). The maximum temperature attained was 139 °C. Approximately 56% removal of the diesel range organics was accomplished in the heated volume. Initial concentrations of 2000-4000 mg/Kg were reduced to 400-1200 mg/Kg. Biodegradation was apparently also stimulated by the heating (AATDF, in press).

5.2.6 Capabilities and Limitations

Each of the heating technologies has proven capable of heating fine-grained soils to boiling or near-boiling temperatures. If adequate temperature can be achieved, volatile and semi-volatile compounds will volatilize and water will be driven off as steam. Most chlorinated solvent DNAPLs are sufficiently volatile that heating groundwater to boiling temperatures should be effective at transferring the DNAPL to the vapor phase. Since the heating technologies do

not recover the contaminants themselves, they must be coupled to another technology for contaminant recovery, typically SVE. Thermal techniques are used when either the permeability to air of the units is too low to allow adequate air flow for conventional SVE or the vapor pressure of a contaminant is too low. Limitations to the combined technology may arise from the difficulty of getting full recovery of mobilized vapor. Aquifer heterogeneities may create difficulties in this regard. Compounds with lower volatility will not be effectively treated. The ultimate level of clean up will depend both upon the heterogeneities, which will limit recovery of vaporized contaminants, and on the type of contamination present. Heterogeneities will also result in non-uniform heating which result in incomplete remediation. Due to the large heat of vaporization of water, the energy cost of boiling off the water may be high.

5.2.7 Further Information

U.S. DOE Office of Technology Development, Innovative Technology Summary Report (April, 1995). Six Phase Soil Heating, demonstrated at the M Area Savannah River Site (Aiken SC) and 300-Area Hanford Site (Richland WA). [DOE.org]

A Citizen's Guide to Thermal Desorption: EPA 542-F-96-005 [clu-in.com]

In Situ Remediation Technology Status Report: Thermal Enhancements: EPA 542-K-94-009, Describes field demonstrations or full-scale applications of *in situ* abiotic technologies for nonaqueous phase liquids and ground-water treatment. [clu-in.com]

Davis, E. L. (1997) How Heat Can Enhance In-situ Soil and Aquifer Remediation: Important Chemical Properties and Guidance on Choosing the Appropriate Technique. EPA Ground Water Issue Paper EPA/540/S-97/502. Includes an extended discussion of mechanisms of thermal enhancement.

5.3 *IN SITU* VITRIFICATION

5.3.1 Description

In situ vitrification involves application of electrical heating to soil to bring it to a temperature sufficient to melt the soil. Upon cooling, the soil forms a glass. Originally developed as a method for stabilizing soils containing metals by turning the permeable soil into impermeable glass (Dragun, 1991), the heating process becomes a thermal extraction/destruction process if DNAPLs are present.

5.3.2 Physical and Chemical Basis

The fundamental principle of vitrification is that if soil is brought to a sufficiently high temperature, it will melt and form a glass when cooled. Required temperatures are in excess of 1100 °C (melt temperatures may exceed 1700 °C, Dragun, 1991). As the thermal front advances, the soil is gradually heated; as the temperature reaches the boiling point of water, soil moisture is volatilized and a dry zone of high permeability at the margins of the melt is produced (Dragun, 1991). As most DNAPL components have boiling points above that of water, but far below the temperature required for melting, they would be volatilized in the dry zone. Vapor phase permeability in the dry zone is higher than in the bulk soil due to the reduced water content, thus the zone provides a preferential pathway for organic vapor migration. If organic components are retained within the melt zone, they may decompose by pyrolysis (thermal decomposition in an anoxic environment).

The process involves inserting electrodes into the contaminated area at sufficiently close spacing to produce uniform heating. Electrical current is passed through the contaminated soil and resistive heating of the soil results. The current is continued until the entire zone to be treated is brought to a molten state; it is then allowed to cool. The process is designed for either saturated or unsaturated conditions to a maximum depth of about 30 feet (9.144 m).

