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In Situ Remediation of DNAPL Compounds in Low Permeability Media Fate/Transport, In Situ Control Technologies, and Risk Reduction

MANAGED AND OPERATED BY
LOCKHEED MARTIN ENERGY RESEARCH CORPORATION
FOR THE UNITED STATES
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ENVIRONMENTAL SCIENCES DIVISION

IN SITU REMEDIATION OF DNAPL COMPOUNDS IN LOW PERMEABILITY MEDIA FATE/TRANSPORT, IN SITU CONTROL TECHNOLOGIES, AND RISK REDUCTION

A Series of Focus Papers by an Ad Hoc Consortium Sponsored by
the U. S. Department of Energy and the American Petroleum Institute

Environmental Sciences Division

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PREFACE

A research and demonstration project was initiated as a joint effort under sponsorship of the Department of Energy (DOE) and the American Petroleum Institute (API). In this project, in situ remediation technologies are being tested and evaluated for both source control and mass removal of dense, non-aqueous phase liquid (DNAPL) compounds in low permeability media (LPM). This effort is focused on chlorinated solvents (e.g., trichloroethylene and perchloroethylene) in the vadose and saturated zones of low permeability, massive deposits, and stratified deposits with inter-bedded clay lenses. The project includes technology evaluation and screening analyses and field-scale testing at both clean and contaminated sites in the U. S. and Canada. Throughout this project, activities have been directed at understanding the processes that influence DNAPL compound migration and treatment in LPM and to assessing the operation and performance of the remediation technologies developed and tested.

DNAPL compounds such as TCE and PCE constitute a major environmental problem across the DOE complex and the industrialized world. In addition, low permeability soil and geologic media represent site conditions that are common and very problematic for environmental restoration. DNAPL compounds can migrate in LPM by preferentially moving into and through naturally occurring fractures where they partition between the gas, aqueous, and sorbed phases within the fracture and matrix system. They may also form isolated "blobs" and "ganglia" known as residuals, as well as connected DNAPL pools. In the vadose zone, DNAPL compounds can continually volatilize into the soil air or leach into percolating water. In the saturated zone, DNAPL compounds can slowly dissolve and contribute contaminants into flowing groundwater.

In situ remediation assessment and technology development have largely overlooked treatment of DNAPLs in LPM. Conventional soil vapor extraction or ground water pump and treatment approaches have been used, but with limited success. Although these technologies provide control of gaseous and dissolved contamination, they have little effect on removing or controlling the mass of DNAPLs within the subsurface. In situ treatment technologies are needed that will remove the sources of DNAPL contamination rather than merely treat DNAPL compounds in soil air or in ground water at extremely low concentrations. Removing DNAPLs in this conventional manner will prove to be very lengthy and very costly. Finally, there is a need to quantify the risk of any residual DNAPL compounds that may be unavoidably left in the LPM following treatment, even when the mass removal efficiency is quite high (e.g., 95%).

The DNAPL in LPM project has been merged with an existing effort by API which has focused on remediation of light, non-aqueous phase liquids (LNAPLs) in LPM. The LNAPL project was initiated in 1992 by API to investigate and study remediation of petroleum hydrocarbons like gasoline in fine-grained soils. It was thus logical for DOE and API to collaborate on a program regarding DNAPLs in LPM. In this collaboration, results from the LNAPL effort will be made available and used to address DNAPL questions whenever applicable. The LNAPL work has produced a series of focus papers describing processes and technologies for LNAPLs. This was followed by a controlled release of gasoline within a 100 m^2 sheet-pile enclosed test cell near Sarnia, Canada. Transport and distribution of the gasoline was monitored and a series of enhanced soil vapor extraction tests were made during the summer of 1993 and 1994. During the summer of 1995, sampling of the cell will be completed for mass balance purposes and microbial characterization. Additionally, large soil cores were collected for subsequent laboratory experiments concerning the mobility and risk associated with residual LNAPL mass.

The initial phase of the DNAPL in LPM project included preparation of a series of focus papers authored by a consortium of experts to document the state-of-the-art for a variety of emerging in situ remediation technologies for DNAPLs in LPM. The focus papers cover transport and fate processes and in situ treatment technologies, including separation and transfer processes (e.g., vapor extraction and subsurface mobilization) and destruction processes (e.g., chemical degradation). Thermal enhancement methods are assessed including hot air and steam injection technologies such as hydraulic and pneumatic fracturing and mixing. This document is a compilation of the focus papers prepared in this project.

The second phase of the DNAPL in LPM project occurred during FY 1994 and 1995 and has included field-scale testing of alternative treatment technologies (i.e., enhanced soil vapor extraction, soil fracturing and hot fluid injection, and soil permeation dispersal of reactive fluids) at clean and controlled-release test sites near Sarnia, Canada, and Cincinnati and Portsmouth, Ohio. Companion testing is also being conducted using large-scale laboratory experiments with packed lysimeters or field-collected cores. During late FY 1995 and into FY 1996, field testing will be conducted at a long-term contaminated site such as the X-231A or X-701B land treatment units at the DOE Portsmouth Gaseous Diffusion Plant in Ohio. This phase of the project will evaluate multiple technologies during side-by-side testing.

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PROCESSES AFFECTING SOIL AND GROUNDWATER CONTAMINATION BY DNAPL IN LOW-PERMEABILITY MEDIA

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Remediation of DNAPL in Low Permeability Media Project

1.0 INTRODUCTION

1.1 Context

This paper is one of a set of focus papers intended to document the current knowledge relevant to the contamination and remediation of soils and ground water by dense, nonaqueous phase liquids (DNAPL). The emphasis is on low permeability media such as fractured clay and till and unconsolidated, stratified formations. These materials are characterized by low-permeability zones bounded by fractures, strata or other features that form preferential flow paths for DNAPL, ground water, or other fluids that may be introduced in the remediation process.

Typical DNAPLs include wood-treating oils, tars from manufactured-gas plants, and chlorinated solvents. Characterization and remediation of DNAPL sites are especially difficult owing to the physical and chemical properties of these fluids (Mercer and Cohen, 1990). Because they are more dense than water, DNAPLs tend to sink in both the vadose and saturated zones. By definition, DNAPLs are immiscible with water and air but are, nevertheless, sufficiently soluble to produce dissolved concentrations orders-of-magnitude greater than maximum concentration levels (MCL) for constituent chemicals. On the other hand, most DNAPLs do not quickly dissolve away. Rather they form persistent sources that may last for many decades and create dissolved plumes several kilometers long (Mackay and Cherry, 1989).

1.2 Purpose of This Paper

Contamination of soils and ground water by DNAPLs and the development of applicable remediation measures are understood within a paradigm quite different from that used to approach contamination problems from more conventional sources (Feenstra, Cherry and Parker, 1995). The purpose of this paper is to set out the salient features of DNAPL behavior that are relevant to the assessment of applicability and performance of various remediation technologies. Basic concepts pertaining to immiscible-fluid mixtures are described and used to discuss such aspects as DNAPL transport, dissolved-phase transport, and equilibrium mass distributions. Finally, several implications for remediation are presented.

2.0 FUNDAMENTAL CONCEPTS

2.1 Interfacial Tension and Wettability

Water, air, and DNAPL may exist simultaneously within the interstices of a porous medium. At sufficiently large scale the fluids appear to form a mixture. However, at the pore-scale, the fluids are seen to remain distinguishable as individual fluids, separated by distinct interfaces at points of contact. The fluids are said to be immiscible. There exists a force in the interfaces between immiscible fluids that can be likened to a stretched membrane (Corey, 1986). This force is called interfacial tension and depends upon the chemical properties of the contiguous fluids. Because the force of interfacial tension acts in directions tangent to the interface, a second force must exist on curved interfaces at equilibrium. This second force on curved interfaces is provided by a pressure difference between the fluids on opposite sides of the interfaces, as shown in Figure 1.

The relationship between the pressure difference across the interface, the interfacial tension, and the radius of curvature of the interface is provided by the Laplace equation:

$$\Delta P = \frac{2\sigma}{r} \qquad \mathbf{1}$$

where ΔP = pressure difference (F/L^2)
σ = interfacial tension (F/L)
r = radius curvature (L)

While this form of the Laplace equation strictly applies only for interfaces with constant curvature (i.e., a subsection of a sphere), it is useful for qualitative discussion of phenomena involving interfaces with more complex geometry. It is clear from Figure 1 that the pressure of the fluid on the concave side of the interface must be the greater in order for a force balance to be established.

It is usually the case that one fluid has a stronger affinity for the solids than does either of the other fluids in the pores or fractures. The fluid with the greatest affinity for the solid is said to be the wetting fluid because it tends to spread over the solid surface. Water is the wetting fluid in practically all DNAPL-water-air-solid systems of interest. For this reason, water is the fluid at lowest pressure in a water-air-DNAPL system.

In the same way that fluids compete to spread on the solid surface, DNAPL and air compete to spread on the water interfaces. DNAPL usually has the greater spreading coefficient and forms a layer between water and air. A schematic representation of the fluid arrangement within a single pore is shown in Figure 2. The DNAPL pressure is intermediate between the water and air pressures.

2.2 Fluid Contents and Capillary Pressure

The traditional quantitative treatment of fluids in porous media makes use of the concept of a representative element of volume (REV). Within an REV, there is a large number of pores and pore throats of different sizes and geometries. Fluid contents, pressures and other variables of interest are expressed in reference to the REV. A common way to express fluid contents is to refer to the fraction of the pore volume in the REV that is occupied by the various fluids. Thus, the water saturation, S_w, is the fraction of pore volume occupied by water. Similarly, we can speak of DNAPL and air saturations. By this definition, the saturations of water, DNAPL, and air must add to unity at all times.

The pressures of the fluids within a REV are considered to be uniform throughout the REV. The aqueous phase has one value of pressure throughout the REV, the DNAPL a different pressure, and the air still a third value. Fluid-fluid interfaces at the pore scale adjust their positions so that the radii of curvature are such that interfacial forces are balanced by forces due to pressure difference across the interfaces. The pressure difference between fluids in the REV determines the radius of interface curvature required and, ultimately, the position interfaces take within the pore structure to accommodate the required curvature. Finally, the location or position of fluid-fluid interfaces dictates the fraction of the pore volume occupied by each fluid.

The difference between the pressures of two fluids in contact is the capillary pressure. The pressure of the fluid at lower pressure is subtracted from the higher pressure so that capillary pressure is positive. In general, any two of the three fluids (water, air and DNAPL) may be in contact. For this reason it is necessary to speak of the DNAPL-water capillary pressure or the air-DNAPL capillary pressure to distinguish the fluid pair under consideration. If only one fluid pair exists in the region of interest (e.g., DNAPL below the water table) then there can be no ambiguity and simply capillary pressure is sufficient.

Figure 3 shows the typical relationship between capillary pressure and water saturation for a DNAPL-water system. The main drying and wetting curves are envelopes that represent the capillary pressure-saturation relationship starting from the extreme conditions of full water saturation (drying curve) and from the minimum water saturation (wetting curve). The main drying curve applies to situations in which DNAPL is advancing into water-saturated media. The main wetting curve applies when water displaces DNAPL as occurs during DNAPL drainage or a waterflood operation. Scanning curves represent drying or wetting processes that are initiated at water saturations between the extreme conditions. Several algebraic formulas have been proposed to describe the capillary pressure-saturation relationship (e.g., Brooks and Corey, 1966; van Genuchten, 1980, Parker, et al., 1987). Luchtner et al., (1989) provide a means of computing the scanning curves.

2.3 Concepts of Entry Pressure and Entrapped DNAPL

Within the context of this paper, there are two particularly important aspects of the capillary pressure-saturation relationship. The first is the concept of entry pressure. Entry pressure is the threshold capillary pressure on the main drying curve at which the DNAPL first becomes continuous throughout the REV. The entry pressure occurs only after the water saturation has been somewhat reduced by the invading DNAPL. This is because the REV can accommodate some invasion by DNAPL before there develops the DNAPL saturation at which DNAPL is continuous across the REV.

The entry pressure is strongly dependent on the characteristic dimension of the pore channel in which DNAPL first becomes continuous and capable of macroscopic flow. The relationship between entry pressure and pore size is indirectly expressed by correlating entry pressure with hydraulic conductivity (McWhorter and Nelson, 1980; Thomas et al, 1968). The empirical equation presented by Thomas et al., after modification of units, is

$$P_e^{aw} = 1.34K^{-0.43} \qquad 2$$

where: P_e^{aw} = entry pressure in cm of water
K = hydraulic conductivity in cm/s

The entry pressure calculated from eqn. 2 is for air into water. The entry pressures for DNAPL into water can be estimated by multiplying the air-water entry pressure by the ratio of interfacial tensions:

$$P_e^{ow} = \frac{\sigma^{ow}}{\sigma^{aw}} P_e^{aw} \qquad 3$$

where: P_e^{ow} = organic-water entry pressure
σ^{ow} = organic-water interfacial tension
σ^{aw} = air-water interfacial tension.

Equation 2 shows that heterogeneity characterized by spatially variable hydraulic conductivities will, also, be reflected by spatially variable entry pressures. In turn, the variable entry pressures have a profound effect on the paths that DNAPL takes as it invades the region below the water table. Kueper and Frind (1991) modeled the distribution of DNAPL infiltrating a heterogeneous aquifer and showed how materials with contrasting entry pressures cause a very complex flow pattern. The effect of spatially variable entry pressures on DNAPL flow patterns is much greater than would be anticipated from our understanding of the effects of permeability variations on water flow. The effect on DNAPL flow of variable entry pressures is somewhat like the effects that random blocks and lenses of strictly impervious materials would have on flow of ground water.

Field evidence of the control that entry pressures exert on DNAPL flow is abundant. One part of a core will be free of DNAPL, yet immediately adjacent, DNAPL is present in material with undiscernibly different properties. DNAPL lenses and flow paths have been observed to be only a few millimeters thick. Macropores such as joints, fractures, and worm and root holes represent preferential flow paths because these features have very low entry pressures. Strata with entry pressures that are large relative to the surrounding material have been observed to cause DNAPL to pool, even though such strata could not be considered aquitards in the usual sense.

The second particularly important aspect of the capillary pressure-saturation relationship is the entrapment of DNAPL during the wetting process. The replacement of DNAPL by water, as during DNAPL drainage or a water flood, is not complete. Chatzis and Dullien (1983) and Mohanty et al. (1987) provide explanations of the processes by which the nonwetting phase becomes entrapped by the wetting phase. The fraction of pore volume occupied by entrapped DNAPL at zero capillary pressure is indicated on Figure 3. The entrapped DNAPL is sometimes referred to as residual DNAPL saturation.

Residual saturations of a variety of organic liquids in different porous media have been tabulated by Cohen and Mercer (1993). Values range from as low as one percent of the pore volume to as high as 50 percent. Poulsen and Kueper (1992) show that residual saturations can be highly variable depending upon sample size and location. In general, bulk samples, say as obtained from a typical core, will indicate rather low residual saturation. Often the scale of the sampling is larger than the scale of heterogeneities controlling the DNAPL distribution and, therefore, low bulk residual values are observed. Very little is known concerning residual DNAPL in fractures. Schwille (1988) reports the fracture retention of tetrachloroethylene in the amount of 0.05 liters per square meter.

A characteristic feature of residual DNAPL is that it is occluded by water. Residual DNAPL is discontinuous at any scale significantly larger than the pore scale. Because it is discontinuous, pressure gradients within a DNAPL globule or ganglia can be induced only by creating pressure gradients in the contiguous aqueous phase. Experiments (Wilson and Conrad, 1984) show that the hydraulic gradient required to induce flow of residual nonwetting fluids is far in excess of that which can be achieved in field settings. Therefore, residual DNAPL represents an in situ, immobile source for dissolved constituents in ground water.

2.4 Darcy's Law and Relative Permeability

The flow of multiple fluids in porous media is calculated by applying the familiar Darcy equation to the individual fluids. A common form is

$$q_{wi} = \frac{-k\,k_{rw}}{\mu_w}\left(\frac{\partial P_w}{\partial X_i} - \rho_w g_i\right) \qquad 4$$

for water (the wetting fluid) and

$$q_{nwi} = \frac{-k\,k_{rnw}}{\mu_{nw}}\left(\frac{\partial P_{nw}}{\partial X_i} - \rho_{nw} g_i\right) \qquad 5$$

for DNAPL (the nonwetting fluid), where:

q = volume flux (L/T)
k = intrinsic permeability (L^2)
k_r = relative permeability
μ = dynamic viscosity
P = pressure
ρ = density
g_i = component of the gravitation constant in direction X_i
X_i = space coordinate

and the subscripts denote the wetting and nonwetting fluids.

The relative permeabilities appearing in eqns. 4 and 5 range from zero to unity as the saturation of the corresponding fluid ranges from zero to unity. Typical relative permeability functions are shown in Figure 4. The coexistence of more than one fluid in the pores reduces the area available for flow of either fluid and increases the tortuosity of the flow path that fluid elements must traverse. It is for these reasons that relative permeabilities are less than unity. Brooks and Corey (1966) and Parker et al. (1987) provide algebraic expressions for the relative permeability functions for both the wetting and nonwetting fluids. The relative permeabilities can also be expressed as functions of capillary pressure.

2.5 Chemical Transport In the Aqueous and Gaseous Phases

The presentation to this point has considered DNAPL as a separate phase, immiscible with both water and soil gas. The foregoing discussion is relevant to understanding the way DNAPLs invade the subsurface and finally distribute themselves in both the vadose and saturated zones. Once in the subsurface, individual chemical constituents of the DNAPL may dissolve into soil gas and subsurface waters. The dissolved chemicals are then transported by diffusion and dispersion-advection.

Dispersion and advection are the transport processes responsible for the development of the dissolved plume exterior to the DNAPL source area. These processes are important, also, in the establishment of effective mass transfer rates from DNAPL pools and residual zones (Anderson et al., 1992a and 1992b). The mass flux of dissolved chemical due to dispersion and advection is expressed by

$$J_i = -D_{ij}\frac{\partial C}{\partial X_j} + Cq_i, \quad \begin{matrix} i = 1,2,3 \\ j = 1,2,3 \end{matrix} \qquad 6$$

where J_i = i-th component of mass flux (M/L^2-T)
D_{ij} = coefficient of hydrodynamic dispersion (L^2/T)
C = mass concentration (M/L^3)
q_i = i-th component of volume flux (L/T)
X_j = spatial coordinate.

The Einstein convention, whereby a repeated index implies summation, is invoked. A common model for D_{ij} is

$$D_{ij} = D_e \delta_{ij} + \left(\alpha_\ell - \alpha_t\right) \frac{V_i V_j}{|\underline{V}|} \qquad 7$$

where D_e = effective diffusion coefficient (L^2/T)
α_l = longitudinal dispersivity (L)
α_t = transverse dispersivity (L)
$\underline{V}$ = seepage velocity vector (L/T)
V_i and V_j = components of the seepage velocity (L/T)
δ_{ij} = identity tensor.

Diffusion is the process in which chemicals dissolved in the soil gas or in water are transported due to concentration gradients. Diffusion may be superimposed on advective transport, but bulk-fluid motion is not required for diffusive transport to occur. Indeed, diffusion is the dominant process only when advection is small or nonexistent. However, in the context of low permeability materials, diffusion processes play an especially important role.

The mass flux due to diffusion is given by Fick's law:

$$J_{\alpha i} = -\phi S_\alpha D_{e\alpha} \frac{\partial C_\alpha}{\partial X_i}, \quad i = 1, 2, 3 \qquad 8$$

wherein $J_{\alpha i}$ = i-th component of mass flux in fluid α ($M/L^2/T$)
ϕ = porosity
S_α = fraction of pore volume occupied by fluid α
$D_{e\alpha}$ = effective diffusion coefficient in fluid α (L^2/T)
C_α = mass concentration in fluid α
X_i = space coordinate (L).