Two configurations have been proposed, melting from the top-down, as practiced by the Geosafe process (EPA, 1995), and a melt from-the-bottom-up process now being developed by DOE. In the bottom-up configuration, the electrodes are inserted to the maximum depth of contamination and then vitrification takes place in a series of steps from deep to shallow as the electrodes are withdrawn. This configuration is claimed to allow deeper melting than practical with the top-down process (DOE, 1996)

5.3.3 Field Trials

1. Geosafe *In situ* Vitrification SITE Demonstration, Grand Ledge, MI: In this test, conducted in 1994-1995, the top-down vitrification process marketed by Geosafe was demonstrated on soils contaminated with mercury and pesticides. The test demonstrated the ability of the process to vitrify soils and provided data on treatment times and costs. No DNAPL was present, so the test provides limited information on remediation of DNAPL sources. The test is fully described in more detail in EPA (1995).

2. Oak Ridge *In Situ* Vitrification Test, Oak Ridge National Laboratory: The test took place at Pit 1 at Oak Ridge, which had once been used for disposal of liquid radioactive waste. The pit had been filled with clean soil and capped, however, an estimated 38 curies of radioactive material (primarily Cs-137) remained. The melting phase of this test began in April, 1996 and continued for 18 days. It was terminated after a release of steam and molten glass occurred causing release of radioactive glass and starting several fires on combustible material around the hood (DOE, 1996). The cause of the steam release is under study; it is believed to be due to the melt front encountering groundwater.

3. Wasatch Chemical Superfund Site: 5500 metric tons of waste contaminated by various organic contaminants was treated using a GeoMelt *in situ* vitrification process. Material was treated in a concrete evaporation pond and waste from outside the treatment area was added to the surface of the pond before treatment. Results indicated that the organics were destroyed and off-gas emissions were below regulatory concern. The vitrified area of the site was declared closed by the EPA (Timmons and Hansen, 1998)

5.3.4 Capabilities and Limitations

The ability to vitrify soils through this process has been demonstrated. No controlled results have been reported for destruction of DNAPL, thus there is not an adequate basis for evaluation of the efficiency of the process for DNAPLs. If the designed temperatures are achieved, as seems probable from the field tests on metal-contaminated soils, extensive destruction/mobilization of most DNAPL components would be expected. The resulting by-products, the degree of capture of the vapors and the control of mobilization of the vapors and condensed DNAPL (if any) has not yet been documented. The melting process is limited to 20 feet (6.1 m) in depth for a single melt (EPA 1995) and requires soils that produce conductive melts. Other configurations have been claimed to allow deeper melts and to be applicable to any soils (DOE, 1996), but there is not sufficient data to evaluate these claims. The problems encountered with the steam release at ORNL suggest that operation at or near the water table poses additional problems.

5.3.5 Further Information

Remediation Case Studies: Thermal Desorption, Soil Washing and *In situ* Vitrification. PB95-182945. Contains case studies of full-scale site cleanups at Superfund sites and Federal facilities. Documents project design, operation, performance, cost, and lessons learned. The reports should be useful to those evaluating the feasibility or design of these technologies at similar sites. [clu-in.com]

EPA. (1995). "Geosafe Corporation *In situ* Vitrification," Innovative Technology Evaluation Report, EPA/540/R-94/520, U.S. EPA Risk Reduction Engineering Laboratory, Cincinnati, OH.

In Situ Vitrification, DOE EM Fact Sheet (1996)
www.ornl.gov/emef/facts/insitu.htm

Timmons, D. and Hansen J.E. (1998) Vitrification Process has appeal for International and U.S. Sites, *Soil and Groundwater Cleanup*, May, 1998, p. 37-40.

6.0 ELECTROKINETICS

6.1 DESCRIPTION

Electrokinetics involves applying an electric potential across the contaminated zone through use of electrodes in the ground. Water and ions migrate under the influence of the DC electrical field. The process has long been effectively used for dewatering fine-grained sediments. The process does not destroy contaminants, it mobilizes them. The contaminants must either be recovered at the electrodes or the process can be coupled with an *in situ* contaminant treatment. Combined electrokinetic migration and treatment for DNAPLs has been done through the LASAGNA[®] process which uses a treatment zone between the electrodes to capture, or break down, contaminants as they are moved by the electrokinetic process.

6.2 PHYSICAL AND CHEMICAL BASIS

Remediation by electrokinetics is based upon the migration of water and ions in an electrical field. The movement of pore water under the influence of an electrical potential is termed electroosmosis, and the movement of ions is termed electromigration. Both processes are well-documented (Cabrera-Guzman et al., 1990; Acar et al., 1993, 1995). It has been demonstrated in both laboratory and field work that water and dissolved ions can be caused to migrate at useful velocities with reasonable electric fields. The mechanism of movement of DNAPL and of non-charged molecules is less well defined. DNAPL molecules, which are non-ionic and generally non-polar, would not be expected to migrate in an electrical field. DNAPLs themselves are typically nonconductive. DNAPL migration may be induced by a combination of osmotic pressure produced by the flow of water, changes in relative saturation due to removal of water and compaction of the unit due to dewatering. In addition, substantial temperature increases that occurred during field trials where DNAPL was suspected to be present may have enhanced volatilization of the DNAPL. There is insufficient data from field trials to evaluate the mechanism of DNAPL migration.

6.3 FIELD TRIALS

There have been a number of field tests of electrokinetics for remediation of metals (Acar et al., 1995). The only field trial of electrokinetics at a known DNAPL site is the LASAGNA[®] Pilot test at Paducah, Kentucky.

1. LASAGNA Field Tests, Paducah KY: Conducted at the USDOE Paducah Gaseous Diffusion Plant, Paducah, KY by a Monsanto, Du Pont, General Electric and DOE. A 3-meter by 4.5-meter zone in silts and clays contaminated with TCE was treated to a depth of 4.5 meters. DNAPL was suspected from high dissolved phase concentrations, although the amount of DNAPL present was not determined. An array of electrodes was operated for 120 days. TCE was reduced from an average concentration of 100-500 ppm to 1 ppm in the soil, or approximately a 99% removal. TCE concentrations in suspected DNAPL zones were reduced to 1 ppm except for a zone at the base of the treatment volume. Since the volume of DNAPL present at the start was not well determined, removal efficiency could not be estimated by mass balance. The contamination was captured on adsorbers placed between the electrodes. Future plans are to utilize iron filing treatment walls instead of carbon adsorption. The LASAGNA[®] test and details of the process are described in Ho et al. (1996) and Hughes et al. (1996).

6.4 CAPABILITIES AND LIMITATIONS

Electrokinetics has demonstrated the ability to induce the flow of both water and ions. Excellent results were obtained in a field trial of the process at Paducah, Kentucky, where DNAPL was suspected to be present. Since the mechanism for DNAPL migration and the amount and distribution of DNAPL was not established prior to the test, the results are difficult to evaluate relative to DNAPL remediation. The technology is designed primarily for fine-grained soils where the hydraulic conductivity is too low to induce adequate liquid flow rates by flushing technologies.

6.5 FURTHER INFORMATION

In Situ Remediation Technology Status Report: Electrokinetics: EPA 542-K-94-007, Describes field demonstrations or full-scale applications of *in situ* abiotic technologies for nonaqueous phase liquids and groundwater treatment. [clu-in.com]

Van Cauwenberghe, L. (July, 1997). Report: Electrokinetics - Technology Overview, Source: Ground-Water Remediation Technologies Analysis Center, Document Number: TO-97-03. [gwrtac.org]

Ho, S., Christopher J. Athmer, C., Sheridan P. and Shapiro, A. (June 1996). Topical Report for Tasks #8 and 10 entitled "Laboratory and Pilot Scale Experiment of the Lasagna Process" DOE Contract Number: DE-AR21-94MC31185 [RTDF.org]

Hughes, M., Ho, S., Athmer, C., Sheridan, P., Shoemaker, S., Larson, J.,

Clausen, J. and Zutman, J. (June 1996). Topical Report for Task #11 entitled "Evaluation of TCE Contamination Before and After the Field Experiment" (Lasagna process) DOE Contract Number: DE-AR21-94MC31185.SVE. [RTDF.org]

7.0 BIOREMEDIATION

7.1 DESCRIPTION

Bioremediation involves the use of biologically mediated reactions to break down contaminants. The process may occur under existing conditions (intrinsic bioremediation) or with the addition of oxygen, nutrients and/or other chemicals. Since biodegradation may be stimulated by the introduction of oxygen, it can be combined with SVE or air sparging. Bioremediation may also be coupled with steam injection in a process in which the steam supplies both oxygen and heat, with electrokinetics where contaminants (and possibly nutrients) are transported by the electrical field or with surfactants, which may increase the bioavailability of contaminants and can serve as a carbon source. The appropriate approach depends upon what is needed to bring about degradation of the contamination at a specific site.