The appearance of the product ϕS_α in eqn. 8 accounts for the reduced cross-sectional area available for diffusion in fluid α due to the presence of solids and other fluids. Of course, S_α is unity if only one fluid is present. The effective diffusion coefficient is given by

$$D_{e\alpha} = \tau_\alpha D_{o\alpha} \qquad 9$$

where τ_α = tortuosity in fluid α
$D_{o\alpha}$ = free-space molecular diffusion coefficient in fluid α (L^2/T).

The free-space molecular diffusion coefficient is the handbook diffusion coefficient for the species of interest in fluid α.

Finally, the tortuosity can be expressed as a function of S_α by

$$\tau_\alpha = \tau_o S_\alpha^{7/3} . \qquad \mathbf{10}$$

This equation for tortuosity, attributed to Milligton and Quirk (Shear et al., 1973), shows that the effective diffusion coefficient declines very rapidly with decreasing fluid saturation. At full saturation of a particular fluid, eqn. 10 predicts the tortuosity is simply τ_o, the intrinsic tortuosity of the medium. The value of τ_o is believed to range from a low of about 0.3 for typical clays to about 0.7 for sands and other granular media. Sometimes the porosity raised to the one-third power is used as an estimate for τ_o.

As closure to this subsection, it is noted that D_o in a gaseous fluid is orders of magnitude greater than in a liquid. Values for D_o in water typically are on the order of $10^{-9}m^2/s$. In contrast, D_o in the gaseous phase is on the order of $10^{-5}m^2/s$.

2.6 Mass Storage Considerations

All of the foregoing developments relate to the ways by which chemicals are transported in the subsurface: as a separate phase (i.e., as DNAPL), by dispersion and advection, and by diffusion. Consideration is now given to the matter of chemical storage in porous and fractured media. The transport processes previously discussed act to change the mass of chemical stored in a reference element. Together, the transport equations and the mass storage equations form a system of partial differential equations that constitute the mathematical bases for transport models.

The contaminating chemical can reside in the subsurface as NAPL, as dissolved chemical in the aqueous phase, as dissolved chemical in the gaseous phase, and as chemical sorbed on solids. The total mass of a particular chemical species per unit volume of porous medium in given by (Feenstra et al., 1991).

$$C_t = \phi S_w C_w + \phi S_g C_g + \rho_b \omega_s + \phi S_n C_n \qquad \mathbf{11}$$

where C_t = total mass of species per unit volume of porous medium (M/L^3)
C_w = mass concentration in the aqueous phase (M/L^3)
C_g = mass concentration in the gaseous phase (M/L^3)
C_n = mass concentration in the NAPL (M/L^3)
ϕ = porosity
S_w = water saturation
S_g = soil gas saturation
S_n = NAPL saturation
ρ_b = dry bulk density of the porous medium (M/L^3)
ω_s = sorbed mass per unit mass of solid.

At thermodynamic equilibrium, the concentrations appearing in eqn. 11 are rather simply related to one another. To an acceptable approximation for most work, the relationship between the aqueous-phase concentration and the concentration of the species in the NAPL phase is given by

$$C_w = \left(\frac{C_{sol} \overline{m}}{\rho_n m} \right) C_n \qquad \mathbf{12}$$

where $\overline{m}$ = number-mean molecular weight of the mixture (M/mole)
m = molecular weight of species (M/mole)
ρ_n = mass density of NAPL (M/L^3)
C_{sol} = solubility of pure species in aqueous phase (M/L^3)
C_n = mass concentration of species in NAPL (M/L^3)
C_w = mass concentration of species in aqueous phase (M/L_3).

If the NAPL is a single chemical species, then $m=\overline{m}$, $C_n = \rho_n$ and C_w is equal to the solubility of the chemical in aqueous phase. Henry's law is used to relate the concentrations in the aqueous and gaseous phases:

$$C_g = K_{HD} C_w \qquad \mathbf{13}$$

where K_{HD} is the dimensionless Henry's constant.
Finally, it is common to account for sorption by a linear isotherm so that

$$\omega_s = K_d C_w \qquad \mathbf{14}$$

where K_d is the distribution coefficient. In turn, the distribution coefficient is related to an organic-carbon partition coefficient by:

$$K_d = f_{oc} K_{oc} \qquad \mathbf{15}$$

where f_{oc} = fraction of organic carbon in the porous medium
K_{oc} = organic-carbon partition coefficient (L^3/M).

By use of eqns. 12-15, the total mass of a species per unit volume of porous medium can be expressed in terms of any desired phase concentration. For example, the total mass per unit volume expressed as a function of aqueous concentration is

$$C_t = \phi \left\{ S_w + S_g K_{HD} + \frac{\rho_b K_d}{\phi} + S_n \left(\frac{\rho_n m}{C_{sol} \overline{m}} \right) \right\} C_w . \qquad \mathbf{16}$$

Of course, the total concentration can be expressed on different bases, as is convenient for the application at hand. Total species concentrations are often expressed as mass of species per unit dry mass of solid, for example. In this case, eqn. 16 becomes

$$\omega_t = \frac{\phi}{\rho_b} \left\{ S_w + S_g K_{HD} + \frac{\rho_b K_d}{\phi} + S_n \left(\frac{\rho_n m}{C_{sol} \overline{m}} \right) \right\} C_w , \qquad \mathbf{17}$$

where ω_t is the total mass of the species per unit dry mass of solid.

It is a simple matter to compute the fraction of total mass that exists in the gaseous, aqueous, sorbed, and NAPL phases provided S_w, S_g, and S_n are known. Feenstra et al. (1991) make use of these storage concepts to compute the minimum value of ω_t consistent with the presence of NAPL. This is accomplished by putting C_w equal to the effective solubility of the species, as S_n approaches zero. The value of ω_t so obtained provides a threshold value to which measured ω_t can be compared to indicate the presence or absence of NAPL in the medium. Cohen and Mercer (1992) provide values of Henry's constants and organic-carbon partition coefficients for an extensive list of DNAPLs.

2.7 Mass Conservation

Mass conservation is expressed by equating the divergence of the sum of the various mass fluxes to the negative rate of change of stored species mass. While all of the various processes discussed above go on simultaneously, it is often possible to focus on a process that is dominant in a particular situation, thereby significantly simplifying the analysis. Then only the flux laws and conservation equations pertinent to the particular application need be considered. Such an approach is adopted in the remainder of this paper.

3.0 CHEMICAL MASS DISTRIBUTIONS AT EQUILIBRIUM

The following discussion pertains to the saturated zone below the water table. That zone presents the greatest difficulty for remediation and is the primary focus of the research project. Also, the focus is on a fractured porous medium consisting of porous matrix blocks bounded by fracture surfaces. Fluids and chemicals can reside in the fractures or in the matrix blocks or both.

3.1 Infiltration of DNAPL

Upon encountering a fractured porous medium, infiltrating DNAPL will preferentially enter the fractures because the entry pressure of fractures is typically small relative to that of the matrix blocks. Table 1 lists estimated fracture entry pressures for three common DNAPLs. The values shown are calculated from

$$P_e = 2\sigma / b \qquad \textbf{18}$$

where P_e = entry pressure (F/L^2)
σ = interfacial tension (F/L)
b = fracture aperture (L),

and are expressed as an equivalent height of water. Equation 18 is based on smooth, parallel-plate fractures and, therefore, the values in Table 1 must be regarded as rough indicators, only.

Entry pressures for typical porous matrix blocks are listed in Table 2. The values shown were computed from eqns. 2 and 3. Clearly, the entry pressures of the matrix blocks are much greater than those of the typical fracture. The contrast in fracture and matrix entry pressures makes it highly unlikely that DNAPL invades the matrix blocks during DNAPL infiltration.

Table 1. Estimated Fracture Entry Pressures For Three DNAPLs

b microns	Entry Pressure, cm of H_2O		
	TCE(1)	PCE(2)	MC(3)
10	70.4	90.6	57.8
20	35.2	45.3	28.9
30	23.5	30.2	19.3
40	17.6	22.6	14.5
50	14.1	18.1	11.6
60	11.7	15.1	9.6
70	10.0	12.9	8.3
80	8.8	11.3	7.2
90	7.8	10.1	6.4
100	7.0	9.1	5.8

(1)σ = 34.5 dynes/cm, (2)σ = 44.4 dynes/cm, (3)σ = 28.3 dynes/cm

Table 2. Estimated Matrix Entry Pressures For Three DNAPLs

Hydraulic Conductivity,(1) cm/s	Entry Pressure, cm of H_2O		
	TCE	PCE	MC
1×10^{-8}	1768	2275	1450
5×10^{-8}	885	1139	726
1×10^{-7}	657	846	539
5×10^{-7}	329	423	270
1×10^{-6}	244	314	200
5×10^{-6}	122	157	100
1×10^{-5}	91	117	75

(1)Hydraulic conductivity of matrix blocks.

Simulations of DNAPL infiltration is a single rough-walled fracture were reported by Kueper and McWhorter (1991). The rough-walled fracture was treated as a porous medium and the two-phase flow formation previously described was used. Figure 5a shows a contour plot of the variable aperture assigned to the fracture. Figure 5b shows the distribution of trichloroethylene after some 40 seconds of infiltration. Clearly, the pattern of DNAPL migration in a rough-walled fracture is quite nonuniform. Portions of the fracture with small aperture may be completely free of DNAPL. Any conceptualization of DNAPL being uniformly distributed in a single fracture, let alone in a fracture network, is very approximate.

The simulations by Kueper and McWhorter (1991) were also used to estimate the times required for DNAPL to penetrate a 5m - thick aquitard in a single, rough-walled fracture. Various pool heights above the aquitard, various mean apertures, and fracture dip angles were analyzed. In all cases, the DNAPL was calculated to travel through the aquitard in a matter of hours to a few tens of hours. It is probable that DNAPL in real fracture networks travels at similarly rapid rates.

3.2 DNAPL Distribution at Mechanical Equilibrium

Fractured porous media often occur as a weathered clay or till. Fracture intensity and apertures are expected to decrease with increasing depth. A downward migrating DNAPL would encounter increasingly larger entry pressures in such a case. Should the entry pressures be sufficiently large, downward migration will cease and the pressures in the water and DNAPL will approach those dictated by mechanical equilibrium. Both the DNAPL and water pressures increase linearly with depth at mechanical equilibrium. Because the density of DNAPL is greater than that of water, the DNAPL pressure increases more rapidly with depth than does that of water. This causes the capillary pressure to increase with depth as shown in Figure 6. This figure and the subsequent discussion apply only for continuous DNAPL, as might occur in a pool.

Downward migration will cease if and when the entry pressures of the flow path exceed the capillary pressure that can be generated at mechanical equilibrium. Because the capillary pressure that can be generated at equilibrium increases with depth, the entry pressures must increase even more rapidly if migration is to cease as a result of this mechanism. Even though entry pressures may increase with depth, so does the ability of the DNAPL to overcome them. Therefore, it is not surprising that DNAPL may migrate to great depths in the fracture network. The tendency to reach large depths is greater for DNAPLs with large density then for DNAPLs with densities near that of water. Coal tars and wood-treating oils, with densities near that of water, are often found in pools at shallow depths. Chlorinated solvents, owing to their large density, are rarely found in thick pools at shallow depth.

3.3 Distribution of Mass Storage Capacity

Constituents of DNAPL in fractures will dissolve in the aqueous phase and diffuse into the matrix blocks. Because the fracture porosity is often orders-of-magnitude less than the matrix porosity, the capacity of matrix blocks for chemical mass storage sometimes exceeds the DNAPL mass storage capacity of the fractures (Parker and McWhorter, 1994). This may be an important consideration in the selection, design, and performance of remediation technologies. For simplicity, the DNAPL is now taken as being comprised of a single chemical species. Then the DNAPL mass in the fracture network is simply

$$M_f = \phi_f S_n \rho_n \quad \textbf{19}$$

where M_f = mass of DNAPL per unit volume of aquifer (M/L^3)
ϕ_f = fracture porosity
S_n = DNAPL saturation in the fracture space
ρ_n = mass density of DNAPL (M/L^3).

The simulations described in Section 3.1 suggest that S_n is less than unity by a substantial margin. Nevertheless, putting $S_n = 1$ in eqn. 19 provides a convenient way to establish the upper bound on the mass of DNAPL that can be accommodated in the fracture network.

The mass storage capacity of the matrix follows from eqn. 16 in which S_n and S_g are put to zero and C_w is equal to the solubility C_{sol}. No DNAPL is considered to exist in the matrix for reasons previously discussed. The assumption of a single-species DNAPL is the reason that $C_w = C_{sol}$. The result is

$$M_m = \phi_m \left(1 + \frac{\rho_b K_d}{\phi_m}\right) C_{sol} \quad \textbf{20}$$

where M_m = mass storage capacity of the matrix per unit volume of aquifer (M/L^3)
ϕ_m = matrix porosity.

It is to be noted that M_m includes both dissolved and sorbed chemical. Equation 20 expresses the storage capacity of the matrix blocks; the actual mass stored may be substantially less than the capacity at any time.

Table 3 shows the distribution of mass storage capacity for a few typical situations. There is a wide variation of mass storage capacity distributions, depending upon fracture porosity and chemical characteristics. The solubility for methylene chloride is 20,000 mg/l, but MC has the lowest organic carbon-partition coefficient (8.7 cm^3/g) of the chemicals considered. On the other end of the spectrum is tetrachloroethylene (PCE) with a solubility of 150 mg/l and organic carbon-partition coefficient of 263 cm^3/g.

An important conclusion is that the matrix storage capacity may exceed the capacity for fractures to store mass in the form of DNAPL. The implication is that DNAPL that moves into the geologic formation in the fractures may eventually disappear as the result of dissolution and subsequent diffusion into the matrix blocks. This matter is considered in more detail in a subsequent section.

Table 3. Distribution of Mass Storage Capacity

Fracture Porosity	Type of DNAPL	Percent of Total Mass Storage Capacity		
		Dissolved	Sorbed	DNAPL
10^{-5}	TCE	25	75	1
	PCE	13	83	4
	MC	82	18	0.2
10^{-4}	TCE	22	70	8
	PCE	10	61	29
	MC	81	17	2
10^{-3}	TCE	13	39	48
	PCE	2	17	81
	MC	71	15	14

$\phi_m = 0.35$, $\rho_b = 1.72$ g/cm^3, $f_{oc} = 0.005$

4.0 DEPLETION OF DNAPL BY DIFFUSION AND ADVECTION

Naturally occurring transport processes tend to deplete DNAPL in fractures, in pools, and in the form of residual. In some cases, these processes can significantly change the DNAPL distribution prior to the initiation of remediation. Also, a discussion of the relevant processes forms a convenient basis for assessing the potential effects of remediation efforts.

4.1 Depletion of DNAPL in Fractures By Diffusion

The potential for DNAPL in fractures to be partially or totally depleted by diffusion into matrix blocks was first recognized by Parker et al. (1994), and further elaborated by Parker and McWhorter (1994). For the purpose of demonstrating the process, matrix blocks are idealized as rectangular parallelepipeds of dimension $L_1 \times L_2 \times L_3$, as shown in Figure 7. At time zero, it is assumed that diffusion is initiated on all six faces into a block initially free of the chemical. The aqueous-phase concentration on the boundaries of the block is assumed to be constant and equal to C_{sol}, owing to the presence of DNAPL in the fractures.

Under these circumstances, the accumulated mass in the matrix block at time t is given by

$$\tilde{M}(t) = C_{to} L_1 L_2 L_3 \left\{ 1 - P_1 P_2 P_3 \right\} \qquad 21$$

where

$$C_{to} = \phi_m \left(1 + \frac{\rho_b K_d}{\phi_m} \right) C_{sol} = \phi_m R C_{sol} \qquad 22$$

in which R is the familiar retardation factor (Freeze and Cherry, 1979). The factors P_i are defined by the infinite series:

$$C_i = \frac{8}{\pi^2} \sum_{n=1,3,5}^{\infty} n^{-2} \exp\left\{ \frac{-n^2 \pi^2 \alpha t}{L_i^2} \right\}, \; i = 1,2,3 \quad . \qquad 23$$

The parameter α in eqn. 23 is the molecular diffusivity and is given as

$$\alpha = \frac{D_e}{R} \quad . \qquad 24$$

Of course the mass accumulated in the matrix blocks occurs at the expense of DNAPL mass in the fractures. Therefore, the time at which all DNAPL mass in the fractures is depleted is computed by finding the time t at which $\tilde{M}(t)$ from eqn. 21 is equal to the initial DNAPL mass given by eqn. 19. Finite disappearance times result only when $C_{to}L_1L_2L_3$ is greater than M_f (i.e., the matrix storage capacity exceeds the DNAPL mass). Again, it has been assumed that the DNAPL is comprised of a single species.

Parker and McWhorter (1994) carried out the above calculations for cubic matrix blocks in a typical fractured clay. Table 4 shows the results of those calculations. These results show that the times required to transfer all the fracture DNAPL mass to the matrix blocks is often small compared to the times that may have elapsed since the release occurred. One can anticipate the existence of fractured porous media sites where little or no DNAPL exists, even though the initial release was in the form of a DNAPL.

Table 4. Disappearance Times for Two Chemicals in Fractured Clay

Chemical	Mass Storage Ratio Matrix:Fracture	Dimension Matrix Block L(cm)	Disappearance Time (days)
TCE	17.7	1	0.002
		10	0.15
		100	15
PCE	9.7	1	0.02
		10	1.8
		100	180

$\phi_m = 0.35$, $r_b = 1.6$ g/cm^3, $f_{oc} = 0.01$, $\tau_o = 0.33$, $R = 5.2$, $D_e = 3.3 \times 10^{-6}$cm^2/s

4.2 Depletion of Pooled DNAPL by Dispersion-Advection

Figure 8 shows ground water flowing over a rectangular DNAPL pool. Mass is transferred vertically from the pool surface in response to a vertically directed concentration gradient. The horizontal motion of ground water carries the chemical laterally. At steady state, this is a classic mass transfer problem discussed in detail by Bird et al. (1960) in the context of diffusion into a falling liquid film. Johnson and Pankow (1992) normalized the rate of mass transfer to a unit area and defined a mass transfer coefficient

$$k_t = 4D_{22}V_1 / \pi L_1^{1/2} C_{sol} \tag{25}$$

in which
k_t = mass transfer coefficient ($M/L^2 \bullet T$)
D_{22} = coefficient hydrodynamic dispersion transverse to the ground water flow (L^2/T)
V_1 = ground water seepage velocity in coordinate direction X_1(L/T)
L_1 = length of pool in direction X_1(L)
C_{sol} = solubility concentration (M/L^3).

The cumulative mass transferred from the pool to the flowing ground water per unit area of pool is obtained by simply multiplying k_t by the time of interest. Alternatively, one can divide the mass in the pool per unit area by k_t to estimate the time to achieve depletion of the pool. According to Johnson and Pankow (1992), decades to centuries are required to deplete pools of TCE ranging from 1 m to 10 m in length with typical ground water flow rates.

5.0 SOME IMPLICATIONS FOR REMEDIATION

The objective of source-area remediation is to reduce the source-area concentrations permanently to the point where ground water leaving the area meets some standard of acceptable quality. Elements of the foregoing presentation bear on technology selection, performance, and associated risks. These subjects are discussed in more detail in the companion focus paper (Freeze and McWhorter, 1995).