7.2 PHYSICAL AND CHEMICAL/BIOLOGICAL BASIS

Biodegradation depends upon the existence of microorganisms that will degrade the compound of interest. The potential for degradation of most common DNAPL components have been demonstrated, although pathways are still being determined (NRC, 1993; Chappelle, 1993; Pankow and Cherry, 1996; McCarty et al., 1998). Specific rates of degradation depend upon many factors including the contaminants present, the concentration of contaminants, nutrients and substrates as well as the extent of contaminant sorption. Degradation requires the presence of primary substrates, nutrients and appropriate redox conditions. The potential for degradation must thus be assessed for each site.

Biodegradation reactions involve either oxidation or reduction of the contaminant and thus require both an oxidizer (electron acceptor) and a reducer (electron donor), the electron donor and acceptor compounds are termed primary substrates. Many organic compounds, including most hydrocarbons, can be used by microorganisms as primary substrates. Oxygen is a common electron acceptor; nitrate, sulfate and iron can also serve as electron acceptors in the absence of oxygen. Chlorinated compounds generally do not act as primary substrates, but may be degraded by cometabolic degradation. In cometabolic degradation, an enzyme produced by degradation of another carbon compound (the primary substrate) fortuitously catalyzes the reduction of the another compound (Lang et al., 1997). Cometabolic degradation of chlorinated compounds has been demonstrated under both aerobic (McCarty et al., 1998) and anaerobic conditions (Pankow and Cherry, 1996).

Cometabolic degradation requires another carbon source as a primary substrate. Abundant organic carbon naturally occurring in an aquifer or an abundant non-

halogenated co-contaminant (hydrocarbons for example) may serve as the primary substrate for anaerobic cometabolism, while several compounds including methane, phenol and toluene have been used to stimulate aerobic cometabolism by injecting them into contaminated zones (McCarty et al., 1998)

Biodegradation reactions require a transfer of electrons, access to nutrients and removal of by-products, all of which are inhibited in the nonaqueous phase. Thus DNAPLs are not likely to be susceptible to direct biodegradation. The DNAPL components may have to be dissolved in groundwater to become bioavailable.

PAHs can serve as primary substrates for aerobic degradation. Considerable success has been achieved at *ex situ* PAH degradation (Loehr and Webster, 1996) with up to 98% removal of PAHs from creosote-contaminated soils demonstrated. *In situ* data are more limited, but the same principles apply. Thus it may be anticipated that degradation can occur *in situ*, but the rate will be limited by oxygen supply and solubility of the heavier PAHs (Brubaker and Stroo, 1992).

7.3 FIELD TRIALS

1. Moffet Field, CA: Conducted by researchers from Stanford University at Moffet Field, CA in a shallow aquifer composed of poorly sorted sand and contaminated with dissolved phase (and sorbed) TCE (Roberts et al., 1990). Biostimulation was accomplished by addition of groundwater containing, alternately, oxygen and methane. Reduction of TCE (20-30%), DCE (45-90%) and vinyl chloride (90-95%) were documented (Semprini et al., 1990; 1992).

2. Moffet Field, CA: Similar to the test described above, in this case phenol and dissolved oxygen were used to accelerate degradation of TCE. Removal of 90% TCE at 1 mg/L was demonstrated with phenol at 25 mg/L (Hopkins et al., 1993)

2. Edwards AFB, CA: Also conducted by the Stanford group, TCE biodegradation in groundwater was demonstrated in a 410-day project of a 22-meter square treatment zone. Toluene, oxygen and hydrogen peroxide were injected into wells and mixed with pumped-in contaminated groundwater. Groundwater was circulated between two wells 10 m apart, screened over two zones from about 9 to 19 m depth in alluvial sediments of approximately 0.005 cm/sec hydraulic conductivity. Initial concentrations of TCE were 680 µg/L in the upper zone and 750 µg/L in the lower zone. Removal averaged 87% in the upper zone and 69% in the lower zone (McCarty et al., 1998).

7.4 CAPABILITIES AND LIMITATIONS

Biodegradation has been shown to be effective at degrading many dissolved-phase compounds including hydrocarbons and, under specific conditions, chlorinated compounds. Weathered samples, notably of PAHs, may degrade very slowly. Degradation of chlorinated solvents requires a separate carbon source.

An important issue for addressing DNAPL source zones is the rate at which degradation will occur from a non-aqueous phase liquid. In general, degradation has been demonstrated for chlorinated compounds only as a dissolved phase. Thus, removal of a DNAPL pool would occur only by dissolution as biodegradation of the dissolved phase allows slow dissolution of the pool. The technology is not a direct source zone remediation technology as currently practiced.

7.5 FURTHER INFORMATION

A Citizen's Guide to Bioremediation: EPA 542-F-96-007. [clu-in.com]

A Citizen's Guide to Natural Attenuation: EPA 542-F-96-015. [clu-in.com]

U.S. DOE Office of Technology Development, Innovative Technology Summary Report (April, 1995). *In Situ* Bioremediation Using Horizontal Wells, demonstrated at the M Area of the Savannah River Site, Aiken, SC. [DOE.gov]

Miller, R. (October, 1996). Report: Bioslurping - Technology Overview Source: Ground-Water Remediation Technologies Analysis Center, Document Number: TO-96-05. [gwrtac.org]

Remediation Case Studies: Bioremediation. PB95-182911. Documents project design, operation, performance, cost, and lessons learned. The reports should be useful to those evaluating the feasibility or design of these technologies at similar sites. [clu-in.com]

Abstracts of Remediation Case Studies: EPA 542-R-95-001, Documents project design, operation, performance, cost, and lessons learned. The reports should be useful to those evaluating the feasibility or design of these technologies at similar sites. [clu-in.com]

Bioremediation Field Initiative Site Profiles. Current information on the status of bioremediation nationally as well as information on sites where field performance evaluations have been and are being conducted. [clu-in.com]

Bioremediation of Hazardous Wastes: Research, Development and Field Evaluations: EPA 540-R-95-532, Results of field evaluation on the use of land treatment for wastes from a wood treatment site. [clu-in.com]

National Research Council, 1993, *In situ* Bioremediation: When Does It Work. National Academy Press, Washington D.C.

8.0 BARRIERS/CONTAINMENT

8.1 PHYSICAL CONTAINMENT

A site with DNAPL contamination will have contamination both in the source zone, the volume actually containing a nonaqueous phase liquid, and as a dissolved-phase plume. The dissolved-phase plume forms as groundwater flows past DNAPL, becoming contaminated as the components of the DNAPL dissolve into it. Depending upon the size of the source zone and the rate of ground-water flow, the plume may be much larger in extent than the source zone. Since several technologies have shown promise in treating dissolved phase plumes, containment of the DNAPL source zone alone may allow remediation of the remainder of the site (Pankow and Cherry, 1996). The problem of delineation of the extent of DNAPL contamination, discussed previously in the introduction, is of paramount importance if containment of the source zone is considered.

The presence of DNAPL at a site poses several concerns for containment technologies. Any penetration of a DNAPL pool during installation of a containment system may result in mobilization of the DNAPL, possibly allowing it to flow downward to previously uncontaminated zones. Additionally, if the ground-water table is impacted by containment system installation, care should be taken that mobilization of the DNAPL will not be induced.

There are a number of technologies for containment of contamination, designed not to remove or destroy a DNAPL, but to prevent the components from migrating. Discussion of these technologies is beyond the scope of this report; common technologies include bentonite slurry walls and sheet piling and innovative approaches such as cryogenic barriers and a variety of grouting techniques. The use of slurry walls and sheet piling walls for containment is well established.

8.1.1 Further Information

U.S. DOE Office of Technology Development, Innovative Technology Summary Report (April, 1995). Frozen Soil Barrier Technology, demonstrated at SEG Facilities, Oak Ridge, TN. [DOE.gov]

Proceedings of the International Containment Technology Conference, St. Petersburg, Florida, February 9 - 12, 1997., pp. 704-710, Florida State University, Tallahassee. A compilation of papers on current barrier wall research.

Rumer, R.R. and Mitchell, J.K., 1995, Assessment of Barrier Containment Technologies. NTIS, U.S. Dept. of Commerce, publication #PB96-180583. An overview of the field as of 1995.