5.1 Steam Flush

A primary intention of steam-flush technologies is to remove DNAPL. The calculations presented in Section 4.1 suggest that most and, perhaps all, of the contaminant mass is likely to reside in the matrix blocks in the form of dissolved and sorbed chemical. In such cases, the performance of steam-flush technologies will be tied to the degree they effect more rapid elimination of dissolved and sorbed chemical from the matrix blocks.

It is important to recognize that a steam front penetrates water saturated media via the process of volatilization, as opposed to hydrodynamic displacement. Therefore, the high entry pressures that form an effective barrier to entry of air, DNAPL, or other nonwetting fluids, do not influence steam-front penetration in the same way. The simultaneous penetration of steam fronts from all faces of a matrix block would appear to require that diffusion of volatilized chemicals be counter-current to the direction of steam flow. After the steam fronts coalesce, the diffusion from the matrix would be enhanced due to the increase in effective diffusion coefficient, owing to the presence of the gas phase.

5.2 Surfactant Flush

Introduction of surfactants can be anticipated to have two effects: 1) reduction of DNAPL-water interfacial tension and 2) enhanced effective solubility. Again, most or all of the mass in fractured porous media may reside in the matrix in sorbed and dissolved form (see Table 3). Surfactant flushes cannot be expected to reduce the mass stored in the sorbed or aqueous phases in a direct way. In fact, enhanced solubilization of DNAPL in the fractures might induce enhanced diffusion into the matrix for a period of time. However, it seems that the overall effect would be to create a low concentration on the block surfaces earlier than would otherwise be the case. Thus, diffusion out of the matrix to the fracture network would be induced. The process of reverse diffusion is significantly slower than the inward diffusion that occurred initially, and the overall rate of improvement would remain a process controlled by aqueous-phase diffusion.

There exists a very real danger of downward remobilization of DNAPL in the fractures. A reduction in interfacial tension produces a corresponding reduction of entry pressure. As pointed out previously, high entry pressures are often responsible for the cessation of downward migration. Even a minor reduction of interfacial tension can be anticipated to remobilize DNAPL halted in a fracture because of high entry pressures.

5.3 Creation of New Fractures

Suppose a matrix block has reached a condition of uniform contaminant concentration. Now the concentration in the bounding fractures is reduced to zero by some means. The fraction of initial mass that remains at time t is given by

$$F = P_1 P_2 P_3 \qquad 26$$

wherein the P_i are as previously defined by eqn. 23. Examination of eqn. 23 shows that the P_i decline with time is much more rapid for small L_i than for large L_i. Thus, an increased fracture intensity (i.e., reduced L_i) promotes enhanced diffusion from the matrix to the fractures. The characteristic diffusion time is inversely proportional to L_i^2. Therefore, the potential for greatly reducing matrix diffusion time exists.

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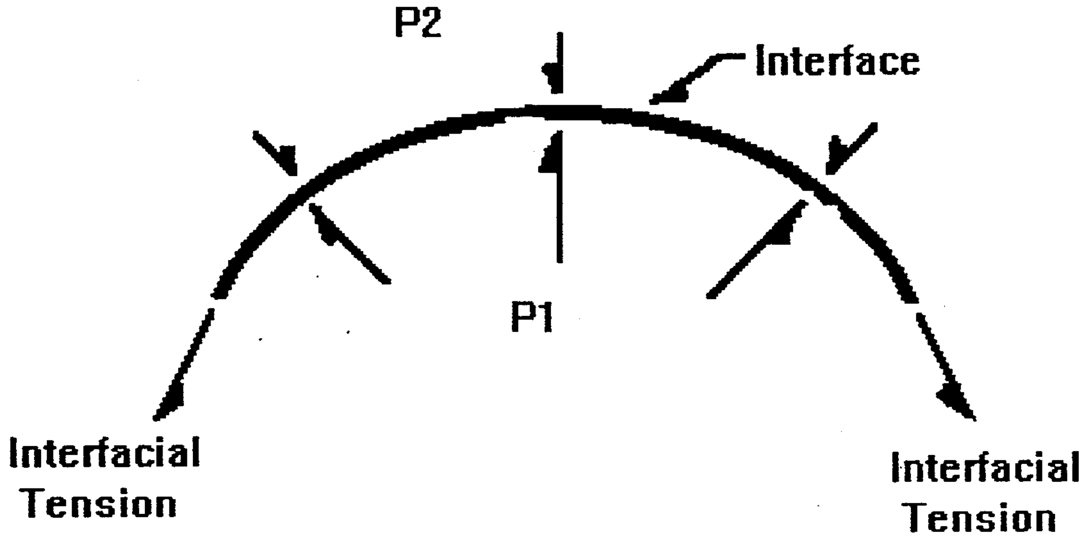

Figure 1. Forces acting on a curved interface.

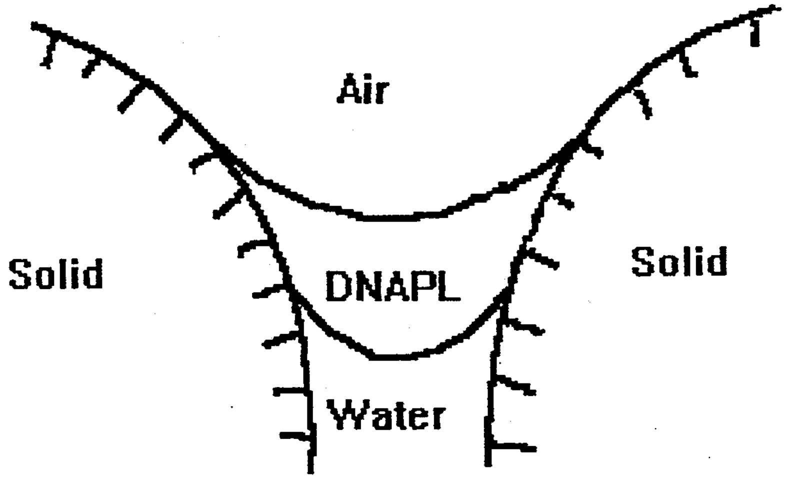

Figure 2. Schematic of fluid arrangement in a single pore.

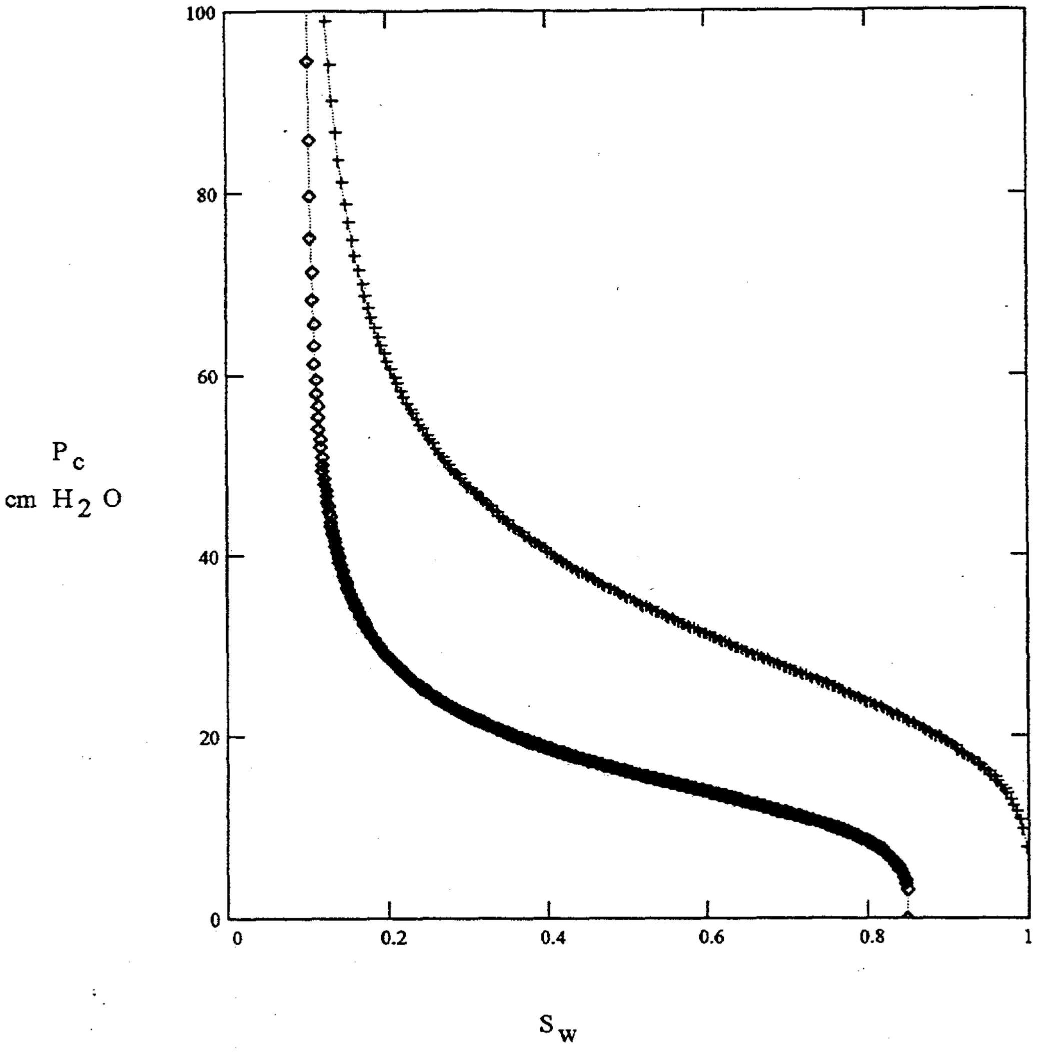

Figure 3. Typical capillary pressure-saturation relationship showing hysteresis between drying (upper curve) and wetting (lower curve). Residual DNAPL saturation is represented by the difference in water saturation where the two curves intersect the axis of zero capillary pressure.

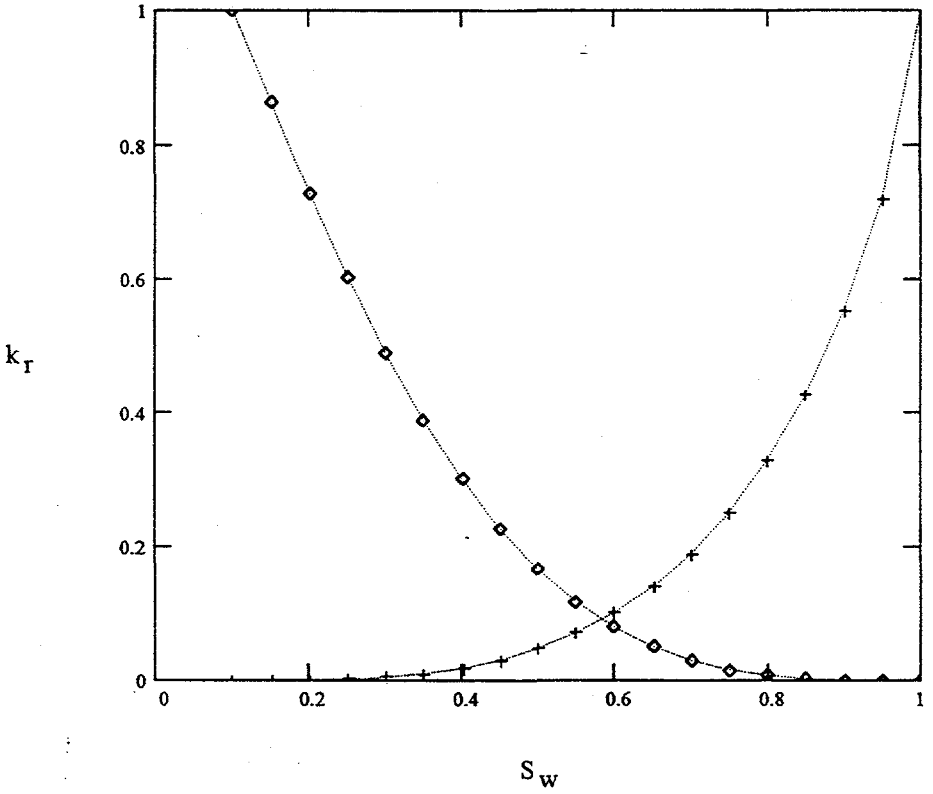

Figure 4. Typical relative permeability relationships. The relative permeability to water (right-hand curve) increases with increasing water saturation. The relative permeability to DNAPL (left-hand curve) decreases as more of the pore space is occupied by water.

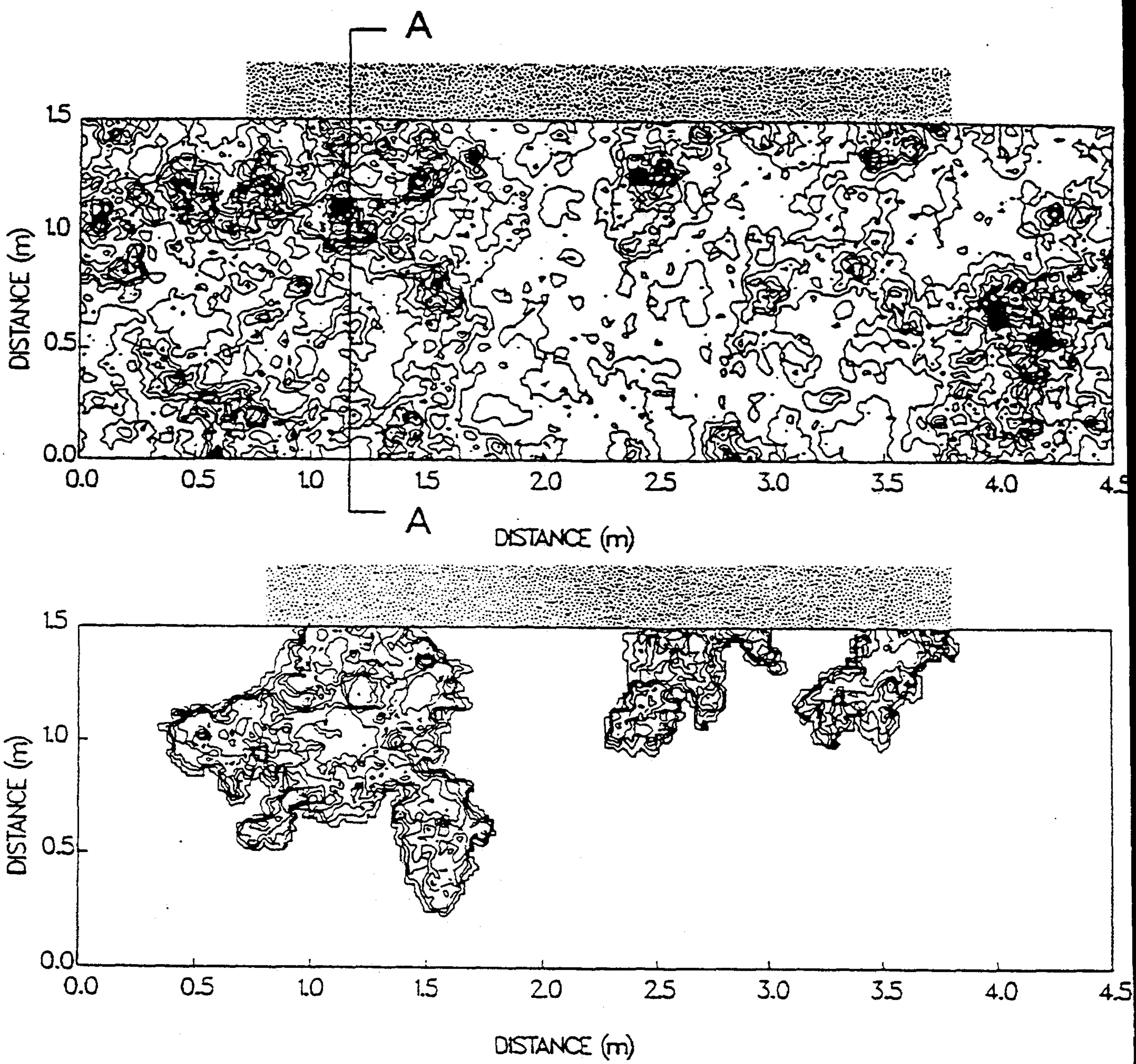

Figure 5. (a) Solution domain of fracture plane simulation. Contours represent fracture aperture, with a spacing of 10 microns. The apertures shown range from 10 to 2010 microns with the dark regions of closely spaced contours corresponding to the highest aperture regions of the fracture. (b) Distribution of trichloroethylene in fracture plane at t = 40.35 seconds. The outermost contour represents 2% saturation of trichloroethylene, with a contour spacing of 15% saturation.

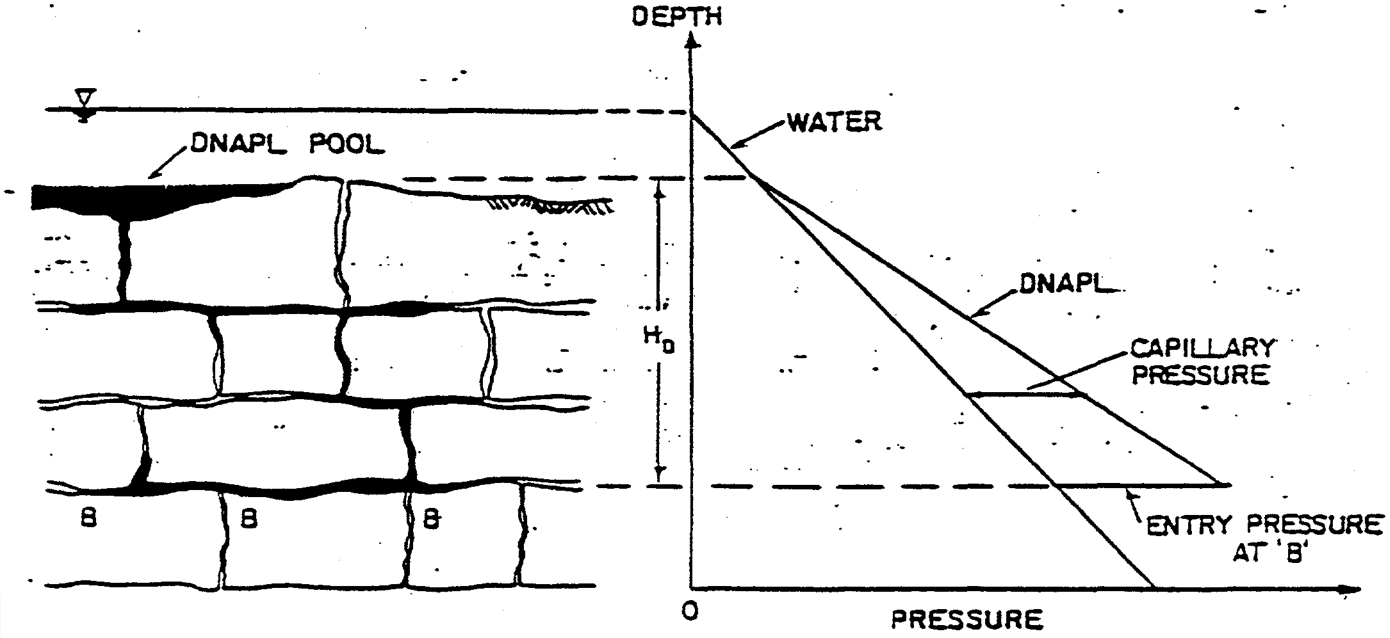

Figure 6. Pressure profiles for DNAPL at hydrostatic equilibrium in a network of fractures.

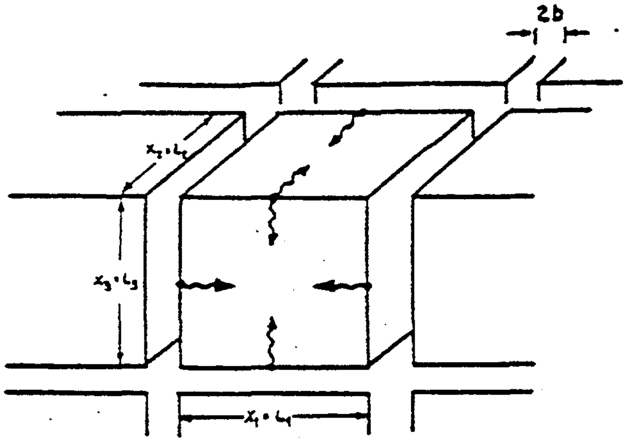

Figure 7. Conceptual model for 3-D finite matrix blocks.

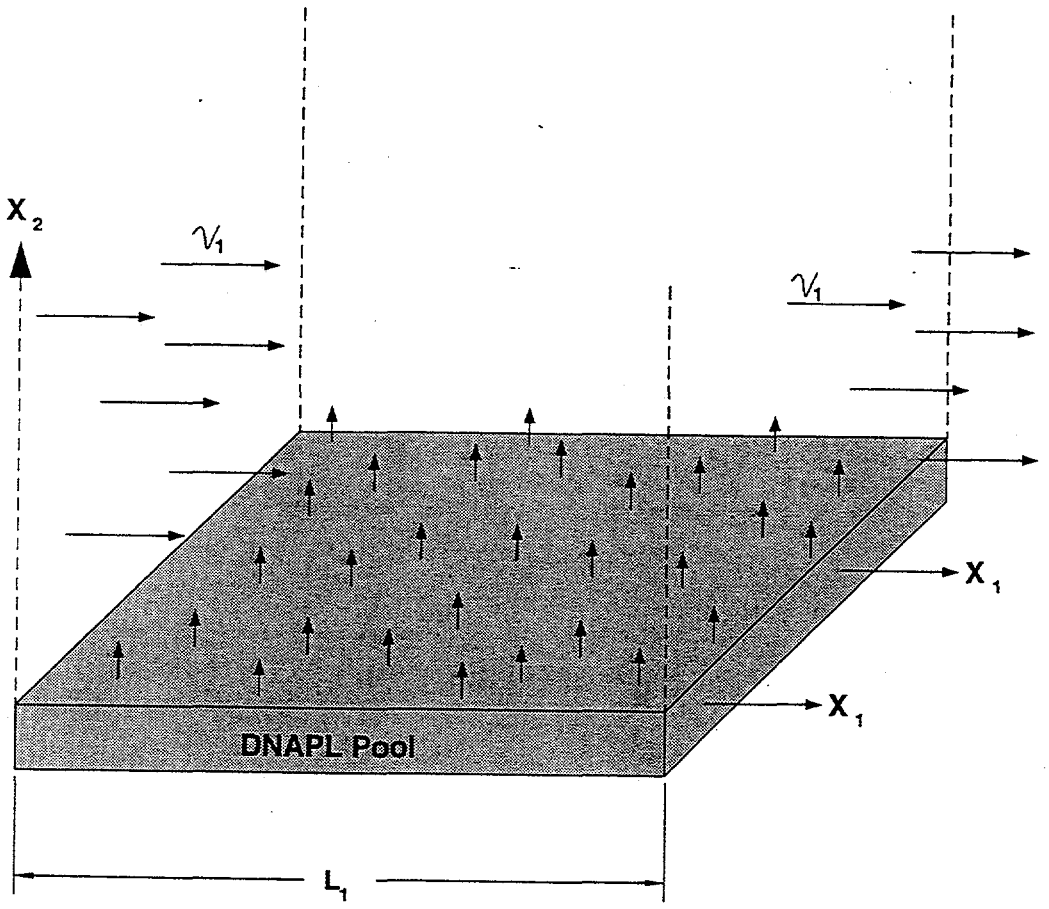

Figure 8. Mass transfer from a DNAPL pool to flowing ground water.

A FRAMEWORK FOR ASSESSING RISK REDUCTION DUE TO DNAPL MASS REMOVAL FROM LOW PERMEABILITY SOILS

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Many emerging remediation technologies are designed to remove contaminant mass from source zones at DNAPL sites in response to regulatory requirements. There is often concern in the regulated community as to whether mass removal actually reduces risk, or whether the small risk reductions achieved warrant the large costs incurred. This paper sets out a framework for quantifying the degree to which risk is reduced as mass is removed from shallow, saturated, low-permeability, dual-porosity, DNAPL source zones. Risk is defined in terms of meeting an alternate concentration level (ACL) at a compliance well in an aquifer underlying the source zone. The ACL is back-calculated from a carcinogenic health-risk characterization at a downstream water-supply well. Source-zone mass-removal efficiencies are heavily dependent on the distribution of mass between media (fractures, matrix) and phases (dissolved, sorbed, free product). Due to the uncertainties in currently-available technology performance data, the scope of the paper is limited to developing a framework for generic technologies rather than making risk-reduction calculations for specific technologies. Despite the qualitative nature of the exercise, results imply that very high mass-removal efficiencies are required to achieve significant long-term risk reduction with technology applications of finite duration.

2.0 INTRODUCTION

2.1 DOE Project

This focus paper has been prepared as part of a U.S. Department of Energy project on In-Situ Remediation of DNAPLs in Low-Permeability Media. The overall objective of the project is to develop a systematic understanding of the processes controlling the migration, remediation, and exposure risk posed by spills and leaks of DNAPLs such as chlorinated solvents in low-permeability soils.

The full project is planned to include laboratory tests, field studies, and modelling analyses of DNAPL migration and spill remediation. The preparation of this set of focus papers represents the first phase of the study. The purpose of these papers is to set down the current state of knowledge with respect to migration processes and exposure risk, and to assess the strengths and limitations of several emerging remediation technologies in low-permeability environments. Among the technologies under consideration are steam injection, surfactant flushing, air sparging, and thermal treatment through electrical-resistance or radio-frequency heating.

2.2 Purpose of This Paper

The remediation technologies under investigation in this project are designed to remove contaminant mass from DNAPL sites. When these sites are in low-permeability media, concern often exists in the regulated communities as to whether sufficient á priori risk exists to warrant remediation, or whether a no-action/monitoring-only strategy ought to be acceptable in many cases. In cases where it is agreed that risk exists, there is concern over whether mass removal actually reduces risk, or whether the small risk reductions achieved warrant the large costs incurred.

The purpose of this paper is to set out a framework for quantifying the degree to which risk is reduced as mass is removed from low-permeability DNAPL sites. The scope is limited to developing a framework rather than making risk-reduction calculations for specific technologies. The latter goal would require more-detailed technology performance data than are currently available. The analysis is also limited to one contaminant in one specific hydrogeological setting. It is hoped that development of this framework will point the way toward more general assessments of the relation between mass removal and risk reduction for a wider suite of contaminated subsurface environments.

2.3 DNAPL-Contaminated Sites

Figure 1 (after Cherry, et al, 1992) illustrates the anatomy of a DNAPL site. Spills and leaks at and near the ground surface often lead to quite localized DNAPL entry locations, but once in the subsurface and below the water table, DNAPL becomes more widely-distributed throughout a source-zone that encompasses the residualized DNAPL and the pools, ganglia and blobs of immobile free product. It is this extended volume of subsurface soil that represents the available source zone for the dissolved plume.

The contaminant mass in the source zone will distribute itself among the available phases according to the migration mechanisms and partitioning principles outlined in the focus paper by McWhorter (this volume). The contaminant mass may exist as: (1) pooled or residualized free product, or it may be (2) sorbed on the soil phase, or (3) dissolved in the water phase. A separate air phase will not exist naturally at depth in the saturated zone, which is the primary zone of interest for DNAPL studies, but it may be necessary to take it into consideration in analyses of air sparging or soil-vapor-extraction from dewatered sites. Air-phase partitioning is not included in the analyses in this paper.

The partitioning of contaminant mass within a source zone between free-product, sorbed, and dissolved mass depends on the hydrogeological environment, the size of the spill, and the nature of the contaminant. Emphasis in the DOE study is on chlorinated solvents. In this paper, trichloroethylene (TCE) has been selected as the contaminant of concern. Table 1 summarizes TCE properties. Of particular importance to the later risk deliberations is the value of the TCE solubility (1100 mg/l) relative to the regulatory standard (0.005 mg/l).

2.4 Hydrogeological Environments

Project studies are focused on an unconsolidated, stratified, low-permeability formation 3 m thick that is overlain by a thin sand and underlain by a sand aquifer. (Figure 2). The low-permeability formation is made up of layers ranging from medium sand ($K = 10^{-3}$ cm/s) to clay ($K = 10^{-6}$ to 10^{-8} cm/s) with an overall bulk hydraulic conductivity less than 10^{-5} cm/s. The water table is at the top of the low-permeability formation. It is assumed that TCE has leaked into the surficial sand layer and then entered the low-permeability formation, creating the source zone indicated on Figure 2.

The clay layers are assumed to contain natural desiccation fractures that are spaced 5-10 cm apart with apertures of 10-40 microns. For this fracture density, the fracture porosity is on the order of 10^{-3}. The matrix porosity for clays is about 0.35. Such media are typically treated as dual-porosity media. Bulk fluid flow is controlled primarily by the network of higher-permeability, fast-flushing, interconnected fractures, but contaminant mass transport is highly influenced by interactions with the isolated, lower-permeability matrix blocks. The nature and timing of natural migration processes, and the feasibility and effectiveness of the various remedial technologies, are largely dependent on the apertures, spacing and degree of connectivity of the fracture network.

There may be risk associated with the source zone itself, but more commonly, concern arises with respect to drinking-water supplies from aquifers that are impacted by plumes that emerge from source zones. Figure 2 shows the situation considered in this paper. Gradients are assumed to be vertically downward through the low-permeability deposits to the underlying aquifer, and horizontal gradients are assumed to exist in the aquifer that could transport dissolved contaminants offsite toward receptors. We assume that the point of exposure (POE) is a downstream water supply well in the underlying aquifer.

We will also consider the case where an underlying aquifer is not present. In that case, there may be no á priori risk, at least from offsite groundwater usage.

2.5 Fate and Transport of Contaminants

The feasibility and efficiency of the various remedial technologies is heavily dependent on the distribution of mass in the source-zone of our saturated, low-permeability, dual-porosity media. McWhorter (this volume) reviews the mechanisms of contaminant transport that control this distribution in such media. These mechanisms include NAPL infiltration, NAPL residualization, NAPL dissolution in water, diffusion of dissolved constituents into the matrix blocks from the fracture network, and sorption of dissolved constituents onto soil particles in the matrix blocks. The reasoning presented in McWhorter (this volume) leads to the following conclusions: (1) It is highly unlikely that free-product DNAPL will invade the matrix blocks during DNAPL infiltration. (2) DNAPL is likely to be very irregularly distributed throughout the fracture network, and within individual fractures. (3) DNAPL can be expected to migrate to significant depths in fracture networks. (4) If matrix storage capacity exceeds DNAPL mass, there is a potential for DNAPL in fractures to be totally depleted relatively quickly by diffusion of dissolved contaminant into the matrix blocks. (5) If total depletion does not occur, residualized DNAPL in the fracture network represents an immobile source for dissolved constituents.

Appendix I provides a rough calculation of the percentage mass distributions that will arise in the source zone after DNAPL infiltration, residualization, dissolution, matrix diffusion, and sorption have reached a state of equilibrium. Mass may reside in any of four states: (1) as free-product DNAPL in the fractures, (2) dissolved in the water in the fractures, (3) dissolved in the water in the matrix, and (4) sorbed on the solids in the matrix. The mass in (2) is very small relative to (1), (3) and (4). Table 2 summarizes the results from Appendix I. These source-zone distribution values are used throughout the rest of the paper as initial conditions for the technology assessments.

It should be noted that the distribution on Table 2 is based on an assumed fracture porosity of 10^{-3}. It is shown in Appendix I that smaller fracture porosities of 10^{-4} or 10^{-5} lead to very different distributions that have strong implications with respect to technology assessment.

As is clear from Table 2, the mass sorbed on the soil matrix, and existing as pooled free product in the fractures, provides the ongoing source of dissolved contamination in the water phase. For TCE in low-permeability source zones, one might expect dissolved concentrations to reach existing solubility limits (1100 mg/l for a single-component TCE source, lesser values based on Raoult's Law for multi-component mixtures). Such values are observed right next to NAPL-filled fractures in carefully-controlled experiments. However, maximum observed TCE concentrations in source zones in the field seldom exceed 100 mg/l. Anderson et al (1993) discuss possible reasons for this observation.

As illustrated in Figure 2, transport to a compliance well and/or a pumped water-supply well will require dissolved-contaminant migration: (1) vertically downward through the low-permeability media to the underlying aquifer and (2) laterally through the aquifer to receptors. Migration will be controlled by advection, diffusion, dispersion and sorption of the dissolved mass. It is likely that diffusion will be dominant in leg (1), advection in leg (2). There may or may not be dilution where the contaminants enter the aquifer. Dilutions from 100 mg/l, to say 10 mg/l might occur in some cases.

Under this scenario, the issue addressed in this paper reduces to the following question: Will the removal of mass from low-permeability source zones reduce downward mass flux to an underlying aquifer to a sufficient degree that offsite risk-based regulatory compliance based on dissolved concentrations can be achieved? This question is addressed in Section 6. In order to get to it, we must first examine the issues of remedial objectives and remedial compliance (Section 3), the concept of risk (Section 4), and the effectiveness of the various technologies in removing mass from the subsurface (Section 5).

3.0 REMEDIATION

3.1 Remedial Compliance

Groundwater remediation takes place in a highly-regulated environment. Most engineers who are asked to design remedial systems will feel that they have satisfied their ethical responsibilities to protect the health and safety of the public if they meet the compliance criteria established by regulatory agencies.

State and federal regulations vary widely, but in most cases, regulatory compliance takes the form of maintaining dissolved TCE concentrations below specified standards at a point of compliance (POC) in the aquifer underlying the low-permeability deposits (Figure 2). For our purposes, the specified standards may take one of two forms: (1) a maximum concentration level (MCL), or (2) an alternate concentration level (ACL) back-calculated from an MCL or a health-risk characterization at a downstream point of exposure (POE). The POE may be a water-supply well, or other receptor such as a stream. If a health-risk characterization is used, it must show that the cancer risk arising from a drinking-water ingestion pathway at specified daily intake rates is less than some acceptable level. In applications of federal CERCLA and RCRA statutes under EPA jurisdiction, the MCL for TCE is 0.005 mg/l, and the acceptable cancer risk lies in the range 10^{-4} to 10^{-6}.

In this paper, a risk-based ACL type of compliance will be presumed. We will assume that the downstream receptor is a water-supply well (Figure 2).

While this type of compliance is loosely based on federal EPA style, we recognize that our approach to future remedial strategies may run contrary to traditional EPA attitudes. We have not tried to adhere to the dictates of any particular state or federal legislation. We recognize that in many cases, the POC is taken as the downgradient boundary of the waste-management area, and the POE is specified at the downgradient edge of the current plume, but we do not limit ourselves to these definitions. We realize that cancer-risk goals for site remediation are usually set at 10^{-6}, but we understand that there may be some state precedent for higher risk goals of 10^{-5} for interim remedial measures of the type described later in this paper.

3.2 Remedial Objectives and Strategies

The primary remedial objective from the perspective of a site owner-operator is to achieve regulatory compliance at minimum cost.

There are two basic strategies that can be contemplated. Compliance can be attempted through: (1) containment, or (2) restoration, or some combination of the two. Cherry et al (1992) discuss these overall strategies. Ross (1993) assesses them from an environmental perspective.

Containment may be attempted at the plume front by creating a capture zone with a pump-and-treat system, or it may be limited to the source zone through the use of cutoff walls, treatment curtains, caps, and/or more localized pump-and-treat. The pump-and-treat containment option is the only strategy to date that has proven feasible, effective, and cost-efficient. However, it has the distinct disadvantage of requiring perpetual aquifer management. It has also been proven at many sites that mass removal rates provided by pump-and-treat are inconsequential. Pump-and-treat provides containment but not restoration (Cherry et al, 1992; USEPA, 1993).

The mass-removal technologies under assessment in the DOE study have aquifer restoration as their goal. Mass-removal technologies usually emphasize the source zone, although mass removal from the dissolved plume can also be contemplated. Mass-removal technologies are appealing in principle because they could lead to aquifer restoration in a finite period of time. However, to date, mass-removal efficiencies have been too low to justify anything but partial restoration, and economic feasibility is still an open question for most technologies at most sites.

Emphasis in this paper will be on assessing potential risk reduction due to partial restoration of low-permeability deposits through source-zone mass removal.

4.0 RISK

4.1 Two Concepts of Risk

The term "risk" is widely used in the waste-management industry in two very different senses: (1) as health risk to receptors in a regulatory health-risk characterization, and (2) as engineering risk to the owner-operator in an engineering decision analysis designed to compare alternative remedial alternatives, using a risk/cost/benefit approach. Both types of risk are pertinent to the risk-reduction issues at hand, and both will be addressed in this paper. The health-risk characterization is described in the following sub-section, and it is then carried through to completion in Section 6. An introduction to engineering risk analysis is presented in Section 7.

4.2 Regulatory Health Risk Characterization

A health-risk characterization must be carried out in support of a risk-based ACL compliance criteria of the type outlined in Section 3.1 The conceptual basis of the methodology, the steps in its application, and issues related to its interpretation are outlined in EPA manuals (1987,1989,1990). Myers (1990) provides specific discussion of ACL scenarios. Hallenbeck and Cunningham (1986) provide a non-EPA treatment of the concepts underlying risk assessment for environmental and occupational health.

A full EPA health-risk assessment involves five steps: (1) contaminant identification, (2) fate-and-transport analysis, (3) exposure assessment, (4) toxicity assessment, and (5) risk characterization.

The first step selects the indicator chemicals, or chemicals of concern (COCs) to be used in the risk characterization. In our case, the COC is assumed to be TCE.

The fate-and-transport analysis leads to an estimate of exposure-point concentrations of the COC. The fate-and-transport analysis may be based on analytical models in early scoping calculations for simple sites, or on numerical models for more sophisticated analyses of more complex sites. The models must include partitioning algorithms that will accurately reflect source-zone distributions of mass between various phases (NAPL-phase, sorbed phase, dissolved phase) and media (matrix, fractures); they must include mass-transfer algorithms to reflect in-situ processes such as sorption and biodegradation; and they must include consideration of transport processes such as advection, dispersion, and diffusion. The latter must be applied to all potential mobile phases, including NAPL, water, and in some cases, air.

The exposure-assessment step involves identifying the pathways to receptors, and estimating chemical intakes by exposed populations. In our case, the pathway is ingestion of groundwater from a water-supply well, and a standard drinking water intake of 2 l/day for a 70-kg adult (or 0.029 l/kg/day) is used. A 70-year lifetime is assumed.

The toxicity-assessment step develops the relationships between the magnitude of exposure to a chemical and the increased likelihood and severity of adverse effects. TCE is considered as a potential carcinogen. For carcinogens, a "slope factor" is defined that provides an upper- bound estimate of the probability of cancer per unit intake of a chemical over a person's lifetime. The slope factor for TCE is 0.011 $(\mathrm{mg/kg/day})^{-1}$.