8.2 REACTIVE BARRIER WALLS

8.2.1 Description

Treatment walls are barriers that are designed to allow groundwater to flow through the barrier and destroy or sorb dissolved-phase contaminants as they pass through the wall. Because these technologies treat only dissolved-phase contamination, they are not true DNAPL remediation technologies. However, the use of reactive barriers to treat the dissolved phase plume is an increasing popular remedy for DNAPL sites, thus the topic is briefly discussed here (the subject has recently been evaluated in a companion GWRTAC Technology Evaluation Report "Treatment Walls" available from GWRTAC including on their web site [gwrtac.org]). Only a brief introduction is given here.

8.2.2 Physical and Chemical Basis

Treatment walls may involve a wide variety of chemical reactions. The most commonly used walls for DNAPL components are zero-valent iron walls that reductively dechlorinate many common chlorinated solvents. Sorption walls utilizing zeolites have also been employed. In principle, any sorbing material could be used.

8.2.3 Field Trials

Numerous field trials of treatment walls are reviewed in the GWRTAC treatment wall report and one example is given here:

1. **Sunnyvale, CA:** A 12-m long, 6-m deep wall composed of granular iron was emplaced between two 75-m long slurry walls to intercept a ground-water plume containing low concentrations of chlorinated solvents (TCE, cis 1-2 DCE, vinyl chloride and CFC 113, all at an average concentrations of less than 1 mg/L). The 1.2 m-wide wall provided a residence time of approximately 4 days. Since installation in early 1995, monitoring wells have yielded no samples above the 0.5 µg/L detection limit.

8.2.4 Further Information

Vidic, R. D. and Pohland F.G. (October 1996). Technology Evaluation Report: Treatment Walls Source: Ground-Water Remediation Technologies Analysis Center, Document Number: TE-96-01. [gwrtac.org]

A Citizen's Guide to Treatment Walls: EPA 542-F-96-016. [clu-in.com]

In situ Remediation Technology Status Report: Treatment Walls: EPA 542-K-94-004, Describes field demonstrations or full-scale applications of *in situ* abiotic technologies for nonaqueous phase liquids and ground-water treatment. [clu-in.com]

Morrison, S. and R. Spangler (March 1998 revision). *In situ* Remediation Technology Status Report: Research on Permeable Barriers, Source: Rust Geotech for the Remediation Technology Forum - Permeable Barrier Working Group, Remediation Technologies Development Forum. [gwrtac.org]

Proceedings of the International Containment Technology Conference, St. Petersburg, Florida, February 9 - 12, 1997., pp. 704-710, Florida State University, Tallahassee. A compilation of papers on current barrier wall research.

Rumer, R.R. and Mitchell, J.K. (1995) Assessment of Barrier Containment Technologies. NTIS, U.S. Dept. of Commerce, publication #PB96-180583.

8.3 PUMP AND TREAT

Pump and treat is the most widely employed technology at DNAPL-contaminated sites. Although it is now known that restoration of a DNAPL-contaminated aquifer by pump and treat may take decades to centuries (NRC, 1994), it can provide effective containment of the dissolved-phase plume. Pump and treat is thus the baseline technology to which emerging technologies will be compared. Pump and treat is effective at containment provided hydraulic control can be established. Numerical modeling is widely used to determine applicability and system design.

8.3.1. Further Information

Alternatives for Ground Water Cleanup, 1994, National Academy Press, [nas.edu]

Keely, J.F., 1989, Performance Evaluations of Pump-and-Treat Remediations, EPA/540/489/005.

9.0 CONCLUSIONS

Several innovative technologies have shown the ability to rapidly remove mass from DNAPL source zones. Other technologies have demonstrated the ability to remediate dissolved-phase contamination. The demonstrated capabilities of the technologies include:

Soil Vapor Extraction has been effective at mass removal of volatile compounds from DNAPL in the vadose zone in homogeneous, permeable soils and, with addition of thermal processes, can be extended to semi-volatile compounds.

Steam has shown the ability to remediate in permeable soil in both the saturated and unsaturated zones. It may be combined with electrical heating when finer-grained layers are present.

Surfactants have demonstrated the ability to nearly completely remove DNAPLs from permeable units under saturated conditions.

Cosolvent Flooding has shown similar potential for rapid removal of complex LNAPLs as surfactants, and should be equally applicable to DNAPLs.