The final risk characterization step uses the concentrations from step 2, the intakes from step 3, and the slope factor from step 4, to calculate the cancer risk:

$$\mathrm{CR} = \mathrm{CDI} \times \hat{\mathrm{C}} \times \mathrm{SF} \tag{4.1}$$

where:

CR = cancer risk for contaminant of concern [-]
CDI = chronic daily intake [l/kg/day]
$\hat{\mathrm{C}}$ = 70-year time-weighed average concentration of contaminant of concern at the exposure point [mg/l]
SF = slope factor for drinking-water ingestion pathway for contaminant of concern $[\mathrm{mg/kg/day}]^{-1}$

For TCE, at the MCL concentration of 0.005 mg/l, the cancer risk is 1.6×10^{-6}.

Let us refer again to Figure 2. Note that because the supply well may draw in clean water as well as potentially contaminated water, the exposure-point concentrations at the wellhead may be much less than the maximum concentrations in the plume. Under such circumstances, the back-calculated ACLs at a compliance point will therefore be much higher than the comparable MCLs. If only 10% of the water captured by the supply well were contaminated, then the ACL could be 10 times the MCL, or 0.05 mg/l. If only 1% of the well water were contaminated, the ACL could be 0.5 mg/l. If a cancer risk of 1.6×10^{-5} were acceptable, the comparable ACLs would be 0.5 mg/l and 5.0 mg/l.

Claff (1993) describes a decision support system for risk and exposure assessment that includes all the above steps. Cushman and Ball (1993) describe the application of such a system at several sites, and the acceptance by a state regulatory agency of risk-based cleanup levels based on ACL-type compliance.

Full health-risk characterization is beyond the scope of this paper. Emphasis will be on assessing the potential for decreasing TCE concentrations at a compliance point through mass removal in the source zone. Fate-and-transport calculations (Step 2) will be presumed for simple hypothetical cases like those analysed by McWhorter (this volume). Steps 3-5 of the health-risk characterization will not be carried out in detail. The linear nature of equation (4.1) insures a direct equivalence between percentage concentration reduction at the compliance point and percentage risk reduction at the exposure point.

4.3 The Question of Timing

The various technologies under consideration remove mass from different phases and media with different efficiencies over different time frames. One can conceive of an "effective technology" such as that shown on Figure 3 that reduces compliance-point concentrations below ACL and leads to large risk reduction relative to no-action/monitoring-only (NAMO). One can also conceive of a "delay technology", say one that removes mass efficiently from the fractures but not the matrix. Early migration to the compliance point is reduced, but reverse matrix diffusion after cessation of remediation, leads to a delayed buildup to NAMO levels at a later time. In this case, the selection of the 70-year period for the calculation of $\hat{C}$ to be used in equation (4.1) is significant. Does the delay in health risk constitute a "risk reduction" of value to the regulatory agency and/or the public?

In many risk assessments, the maximum anticipated concentration is used for the full 70-year CR calculation (cf. Cushman and Ball, 1993). However, this may be an example of the over-conservative nature of "upper-bound" risk characterization that upsets many site owner-operators and industry representatives. See Lehr (1990a,b) and Harris (1993) for discussions of this issue.

Our approach will be to differentiate between interim remedial measures (IRMs) and final records of decision (RODs). For IRMs, the CR should be calculated for the next 70 years and the predicted C(t) time series over that period should be used to calculate $\hat{C}$ in equation (4.1). For IRMs, delay technologies will lead to short-term risk reduction. For RODs, the CR should be calculated for the 70-year period in the future with the highest C. With this approach, long-term risk reduction must involve decreased maximum concentrations at compliance points, not just delays in reaching them. This differentiation between short-term risk reduction (decades) and long-term risk reduction (centuries) seems to fit well into the EPA's new guidance with respect to technical-impracticability (TI) issues at DNAPL sites (EPA, 1993). Short-term risk reduction during the IRM period may be valuable in terms of waiting for technology improvements in restoration technologies in the next few decades. If forthcoming, the improved technologies can be the basis of long-term risk reduction in the final ROD. Site containment through pump-and-treat or other measures represents the classic-case of short-term IRM risk reduction.

5.0 TECHNOLOGY PERFORMANCE

In order to assess risk reduction, it is necessary to analyze two cases: (1) the base case of NAMO natural migration, and (2) the remedial case, after completion of the application of the remedial technology (or, if not after completion, then after some specified period of remedial action). The risk reduction is the difference in risk between the two cases.

In order to carry out the base-case analysis, it is necessary to know the initial distribution of contaminant mass in the various phases and media of the low-permeability deposit, and the fate-and-transport mechanisms in the low-permeability deposit and in the underlying aquifer to compliance points and receptors. We will use Table 2 as an estimate of initial mass distribution. We assume vertical diffusion across the low-K unit and horizontal advection in the aquifer.

In order to carry out the remediated-case analysis, it is necessary to have technology-performance information in addition to the two items above. Ideally we would like to have estimates of timing and effectiveness of mass removal by the technology from the various phases and media in the low-K deposit. These might take the form of Table 3 or Figure 4, which are provided as an example. They provide a rough estimate of the performance characteristics that might be expected for a source-zone pump-and-treat system using a dual-well (water/NAPL) removal configuration. Efficiency is thought to be highest for dissolved mass in the fractures (which is a very small percentage of the total mass) and then NAPL in the fractures. If dissolved and sorbed mass in the matrix were to remain in equilibrium, then these two removal efficiencies should be the same. We feel the sorbed mass will be harder to remove and that disequilibrium will arise. The value for total mass removal on Table 3 takes into consideration both the performance estimates, and the estimate of initial mass distribution from Table 2.

Unfortunately, detailed performance information is not yet available for most of the emerging technologies under investigation in this study. Realistically, it may be necessary to work with simpler performance information such as total endpoint mass-removal effectiveness (as a % mass removal) and general timing (months, years, decades), as indicated on the right-hand-end of Table 3.

In principle, it would be desirable to carry out analyses of the remediated case for each technology (air sparging, steam injection, surfactant flushing, etc). In practice, even the simpler performance information indicated above may not be available for most of the technologies. For the purposes of this paper, therefore, we will fall back on making qualitative sample calculations for hypothetical technologies (Technology A, Technology B, etc) with specified mass-removal performance characteristics similar to the suite of actual technologies under investigation in the DOE study. It is hoped that in the future, as more complete performance data become available for the various technologies from laboratory and field testing, the framework suggested here will prove suitable for more technology-specific risk-reduction calculations.

Table 4 lists four generic technologies with their assumed mass removal efficiencies; Figure 5 provides a qualitative view of assumed timing. Technology A is a repeat of Table 3 and might represent NAPL/water removal by pump-and-treat. Technology B is meant to represent a rapid-flushing thermal treatment option such as steam flushing that is effective in removing NAPL from fractures. Technology C is an enhanced version of Technology B, perhaps based on hydraulic or pneumatic fracturing to reduce matrix diffusion paths and increase mass removal efficiencies from the matrix. Technology D is a remedial approach that is effective in both fractures and matrix but which is slow-acting.

The mass removal efficiencies are largely dependent on the ability of circulating fluids (water, air, steam, surfactants, etc.) to contact contaminant mass. The distribution of mass is in turn largely dependent on site-specific hydrogeological factors. The total-mass-removal figures on Table 4 are controlled by the NAPL-removal effectiveness from the fractures and the removal of sorbed mass from the matrix, given that 87% of the initial mass is assumed to be in these two modes. Sites with less NAPL might exhibit different mass-removal profiles and different levels of total effectiveness. In general, the values presented on Table 4 are thought to be optimistic rather than pessimistic.

6.0 HEALTH RISK REDUCTION

6.1 Summary of Conditions

The framework and general conclusions presented in this section with respect to health risk reductions are based on the (somewhat restrictive) set of conditions that have been developed through the preceding four sections. These can be summarized as follows:

(1) The contaminant of concern is TCE.
(2) The low-permeability hydrogeological environment is a dual-porosity medium consisting of fractures and matrix. Two cases are considered, one with an underlying aquifer, and one without.
(3) Initial mass distribution in the source zone is 48% pooled and residual NAPL in the fractures, 39% sorbed on the matrix, and 13% dissolved. Dissolved-phase concentrations of TCE in the source zone are on the order of 100 mg/l.
(4) Mass transport of dissolved contaminants from the source zone to receptors occurs as vertical diffusion across the low-permeability deposit and horizontal advection through the aquifer. Dilution of dissolved TCE concentrations from 100 mg/l to 10 mg/l may occur where the vertical plume enters the horizontal aquifer.
(5) The exposure pathway is drinking-water ingestion from a downstream water-supply well in the aquifer. Regulatory compliance is with respect to an ACL at a monitoring well between the source and the receptor, with the ACL established on the basis of 10^{-4} to 10^{-6} carcinogenic health risk. Depending on the risk level deemed acceptable and the percentage of contaminated water captured by the supply well, the ACL could lie anywhere in the range 0.005 mg/l to 5.0 mg/l.
(6) The percentage reduction in health risk at the receptor is equivalent to the percentage reduction in contaminant concentration at the compliance point.
(7) Differentiation is made between short-term IRM risk and long-term ROD risk.
(8) Discussions of risk reduction are carried out with respect to containment and with respect to four generic mass removal technologies A,B,C and D.

6.2 Case 1: No À Priori Risk

If there is no aquifer underlying (or connected in some way to) the contaminated low-permeability source zone, or if the aquifer contains saline (or otherwise non-potable) water, or if there are no receptors of water from the aquifer (and never will be), then it can be argued that there is no à priori health risk due to groundwater usage. In such cases, mass removal from the source zone cannot provide risk reduction. This is a trivial conclusion, but one that is relevant to many sites. At such sites, there may still be well-placed and defensible societal pressures to provide site cleanup, but given the limited amount of societal resources that can be directed to environmental concerns, and the pressing needs at many sites where meaningful risk reduction can be achieved, it may be that a no-action decision is the correct one, even from a societal perspective.

6.3 Case 2: NAMO

In cases where an underlying aquifer is present, and migration routes exist between source and receptor, the calculation of risk reduction that can be achieved by mass removal from the source zone requires comparison of the remediated case against the NAMO case of natural migration.

Consider Figure 6a. The dissolved TCE concentration in the source zone is 100 mg/l. Diffusion across the low-K unit will lead to a mass-flux rate into the underlying aquifer across AB. Dilution to a concentration of 10 mg/l may occur. If so, advection in the aquifer will ultimately lead to a maximum concentration of 10 mg/l or less at the compliance monitoring well. Retardation due to sorption in the aquifer will delay it but not reduce it. Dispersion could reduce it. If the maximum concentration is less than the ACL, no à priori risk exists. If the concentration is greater than the ACL, à priori risk exists, and an analysis of potential risk reduction through alternative remedial actions is called for. On Figure 6a, Δt_1 is the time required for contaminants to diffuse through the low-K layer from the source zone to the aquifer, and Δt_2 is the time required for contaminants to advect through the aquifer to the POC.

6.4 Case 3: Containment: Plume Capture by Aquifer Pumping

Consider Figure 6b. A groundwater pump-and-treat system is installed in the aquifer downstream of the contaminated site, such that all mass flux across AB is encompassed in the capture zone of the pump-and-treat system. The TCE concentration at the compliance well will decline, ultimately (in principle) to zero, leading to significant (or even complete) risk reduction. However, if the system is turned off, concentrations will increase to their former level. Short-term risk reduction will be significant, but unless pump-and-treat containment is maintained in perpetuity, long-term risk reduction is not achieved (Table 5).

6.5 Case 4: Technology A

Technology A (Table 4) sweeps only 50% of the NAPL from fractures, and has an overall removal efficiently of just 33%. It is unlikely that such a removal efficiency will significantly impact NAPL dissolution in water. It is likely that dissolved concentrations in the source zone will remain at 100 mg/l. Under these circumstances mass flux to the aquifer by diffusion will not be reduced (Figure 6c) and significant risk reduction will not be achieved on either the short-term or the long-term (Table 5).

6.6 Case 5: Technology B

Technology B (Table 4) removes 90% of the NAPL from fractures and has an overall efficiency of 52%. Such a removal efficiency is likely to clean some volume elements of the fractures completely, but leave others with sufficient residual NAPL to maintain dissolution rates and concentration levels at 100 mg/l. This partial restoration could lead to a reduction in mass flux to the aquifer but it may not lead to sufficient reduction in concentration at the compliance point to cross the ACL threshold (Figure 6c). If not, then short-term risk reduction will not be significant (Table 5). Technology B does not remove mass from the matrix efficiently, so long-term risk reduction after cessation of the remediation will also not be significant (Figure 6c, Table 5).

6.7 Case 6: Technology C

Technology C is an enhanced fast-flushing technology with improved NAPL-removal efficiency from fractures (95%) and improved efficiency in the matrix (50% for sorbed, 75% for dissolved). The overall efficiency is 78%. As indicated on Figure 6c and Table 5, such fracture efficiencies might lead to significant short-term risk reduction, but the matrix efficiencies are not likely to lead to long-term risk reduction. Reverse matrix diffusion after cessation of remediation will likely lead to a buildup of concentration that will ultimately exceed the ACL again.

6.8 Case 7: Technology D

It is possible that Technology D (Table 4) with an overall efficiency of 95%, could provide both short-term and long-term risk reduction (Figure 6c, Table 5) from application over a finite period of time.

6.9 Disclaimer

The above analyses are conceptual. We recognize that readers may be somewhat let down by the qualitative nature of our fate-and-transport analysis. We do not feel it is reasonable to include quantitative fate-and-transport calculations, given the qualitative understanding and large uncertainties associated with technology performance. Detailed site-specific modelling would be needed to determine the actual threshold values for removal efficiencies from fractures and matrix that would lead to significant risk reduction. It is not known whether the 95% value used in Section 6.7 is realistic, or whether higher efficiencies would be needed, or lower efficiencies adequate. The threshold value is dependent on the size and nature of the source zone, the hydrogeological environment, the ACL value, and the compliance location.

6.10 Summary of Analysis of Health-Risk-Reduction

The ultimate goal of a risk-reduction framework of the type presented here might be to produce a summary plot of the type shown in Figure 7. Once again, the disclaimer of Section 6.8 applies: the figure is conceptual, the values on the figure have qualitative but not quantitative significance.

Figure 7 is a plot of concentration reduction at the compliance point (relative to no action) achieved by technologies with different total-mass-removal efficiencies. The four generic technologies from Table 4 are plotted, using the qualitative performance indicated on the bottom plot of Figure 6c. Two curves are presented on Figure 7, one corresponding to short term achievements, and one corresponding to long-term achievements.

Because concentration reduction is linearly related to risk reduction in our framework (Section 4.2), the vertical scale on Figure 7 can be considered equivalently as a concentration-reduction ordinate or a risk reduction ordinate. Significant risk reduction is achieved only if the ACL threshold is crossed.

Even in qualitative form, Figure 7 implies that very high total-mass-removal efficiencies are required to achieve significant long-term risk reduction with technology applications of finite duration. It is unlikely that current technologies can achieve such efficiencies in heterogeneous low-permeability soils that exhibit dual-porosity properties and preferential pathways.

We are quite concerned that the message of this paper will be misread as an argument for no action at contaminated sites. Nothing could be further from our intention. We support containment of currently contaminated sites, and we encourage further research into mass-removal technologies. However, given the limited social funds available for environmental protection, it is important to insure that public policies utilize these funds for maximum public benefit, and do not waste them on efforts that are outside the current range of technical feasibility. We concur with Cherry et al (1992) that the primary goal of current remediation should be short-term risk reduction, with the aim to pass on to future generations site conditions that are well-suited to the future application of emerging technologies with improved mass-removal capabilities.

7.0 ENGINEERING RISK REDUCTION

7.1 Introduction

In Section 4.1, two concepts of risk were introduced: (1) health risk, and (2) engineering risk. In Section 6.0, emphasis was placed on health-risk characterization. Such a characterization is usually carried out by the owner-operator of a contaminated site for the purpose of establishing a risk-based alternate concentration level (ACL) that he or she hopes will be accepted by a regulatory agency as a compliance standard. Comparisons of alternative remedial technologies are carried out only from the point of view of whether or not they will lead to compliance, either on a short-term basis using an interim remedial measure (IRM), or on a long-term basis in a final record of decision (ROD). There is no consideration in this approach of the relative costs of the alternative technologies, or of the relation between costs and the level of risk reduction achieved. These latter questions fall into the domain of engineering decision analysis, utilizing the concept of engineering risk.

As noted in Section 3.2, the primary remedial objective from the perspective of a site owner-operator is to achieve regulatory compliance at minimum cost. Let us assume that an ACL has been established at a specified monitoring-well compliance point in an aquifer underlying a low-permeability site (Figure 2) on the basis of a health-risk characterization. The owner-operator wishes to select the technology that will meet the ACL at minimum cost. The techniques of hydrogeological decision analysis (Freeze, et al, 1990, 1992) can be applied. This brief introduction to the approach covers: (1) the definition of an economic objective function, (2) the selection of a suite of alternatives, (3) the concept of hydrogeological uncertainty, (4) the use of stochastic fate-and-transport models, (5) a summary of the methodology, and (6) a hypothetical example.

7.2 Objective Function

Alternative technologies are compared using an economic objective function defined as the net present value of the future stream of benefits, costs and risks, taken over an engineering time horizon, and discounted at the market interest rate. In a site remediation context, there are no direct benefits (that is there is no income that accrues to the decision maker from the remedial decision). The objective function is therefore a risk-cost minimization:

$$\Phi_j = \text{Min} \sum_{t=0}^{T} [1/(1 + i)^t] \; [C_j(t) + R_j(t)] \tag{7.1}$$

where
Φ_j = objective function for alternative j [\$],
$C_j(t)$ = costs of alternative j in year t [\$],
$R_j(t)$ = risks of alternative j in year t [\$],
T = engineering time horizon [years], and
i = annual market discount rate [decimal fraction].

In this context, the risks in (7.1) are defined as the expected costs associated with a probability of failure:

$$R_j(t) = Pf_j(t) \cdot Cf_j(t) \tag{7.2}$$

where
$Pf_j(t)$ = probability of failure of alternative j in year t [decimal fraction]
$Cf_j(t)$ = costs associated with failure of alternatives j in year t [\$]

Failure is defined as not meeting the ACL at the compliance point.

The direct costs, $C_j(t)$, in (7.1) are the capital costs of building the technology (wells, pumps, heaters, treatment plants, etc). The risk costs, $Cf_j(t)$, in (7.2) are the probabilistic costs that would have to be borne in the event of failure (additional remediation, regulatory penalties, litigation costs, loss of goodwill in the community, etc). In reality, these costs will either have to be borne or they will not, depending on whether the technology succeeds or fails. But at the decision-making stage they are treated probabilistically, because it is not known what the future holds with respect to success or failure.

The technology with the lowest value of Φ is the technology that is selected for application.

7.3 Alternatives

The alternative technologies under consideration might be: (1) NAMO, (2) containment by pump-and-treat, and (3) technologies A,B,C or D. The performance of these technologies was discussed in Section 5.0, Table 4, and Figure 5. Their ability to meet the ACL at a compliance point was discussed in Section 6.0, Table 5, and Figure 6. These data would provide qualitative input for estimates of the necessary time horizon, T, and probability of failure, $Pf_j(t)$ for each technology. In addition, it would be necessary to develop estimates of capital costs, operating and maintenance costs, and closure costs for each technology. Depending on the anticipated costs associated with failure, $Cf_j(t)$, it could be more advantageous to the owner-operator to select a low-cost/high-risk technology, or a high-cost/low-risk technology.

Alternatives can be specified within technology classes as well. It may be necessary to compare several pump-and-treat containment options, for example, each with different numbers of wells, locations of wells, and pumping rates; each producing a more-or less-robust capture zone; each with different costs and probabilities of failure.

7.4 Hydrogeological Uncertainty

The reason that failure or success of a remedial technology cannot be predicted with certainty is because of the many uncertainties in the system that must be analysed. These include uncertainties in : (1) the geological stratigraphy and pattern of dual-porosity elements, (2) the spatial pattern of values of the heterogeneous hydrogeological parameters such as porosity and hydraulic conductivity, (3) the mass and extent of contamination, and the degree of partitioning between NAPL, water, air, and soil, and between matrix and fractures, and (4) the mass-removal efficiencies of the remedial technologies.

The emerging techniques of geostatistics can be used to provide statistical descriptions of the parameters for items (1), (2) and (3) above. These descriptions take into account both the most likely values for the parameters, and the uncertainties associated with these estimates. In the application at hand, it may or may not make sense to employ complex geostatistical models. The greatest uncertainties are likely associated item (4), the mass-removal efficiencies of the remedial technologies.

7.5 Stochastic Fate-and-Transport Models

If there were no uncertainties in the technologies or in the hydrogeological system, then it would be possible to define all the input parameters exactly, carry out a deterministic fate-and-transport simulation, and determine the success or failure of a proposed remedial technology with certainty. In the traditional engineering approach, this deterministic style is usually followed, using the most-likely estimates of the parameters in a single fate-and-transport simulation. The influence of uncertainty is implicitly taken into account by carrying out sensitivity analyses, and invoking a safety factor in the engineering design.

The emerging risk-based style is to explicitly include consideration of uncertainties by using probabilistic distributions to define initial mass distributions and technology efficiencies and geostatistical patterns to define hydrogeological input parameters then performing the fate-and-transport simulations in stochastic mode. If the simulation is analytical, there are uncertainty propagation methods available. If the simulation is numerical, then Monte Carlo runs are usually carried out.

The output from a stochastic simulation is a probabilistic distribution of concentrations as a function of time at the compliance point. Comparison with the ACL allows definition of the probability of failure, $Pf_j(t)$, in any given year, for any given technology.

7.6 Summary of Engineering-Decision-Analysis Methodology

The steps required in the decision analysis to select the best remedial technology at a contaminated site are as follows:

(1) Define the economic objective function as a risk-cost minimization.
(2) Decide on the alternative technologies under consideration, and estimate the costs associated with each.
(3) Estimate the costs that would be associated with a failure to meet regulatory compliance standards.
(4) Use available site data to develop geostatistical descriptions of the input parameters.
(5) Carry out the fate-and-transport analysis in stochastic mode to produce an estimate of the probability of failure for each technology.
(6) Use steps (3) and (5) to calculate the engineering risk, combine them with the costs from (2), and calculate the value of the objective function (1) for each technology.
(7) Select the technology that minimizes the total expected sum of cost and risk.

7.7 Hypothetical Example

Consider a site similar to that shown in Figure 2. A short-term IRM is under consideration. The time horizon for comparing remedial alternatives is 5 years. A nearby downstream compliance well is contaminated. A regulatory consent order decrees that if the well is not in compliance at the end of the 5-year period, the site must be excavated. Two technologies are under consideration: (1) Containment by plume capture through aquifer pumping, as illustrated in Figure 6b, and (2) Technology C, an enhanced rapid-flushing thermal treatment option such as steam flushing, with source-zone performance characteristics illustrated in Figures 5 and 6c.

The direct costs and risk costs for each of these technologies, as well as the NAMO option, are listed on Table 6. The ultimate result is the value of the objective function, as calculated from Equation (7.1), on the right-hand column of Table 6. The values on Table 6 are in dimensionless dollar units. Depending on the scale of the site, the units could be viewed as \$10,000, \$100,000 or \$1,000,000 each. The cost of excavation at the end of year t=5 is assumed to be 100 units. It is assumed on Table 6, that monitoring wells have already been installed, and that sampling-and-analysis costs would be equal for all three options. For this reason, monitoring costs are not included on Table 6. The discount rate is taken as 10%.

The NAMO option involves no capital costs at t=0 and no operation and maintenance (O&M) costs in years t=1 to t=5. The probability of failure is 100% (Pf=1); the cost of failure CF is the excavation cost of 100 units; the risk cost R, which occurs at the end of year 5, is therefore 100 units. The discounted risk (Equation 7.1), which is the only component of the objective function, is 62 dollar units.

Containment by plume capture through aquifer pumping is assumed to have capital costs of 10 units, O&M costs of 2 units/year, and robust performance with a probability of failure of only 10%. The net-present-value objective function is 24 dollar units.

Technology C has larger capital costs of 20 units, a one-time-through O&M cost of 4 units in year t=1, and a less-certain performance with Pf=30%. The objective function is 42 dollar units.

For this hypothetical example, then, the owner-operator of the site would select the containment option rather than Technology C. Both represent considerable engineering-risk reduction over NAMO.

We emphasize that this example is purely hypothetical. The values on Table 6 have no generic significance. It is not meant to imply that containment is always preferable to mass removal. Different hydrogeological environments, different remedial objectives, and different economics, will lead to unique conclusions for each site investigated. The hypothetical example is presented for the sole purpose of illustrating the engineering-decision-analysis methodology.

8.0 ACKNOWLEDGEMENTS

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APPENDIX I
CALCULATION OF ROUGH ESTIMATE OF PERCENTAGE MASS DISTRIBUTIONS IN SOURCE ZONE

Given the fate-and-transport mechanisms discussed in McWhorter (this volume), DNAPL mass introduced into a dual-porosity, low-permeability medium will begin to partition itself between the two media (fractures, matrix) and the three phases (water, free product, solid) such that an equilibrium distribution is eventually reached. Mass may ultimately reside in any of four states:

(1) as free-product DNAPL in the fractures.

(2) dissolved in the water in the fractures.

(3) dissolved in the water in the matrix.

(4) sorbed on the solids in the matrix.

The mass of free-product NAPL in the fractures is given by:

$$M_{nf} = \phi_f S_{nf} \rho_n \tag{I.1}$$

where:
M_{nf} = mass of NAPL in fracture per unit volume of dual porosity medium [M/L^3]
ϕ_f = fracture porosity
S_{nf} = NAPL saturation in the fracture space
ρ_n = mass density of NAPL [M/L^3]

The mass dissolved in the water in the fractures is given by:

$$M_{wf} = \phi_f S_{wf} C_{wf} \tag{I.2}$$

where
M_{wf} = dissolved mass in fracture per unit volume of dual-porosity medium [M/L^3]
S_{wf} = water saturation in the fracture space
C_{wf} = mass concentration in the water phase in the fracture [M/L^3]

The mass dissolved in the water in the matrix is given by:

$$M_{wm} = \phi_m C_{wm} \tag{I.3}$$

where
M_{wm} = dissolved mass in matrix per unit volume of dual-porosity medium [M/L$^{3]}$
C_{wm} = mass concentration in the water phase in the matrix [M/L^3]
ϕ_m = matrix porosity

The mass sorbed on the solids in the matrix, assuming a linear sorption isotherm, is given by:

$$M_{sm} = \rho_b f_{oc} K_{oc} C_{wm} \tag{I.4}$$

where M_{sm} = sorbed mass on the matrix solids per unit volume of dual -porosity medium $[M/L^3]$
ρ_b = dry bulk density of soil $[M/L^3]$
f_{oc} = fraction organic carbon in the matrix
K_{oc} = organic-carbon partition coefficient $[L^3/M]$

Calculations have been carried out using equations (I.1) through (I.4) to determine the equilibrium mass distribution, assuming the DNAPL is single-species TCE. In these calculations it was assumed that the fractures were almost saturated with DNAPL, so that S_{nf} approaches unity and S_{wf} approaches zero. This has little impact on M_{wf}, which is very small regardless of the assumption on S_{wf}, but it may overestimate M_{nf}. It was also assumed that $C_{wf} = C_{wm} = C_{sol}$, where C_{sol} is the solubility of TCE, equal to 1100 mg/l. This may lead to overestimates of both M_{wm} and M_{sm}, but will not affect their ratio. Other parameter values are as follows: $\rho_n = 1.46$ g/cm^3, $\phi_m = 0.35$, $\rho_b = 1.72$ g/cm^3, $f_{oc} = 0.005$, $K_{oc} = 126$ cm^3/g, and $\phi_f = 10^{-3}$.

The results of the calculations indicate $M_{nf} = 1.46$ kg/m^3, $M_{wf} = 0$, $M_{wm} = 0.39$ kg/m^3, and $M_{sm} = 1.19$ kg/m^3. In percentages, $M_{nf} = 48\%$, $M_{wf} = 0\%$, $M_{wm} = 13\%$, and $M_{sm} = 39\%$. These are the percentages that are presented in Table 2 and used in the subsequent calculations in the main body of the paper.

It is worth noting that the mass-distribution percentages are very sensitive to the fracture porosity, ϕ_f. Table I.1 shows the distributions for $\phi_f = 10^{-3}$, 10^{-4}, and 10^{-5}.

Table I.1. Percentage Mass Distribution of TCE for Various Values of Fracture Porosity

Fracture Porosity	Sorbed on Soil Phase		NAPL Phase		Dissolved in Water Phase	
	Matrix	Fractures	Matrix	Fractures	Matrix	Fractures
10^{-3}	39	0	0	48	13	0
10^{-4}	70	0	0	8	22	0
10^{-5}	75	0	0	< 1	25	0

Table 1. Properties of TCE

Density	1.46 g/cm^3
Solubility	1100 mg/l
Vapor Pressure	58.2 mm Hg
Henry's constant	0.30
Log octonal-water partition coefficient	2.4
Regulatory standard: SDWA MCL	0.005 mg/l

Table 2. Rough Estimate of Percentage Mass Distributions in Source Zone

Sorbed on Soil Phase		NAPL Phase		Dissolved in Water Phase	
Matrix	Fractures	Matrix	Fractures	Matrix	Fractures
39%	0	0	48%	13%	<1%

Table 3. Rough Estimate of Percentage Mass Removal from Source Zone by Dual-Well (NAPL/Water) Pump-and-Treat System

Sorbed on Soil Phase		NAPL Phase		Dissolved in Water Phase		Total	Timing
Matrix	Fractures	Matrix	Fractures	Matrix	Fractures		
15%	-	-	50%	25%	100%	33%	Years

Table 4. Mass Removal Percentages for Four Generic Technologies

	Sorbed on Soil Phase		NAPL Phase		Dissolved in Water Phase		Total	Timing
	M	F	M	F	M	F		
Technology A	15%	-	-	50%	25%	100%	33%	Years
Technology B	15%	-	-	90%	25%	100%	52%	Months
Technology C	50%	-	-	95%	75%	100%	78%	Months
Technology D	95%	-	-	95%	100%	100%	95%	Decades

Table 5. Health-Risk Reduction

Case	Objective	Technology	Significant Risk Reduction?	
			Short-Term IRM	Long-Term ROD
3	Containment by Plume Capture through Aquifer Pumping	A	Yes	No
4	Mass-Removal	B	No	No
5	Mass-Removal	C	Maybe	No
6	Mass-Removal	D	Yes	Maybe

Table 6. Engineering-Risk Reduction

	DIRECT COSTS						RISK COST			OBJECTIVE FUNCTION
	Capital Costs	0&M Costs					Pf	Cf	R	Φ
	t=0	t=1	t=2	t=3	t=4	t=5	t=5	t=5	t=5	
NAMO	0	0	0	0	0	0	1	100	100	62
Containment by Plume Capture through Aquifer Pumping	10	2	2	2	2	2	0.1	100	10	24
Technology C	20	4	0	0	0	0	0.3	100	30	42

All values in dimensionless $ units.
Time horizon = 5 years
Discount rate = 10%

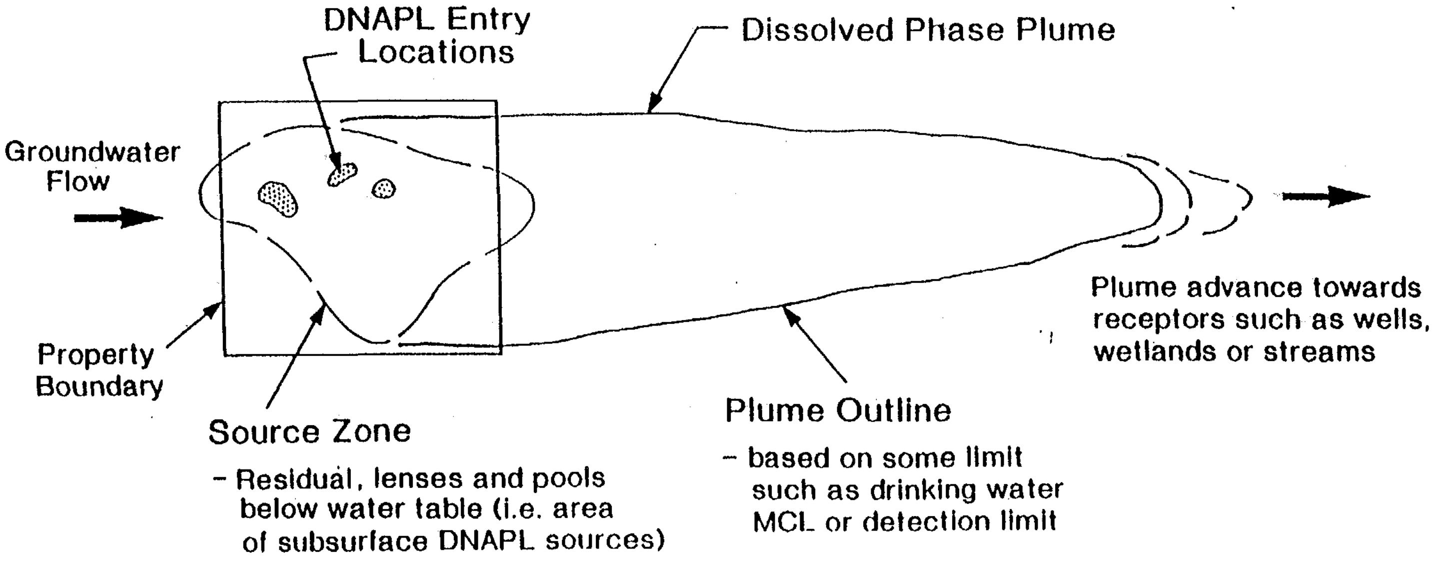


Figure 1. The anatomy of a DNAPL site (after Cherry, et al., 1992).

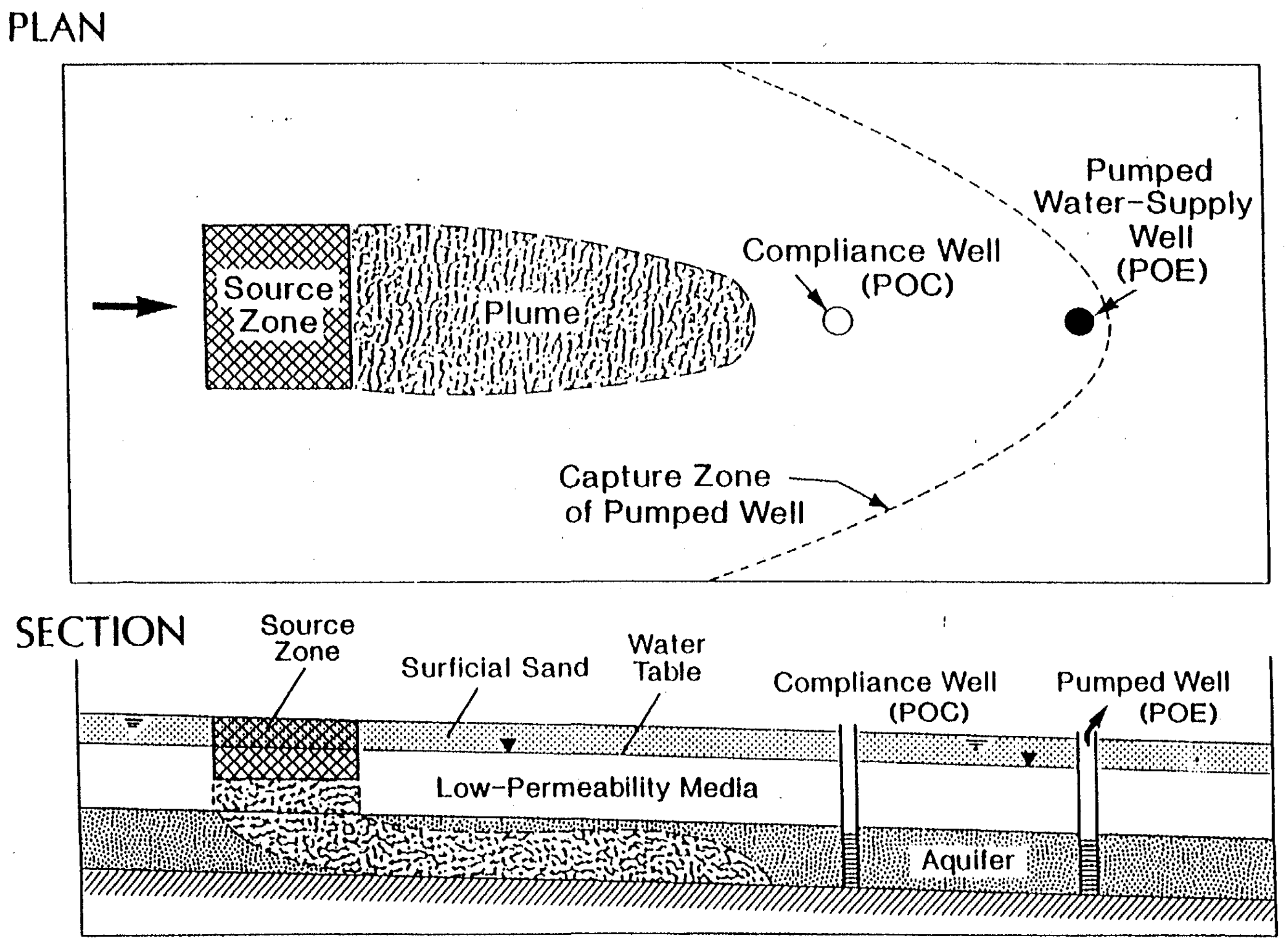
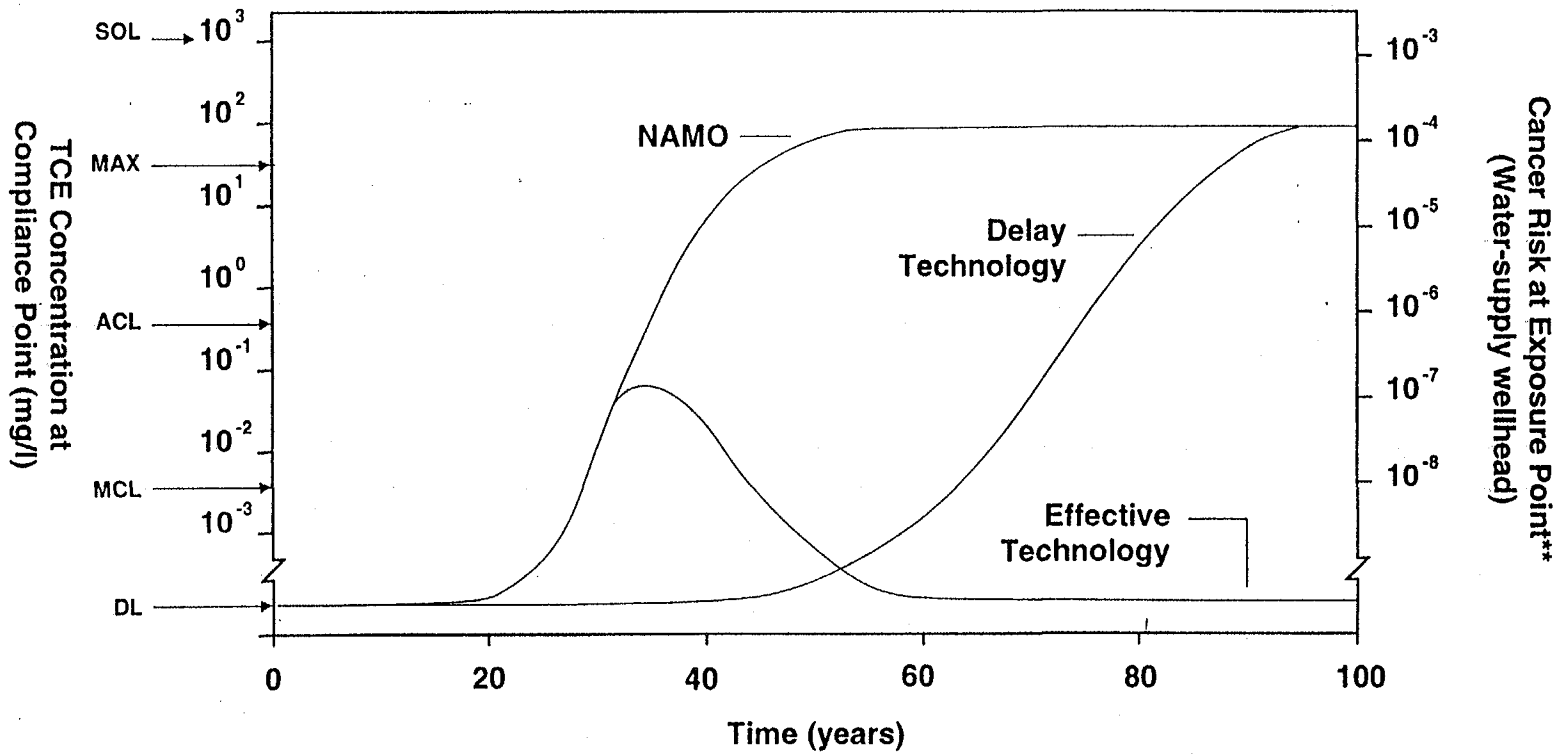


Figure 2. Hydrogeological environment assumed in analysis.