In Situ Oxidation has proven to be effective at destruction for specific chlorinated DNAPL compounds in permeable, relatively homogeneous soils.

Electrical Heating and Electrokinetics have shown potential for remediation of DNAPL in low permeability units. Both must be accompanied by some form of contaminant retrieval/destruction. There is not yet adequate data to determine the effectiveness of electrokinetics for DNAPL source zones.

Biodegradation of both chlorinated compounds and PAHs as dissolved phase has been demonstrated. Degradation apparently takes place primarily in the dissolved phase, thus treatment of DNAPL source zones may require an extended time.

In Situ Vitrification has demonstrated the ability to vitrify soil and produce temperatures that should lead to the destruction/mobilization of DNAPL compounds. There is not sufficient data on applicability to DNAPL sites to provide a meaningful evaluation at this time.

Reactive Barrier Walls have shown great promise for treatment of chlorinated solvent dissolved phase plumes. They do not directly address the DNAPL source zone. Barrier walls, with or without reactive components, may, however, provide containment of the DNAPL source zone.

Clean Up Goals - Due to the lack of carefully controlled field tests at DNAPL sites, the ultimate level of clean up attainable for each technology has not yet been documented. Each of the technologies discussed in this report is based on well established chemical and physical principles; their performance under field conditions are thus more likely to be limited by the hydrogeologic conditions rather than by limitations of the processes themselves.

Metals and Radionuclides - At many sites, contamination includes both DNAPL and metals or radionuclides (many radioactive contaminants are metals, but since regulations differ significantly for radioactive and nonradioactive contaminants, radioactive contaminants are classified separately). A few technologies, including electrokinetics and barrier walls have been applied to both organic and some inorganic contaminants. Those based on solubilization (surfactants and solvents), volatilization (steam, SVE, air sparging) or biodegradation will not be directly applicable to metals or radionuclides. A review of the applicability of the technologies to sites with a mix of organic and inorganic contaminants is beyond the scope of this report, since the applicability of a given technology depends upon the specific contaminants present. It is likely that such wastes may require treatment by more than one technology.

Geological Heterogeneities are the prime limitation for remediation. Variation in hydraulic conductivity within the contaminated zones results in two types of problems; regular lithologic variation produces channeling of flow, while inter-unit heterogeneity results in unequal access to the unit. Where some layers have higher conductivity than others, typical of layered sedimentary sequences, flow will preferentially occur in the higher conductivity units. Pumping of any fluids, whether it be vapor or liquid, will require a longer time in the lower conductivity units, resulting in much larger-than- necessary volumes being pumped through the high permeability units. Variations within a given unit, such as horizontal grain size variation, cause some areas to receive less flow than others within the same horizon. This may result in some zones getting little or no treatment if a fluid is pumped in or out of the zone. Heterogeneities also tend to produce more irregular DNAPL distribution and, hence, increase both the difficulty of characterization and of remediation. The degree of problems produced by heterogeneities can often be predicted if an accurate site assessment is performed.

Because an accurate characterization of the occurrence of DNAPLs is essential for design of a remediation system, and an accurate knowledge of geological heterogeneities is vital for evaluating the hydrogeological limits on remediation, a thorough site characterization is required for DNAPL sites. Once site assessment has provided the required site-specific data, the applicability of the technologies discussed in this report may be evaluated and the probable limitations of remediation estimated. Comparison can then be made to baseline technologies such as excavation and pump and treat.

Cost Comparison of technologies is not yet possible due to the very limited amount of data on most emerging technologies. There have been virtually no large-scale DNAPL source-zone remediation projects completed. Some technologies including soil vapor extraction and bioremediation have been widely implemented, but not for DNAPL remediation, thus while cost of installation may be estimated, the time and hence cost of operation is unknown. Other technologies including surfactants, solvent flooding and *in situ* oxidation have been implemented only in small-scale field trials, however the cost data cannot easily be scaled up due to the difficulty of separating research and development

costs from technology costs. Finally, the costs are highly site-dependent and because only a very few field trials have been completed for most emerging technologies, it is difficult to compare costs for technologies tested at different sites. Until cost estimates become available, potential vendors will have to be contacted for estimates for each site.

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Note: Additional references are given after the discussion of each technology; they are included in the "further information" section included with each technology discussion.