SOL=Solubility
MAX=Maximum Observed Concentration
ACL=Alternative Concentration Limit
MCL=Maximum Concentration Limit
DL=Detection Limit

**** Assuming TCE concentration on left-hand scale horizontally across from these values used for $\bar{C}$ in Eq. 4.1**

Figure 3. Timing of risk reduction with effective technology and "delay" technology, relative to no-action/monitoring-only (NAMO).

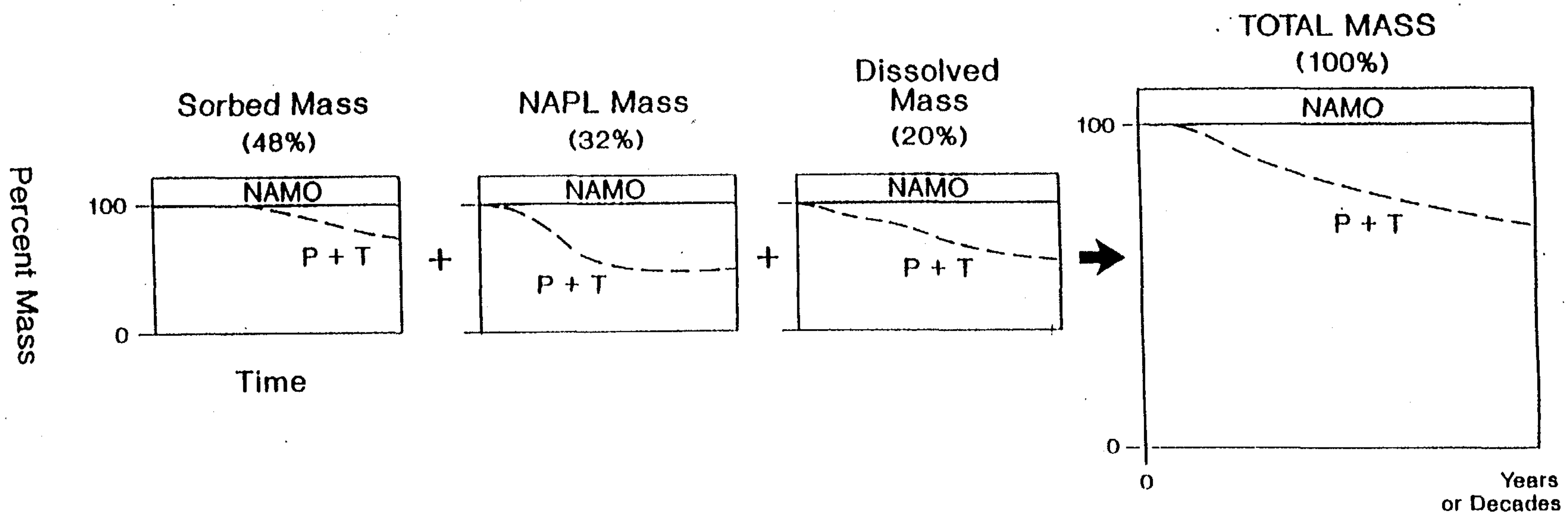


Figure 4. Hypothetical technology performance plots of mass reduction vs time. Example is rough estimate for a source-zone pump-and-treat (P&T) system using a dual-well (water/NAPL) removal configuration.

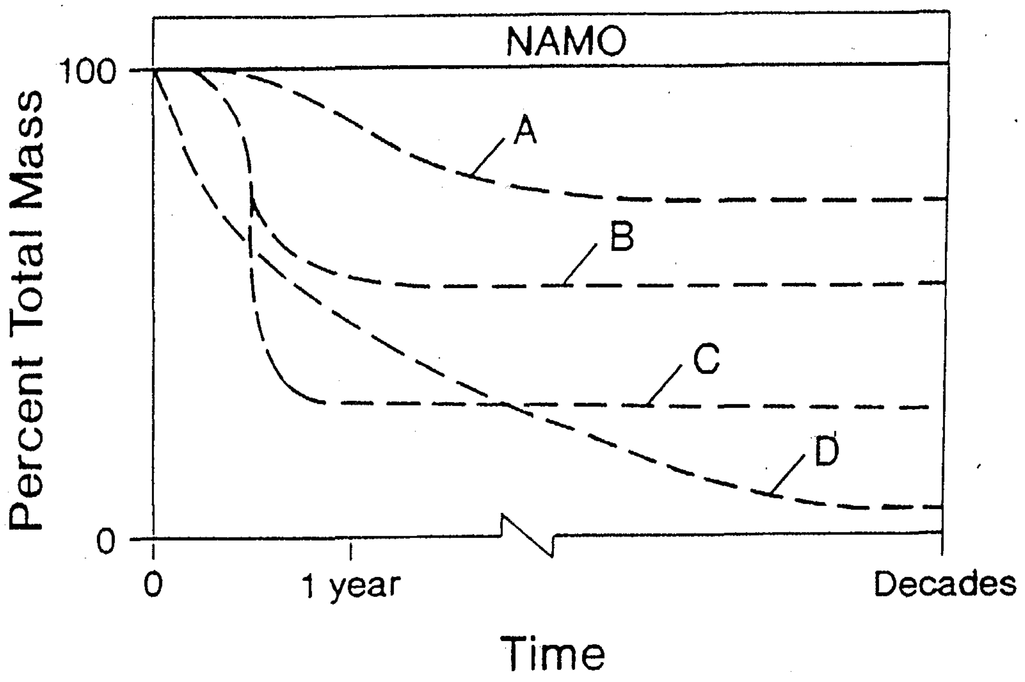


Figure 5. Hypothetical plots of total mass reduction vs time for four generic technologies, A, B, C and D.

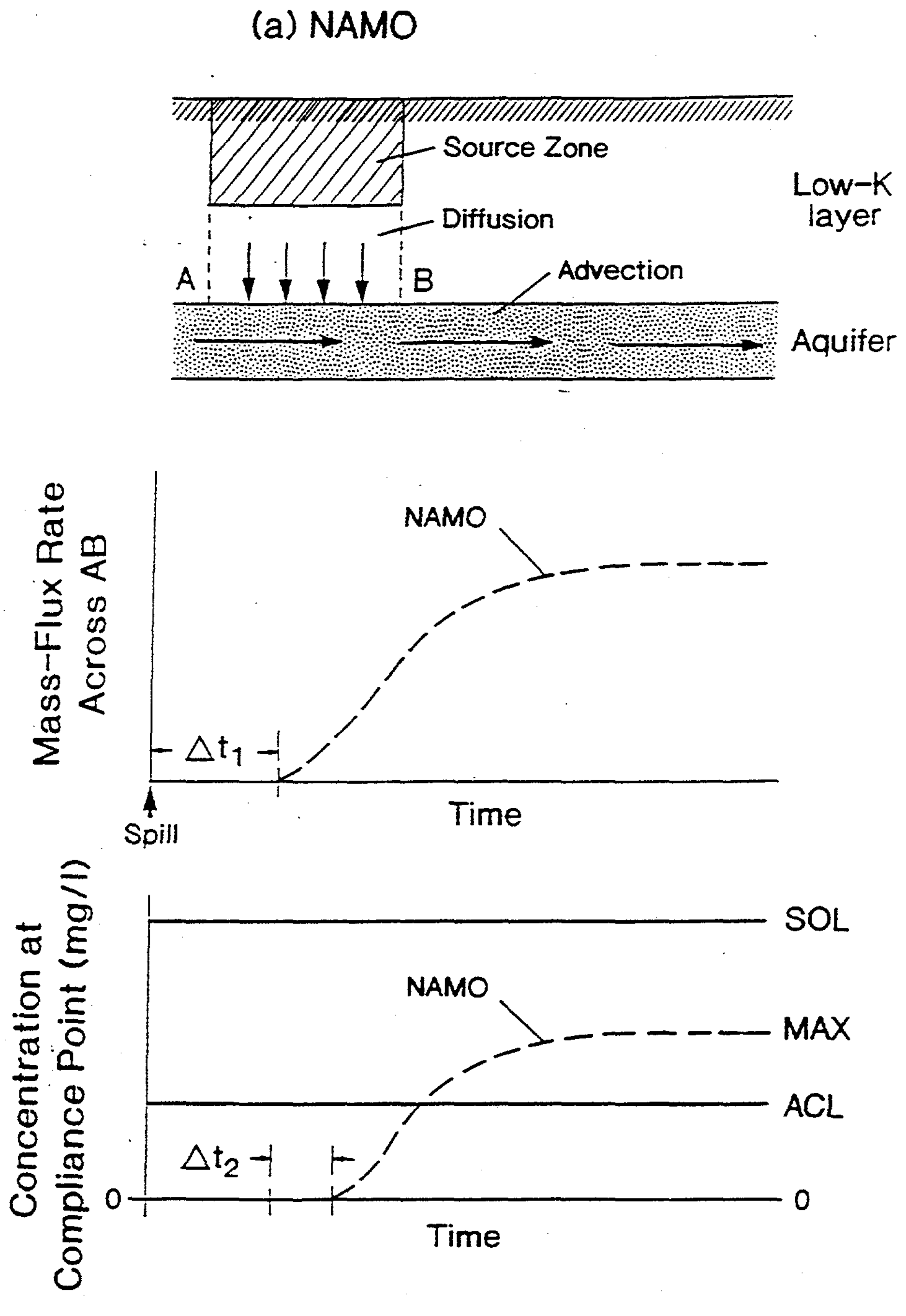


Figure 6a. Hypothetical mass flux rates into the underlying aquifer from the source zone, and TCE concentration at the compliance point for no-action/monitoring-only.

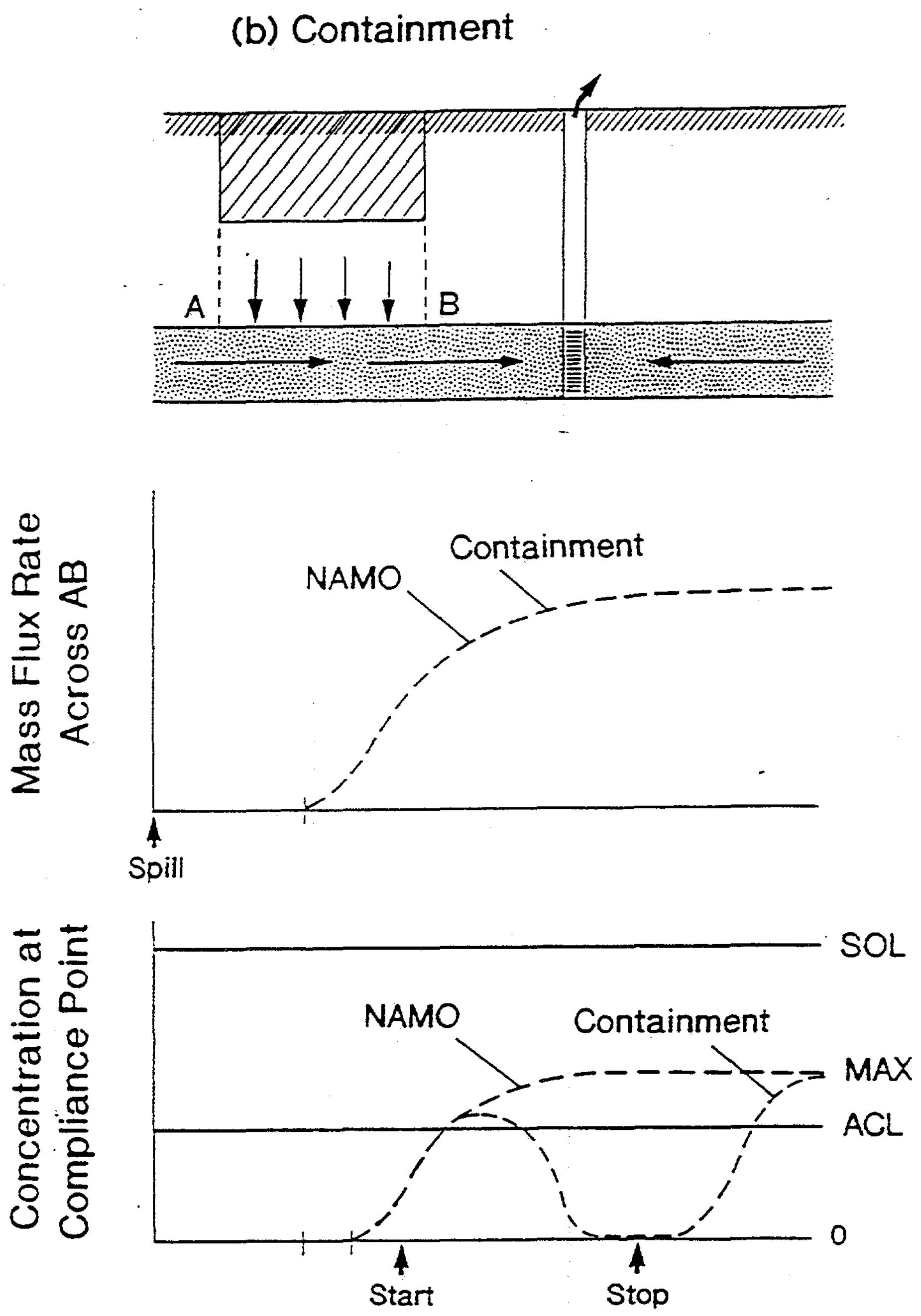


Figure 6b. Hypothetical mass flux rates into the underlying aquifer from the source zone, and TCE concentration at the compliance point for containment by plume capture through aquifer pumping.

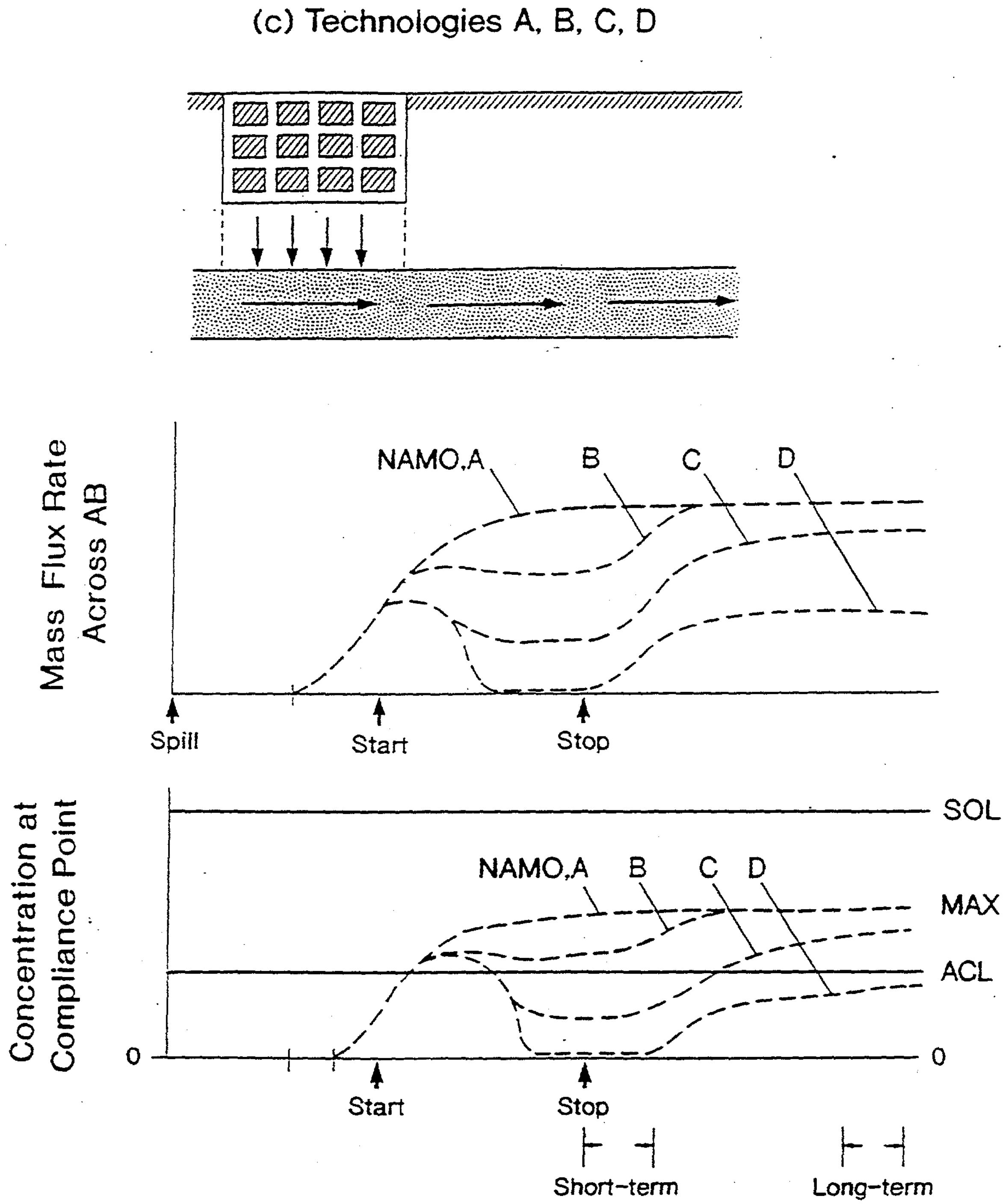


Figure 6c. Hypothetical mass flux rates into the underlying aquifer from the source zone, and TCE concentration at the compliance point for technologies A, B, C and D.

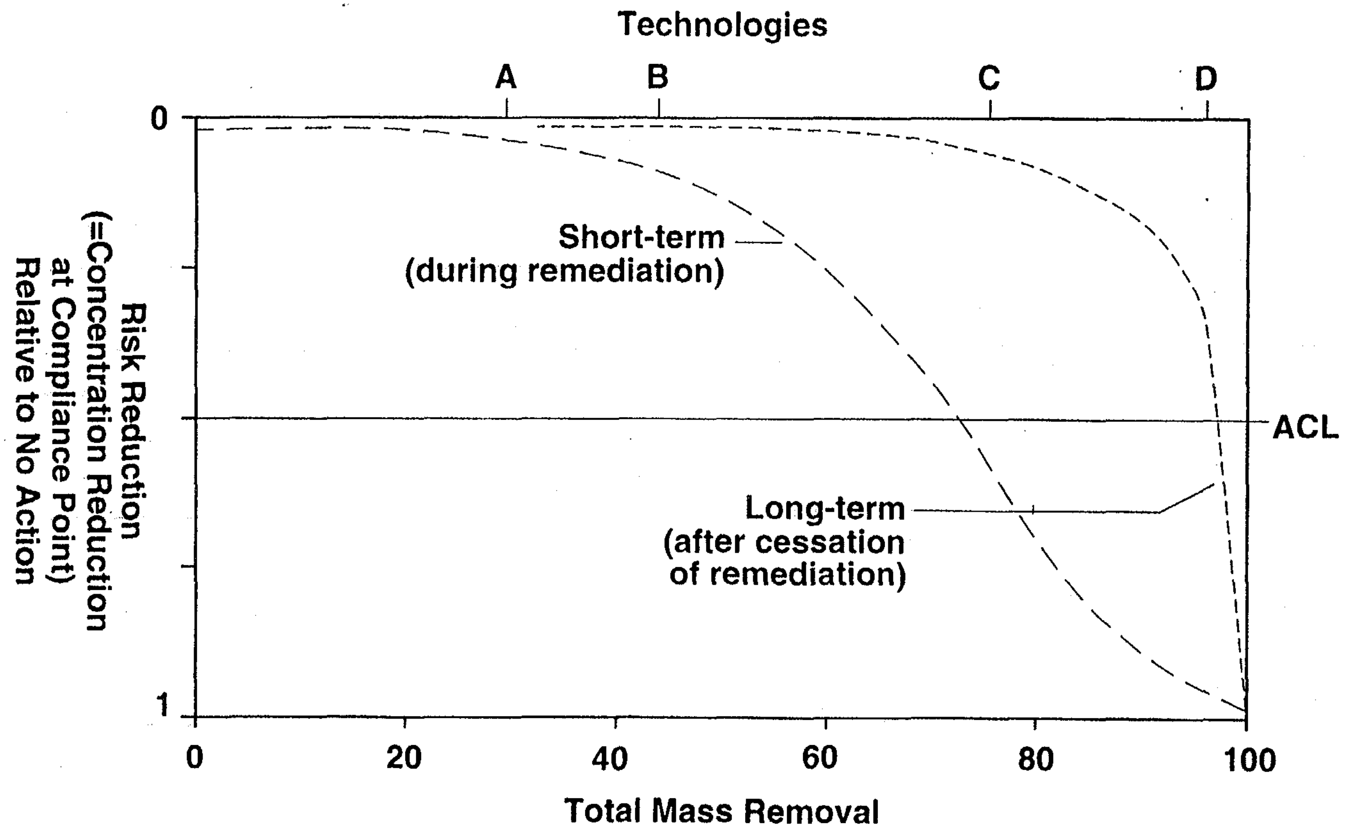


Figure 7. Short-term (IRM), and long-term (ROD) risk reduction vs total mass removal for technologies A, B, C and D.

BIOLOGICAL DEGRADATION OF DENSE NONAQUEOUS PHASE LIQUIDS (DNAPLs)

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Sponsored by
U.S. Department of Energy
and
American Petroleum Institute

Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

In situ bioremediation is a very attractive, safe and efficient method of not only removing, but eliminating hazardous compounds from the environment. However, the quickest and most efficient method of restoring a hazardous waste site would be to link several remediation processes. In situ biodegradation can involve the addition of nutrients, oxygen, electron donors, electron acceptors, organisms or all the above. These amendments can be introduced and coupled to a variety of other technologies such as permeability enhancements, chemical treatments and/or physical processes. In addition to in situ technologies, bioremediation in bioreactors is an efficient tool facilitating mineralization of contaminants. Overall, biodegradation has a significant potential to increase the rate of site restoration and decrease overall costs.

2.0 DESCRIPTION OF THE TECHNOLOGY

Microorganisms can degrade most dissolved organic contaminants. Cellular enzymatic processes oxidize or reduce a wide variety of complex organic compounds to simple molecules, such as carbon dioxide or methane (i.e. mineralization). However, dense nonaqueous phase liquids (DNAPLs) present specific barriers to biodegradation in terms of the various classes of contaminants and their availability for degradation.

Commonly observed contaminants include halogenated organics such as tetrachloroethylene (PCE), trichloroethylene (TCE) and trichloroethane. Microorganisms can aerobically attack some of these molecules causing epoxidation and dehalogenation, forming end products such as chloride salts, CO_2, or organic acids. Under anaerobic conditions microorganisms transfer electrons to halogenated organics, causing reductive dehalogenation and the formation of less chlorinated daughter products including dichloroethylene (DCE), vinyl chloride (VC), ethylene and ethane from PCE and TCE.

Numerous types of in situ remediation technologies exploit biological catalysis for the degradation of contaminant compounds. Nutrients have been added to contaminated aquifers to increase the activities or population densities of indigenous organisms and thereby increase their activity and the degradation rates of chlorinated organics. Other approaches include the addition of contaminant degrading microorganisms with or without additional nutrient supplementation. These organisms move through the zone of contamination and degrade dissolved chlorinated substrates. Additional alternatives include engineering designs that direct contaminated water through trenches or wells packed with a solid supporting material and immobilized microorganisms. This in situ filter approach (biofilter system) cleans contaminated groundwater as it passes through a zone of enhanced microbial activity.

A primary problem with biological treatment is low solubility or sorption of the contaminants to the soil matrix. Since biodegradation takes place in the liquid phase, contaminants that are not soluble are usually not available for microbial degradation. Thus, even if all other parameters are optimized, the rates of degradation may often be limited by mass transfer problems. The addition of (bio)surfactants, synthetic surfactants, and/or commercially available bioenhancers may increase the bioavailability and rates of contaminant degradation. Surfactants have also been used in soil washing (discussed by T. Sale, "Surfactant and Chemical Floods") or for enhanced in situ degradation.

Synthetic surfactant or microbiologically produced biosurfactant could be introduced into the aquifer to increase solubilization and bioavailability of sorbed contaminants. High concentrations of surfactants can inhibit or reduce the rates of microbial degradation, thus the optimization of surfactant concentration is critical in treatability experiments and site assessments. A second method of surfactant enhanced degradation is selective stimulation of indigenous microorganisms to produce biosurfactants. Specifically, the use of oleophilic fertilizers (which also have surfactant-like properties) could shift the microbial community structure to one of biosurfactant producers. These biosurfactants could facilitate contaminant desorption thereby increasing biodegradation. A remediation program may benefit by using and introducing biosurfactant synthesizing bacteria as part of in situ remediation. Under these conditions it would be advantageous to introduce microorganisms previously isolated from the subsurface over those isolated from surface soils, plants, or animals to increase the likelihood of survival or persistence in situ. Successful use of these bacteria will rely on knowing the conditions necessary to stimulate biosurfactants in the subsurface. Regardless of the method of addition, surfactants can increase contaminant solubilization for either in situ remediation or removal for above-ground treatment.

2.1 Key Physical and Chemical Processes

Accelerated remediation of an existing pump and treat system involves pumping groundwater through recovery and injection wells to modify conditions in the subsurface for increased rates of biodegradation. Groundwater is pumped to the surface, nutrients, oxygen or other electron acceptors are added, and pH may be adjusted. The amended groundwater is reinjected into or near the contaminant plume. Microorganisms may also be introduced during these processes to enhance biological activity. Microorganisms migrate through aquifer material carried by advective flow, diffusion, and swimming (motility) in the water stream. Microorganisms can display a characteristic of movement towards certain chemicals which may play an important part in bioremediation. Chemotactic responses of microorganisms towards contaminants have been studied and positive chemotactic responses towards trichloroethylene have been found (1). This movement can be independent of the hydraulic flow in the aquifer, increase the dispersion of microorganisms through the zone of contamination, and even cause the organisms to move directly towards the contaminant.

2.2 Aerobic Oxidation Processes

A variety of aerobic microorganisms produce oxygenase enzymes that can attack many chlorinated hydrocarbons; chloroform, TCE, DCE, VC and dichloromethane. This oxidative metabolism occurs co-metabolically, i.e., enzymatic degradation of chlorinated hydrocarbons only occurs fortuitously with no microbial energy gain. The co-metabolic nature of these reactions means that aerobic TCE oxidation requires the simultaneous presence of compounds such as methane, ammonia, or other aromatic hydrocarbons such as phenol or toluene (2). Alkane and aromatic hydrocarbon oxidizing bacteria can oxidize TCE at rates ranging from 1 to 8 nanomoles TCE oxidized/min/mg microbial protein (3). Certain methane oxidizing bacteria (i.e., methanotrophs) (4) have oxidation rates as high as 150-400 nanomoles TCE/min/mg cell protein. These rapid rates enable bacterial populations to reduce TCE from 10 ppm to $\leq$10 ppb (99.9% degradation) within 3-6 hours. These rates were measured under optimized laboratory conditions and only describe degradation of soluble TCE.

2.3 Anaerobic Dehalogenation Processes

Some anaerobic microorganisms can transfer electrons from reduced molecules, such as hydrogen, formate or aromatic hydrocarbons, to halogenated organic compounds including polychlorinated biphenyls, hexachlorobenzene, pentachlorophenol and PCE. Generally, dehalogenation converts halo-organic compounds into less toxic and more readily degradable products. There are two types of reductive dehalogenation that involve the loss of a halogen with the simultaneous addition of electrons. The first process is hydrolysis, or the replacement of halogens with hydrogen. The second process results in the loss of two halogens from adjacent carbon atoms with the formation of an additional bond (5).

Although most studies of reductive dehalogenation have used undefined microbial consortia, some pure culture studies have identified possible mechanisms for this phenomenon. Many enzymes contain transition metal complexes that catalyze one electron transfer from the metal to a halo-substituted carbon atom forming an alkyl radical and releasing the ion. Occasionally, two carbon atoms can form an additional bond under vicinal reduction. Transition metal complexes, including iron, cobalt and nickel-containing porphoryns are capable of catalyzing reductive dehalogenation. Some enzymes and cofactors have been identified as reductive dehalogenation catalyzers. Groups of acetogenic and methanogenic microorganisms as well as sulfate and nitrate reducing bacteria have all been associated with reductive dehalogenation.

Partial reductive dehalogenation of contaminant compounds such as PCE or carbon tetrachloride results in the formation of chloroform, DCE or VC (6, 7). Partial dehalogenation generally decreases the toxicity of a molecule and makes it more available to subsequent degradation. However, VC is a toxic product and steps must be taken to prevent its formation, insure complete dehalogenation or link VC degradation to an aerobic process.

Several instances of complete microbial dehalogenation under anaerobic conditions have recently been reported. PCE was degraded to ethane by anaerobic river sediment in the presence of lactic acid as an electron donor (8). Other workers have reported the complete dehalogenation of PCE and TCE with formate as an electron donor. One organism has been isolated that uses PCE as an obligatory electronic acceptor; the organism cannot grow in the absence of this compound. This culture dechlorinates PCE to ethene and ethane without a measurable accumulation of VC at rates of 3.7 μmoles of PCE reduced per liter per hour at a temperature of 10°C.

Under laboratory conditions reductive dehalogenation reactions proceed more slowly than oxidation reactions; however, this may be advantageous. It may be relatively simple to stimulate reductive dehalogenation since anaerobic conditions exist within many contaminated aquifers. Thus, under the appropriate natural or induced environmental conditions, microorganisms may be able to completely dehalogenate contaminants found in DNAPLs.

2.4 Overall Strengths and Weaknesses of the Technology

Biological treatment of dense nonaqueous phase contaminants is potentially a low cost process particularly when remediation is needed below the water table. Once site characteristics, biology, soil chemistry and interactions with the contaminant are established, the use of organisms is operationally simple as evidenced by widespread sewage and soil treatment methods. Destruction can be relatively rapid compared to methods such as pump and treat and can remove contaminants to concentrations below regulatory concern. Furthermore, in situ bioremediation does not result in the generation of any secondary waste, and usually does not require further treatment of groundwater or volatile contaminants ex situ. In situ remediation minimizes worker exposure and reduces above ground activities.

The weaknesses of this technology include sensitivity to site conditions such as the presence of other contaminants, heavy metals, low pH or extremes of temperature. Mesophilic microorganisms have restricted temperature activity ranges and may not be active during winter months or at temperatures above 40°C. Furthermore, the direct application of microorganisms to the subsurface environment is poorly understood. Site conditions often dictate whether microorganisms can be used and whether a contaminant is completely degraded.

Biological degradation of contaminants in low permeability media raises questions as to whether microorganisms can efficiently penetrate to the source of contamination and whether the degradation occurs within a reasonable time frame. The sensitivity of organisms to very high concentrations of organic solvents (e.g. nonaqueous phase liquids) could include the area in the proximity of the contaminant pools. Coupling hydraulic fracturing and controlled hydraulic flow may provide enhanced distribution. Problems involving the necessity for some hydraulic flow to permit continuous introduction of nutrients stimulating metabolism or degradation should also be addressed.

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

3.1 Soil and Groundwater

Biological treatment methods can degrade contaminants in both soil and groundwater. However, stimulating contaminant degradation in the vadose zone can be problematic and difficult to control. Integrating biodegradation with most remediation options (e.g., soil venting or other unsaturated zone treatments) would be the most efficient and rapid treatment. Current models predict that microorganisms primarily degrade aqueous contaminants and are incapable of attacking sorbed or nonaqueous phase material.

3.2 Petroleum and Chlorinated Hydrocarbon Remediation

Biological oxidation processes can be used to remediate both petroleum and chlorinated hydrocarbons and, in fact, it has been shown that some petroleum hydrocarbons, such as toluene, stimulate the oxidation of chlorinated hydrocarbons. Many components of petroleum are more easily and rapidly degraded than chlorinated hydrocarbons, and organisms or cultures adapted to petroleum hydrocarbon metabolism will often show activity against chlorinated hydrocarbons.

Synthetic surfactants, although quite expensive, can increase solubilization rates and make sorbed organics more amenable to pump and treat technologies. The addition of surfactants and biosurfactants into contaminated soils is known to increase desorption rates. Synthetic surfactants have been used at high concentrations for soil washing (9). The contaminants partition into the micelle and can be pumped to the surface. However, surfactants at these concentrations can reduce or inhibit degradation rates by making them less bioavailable within the hydrophobic micelle cores. Recent reports have discussed using surfactants at low concentrations to obtain increased aqueous phase bioavailability thereby increasing degradation rates (10). Both surfactants and biosurfactants can increase degradation of toluene and naphthalene in the aqueous phase and soil slurries if added at low concentrations (11). Biosurfactants and some synthetic surfactants are biodegradable, which could be a concern if these compounds were preferred as a carbon source over the contaminant material. However, biodegradation of surfactant is also an attractive feature because after contaminant desorption is complete, biodegradable surfactants will not persist within the aquifer.

3.3 Depth of Remediation

The maximum depth of remediation by microorganisms is unknown. Organisms have been isolated from depths >1000 meters below surface; however, the metabolic rates and activities at these depths has not been characterized. The most reliable basis for extrapolation regarding the use of microorganisms to treat DNAPLs can best be drawn from current practices of microbial enhanced oil recovery (MEOR). It is conceivable that current technology would permit treatment of contaminants up to a few hundred feet provided other site conditions, such as hydraulic flow, could be met.

3.4 Utility Operations

It is anticipated that most utility, operation and maintenance requirements will be routine. Field examples of biological treatment (discussed below) rely upon relatively simple methods, such as pumps and wells with relatively low maintenance and energy requirements.

3.5 Secondary Waste

Typically, secondary waste streams of contaminated water or air are not produced under bioremediation regimen. Once in operation, all organic degradation is below the surface. No secondary treatments, adsorbent regeneration or landfill disposals are required. Furthermore, none of the materials required for operation will likely cause equipment deterioration.

3.6 Environmental Impact and Safety

Safety and public relation issues are a consideration in the application of biological treatment processes. Many of the aerobic microorganisms that degrade chlorinated hydrocarbons belong to the species *Pseudomonas*. Pseudomonads and other genera useful in bioremediation include some human and plant pathogens. For a microorganism to be introduced into a contaminated site, particularly groundwater, concerns would be raised by regulatory agencies as to whether the introduced microorganism was a plant or animal pathogen. It can be extremely difficult to "prove" that an organism is not a pathogen. Many soil isolates are not well characterized as to their pathogenic potential and it is widely recognized (12) but seldom discussed that even stimulating the indigenous microorganisms at the site to degrade organic contaminants may cause an increase in the population of potentially pathogenic organisms, at least temporarily. The risk presented by potential pathogenicity of degradative microorganisms is primarily one of perception.

Another public perception and regulatory issue that could arise with bioremediation is the use of genetically engineered microorganisms (GEMS). The use of GEMS could have significant beneficial effects on in situ bioremediation and may be especially applicable to the co-metabolic processes that are most promising for the degradation of chlorinated solvents (13, 14, 15, 16). In these co-metabolic processes, the chlorinated solvents are metabolized by enzymes that are induced by other substrates (e.g., methane or toluene) which in turn also act as competitive inhibitors for the chlorinated compound degradation (17, 18). Thus, it is difficult to optimize these processes for degradation. Although innovative bioreactor designs may address these problems for ex situ applications (19) these approaches are not applicable to in situ remediation. Also, the inducers (e.g. toluene, phenol) for the aromatic degraders that oxidize TCE are hazardous substances and will be difficult (from a regulatory viewpoint) to use for in situ applications. The use of genetically engineered strains could overcome these problems. However, before this or any other

GEM can be used in the field for bioremediation a clear path through the regulatory hurdles must be established.

3.7 Models

Although the overall bioremediation of DNAPLs has not been modeled, there are models describing the movement of microorganisms in both low and high permeability media, with and without hydrological gradients (20). The simultaneous movement of microorganisms and stimulatory nutrients associated with degradation of DNAPLs has never been established. Limited models exist for the extrapolation of microbial movement and nutrient enhanced contaminant degradation.

The in situ bioremediation demonstration (methane biostimulation) of the Savannah River Site (SRS) Integrated Demonstration Project DOE/OTD was designed to demonstrate in situ bioremediation of groundwater and sediment contaminated with chlorinated solvents. Indigenous microorganisms were stimulated to degrade TCE, PCE and their daughter products in situ by the addition of nutrients into the contaminated aquifer and adjacent vadose zone. The principle carbon and energy source used in this demonstration was methane (natural gas). Modeling studies by Los Alamos National Laboratory (LANL) using history matching techniques has shown that ca. 41% more TCE was remediated with the biological components versus physical stripping alone. The Bioremediation Technical Support Group (expert panel) of the project is producing several technology reports and peer-reviewed papers regarding this demonstration. These reports will deal with preliminary technology status, nucleic acid probe analyses, community structure analyses, biodegradation analyses, site preparation and field engineering, modeling, and the final summary report.

The preliminary technology evaluation of this demonstration has shown that: (1) bacteria capable of degrading TCE and PCE can be stimulated in situ using relatively simple nutrients, (2) biostimulation and biodegradation occurred in situ without the production of toxic daughter products, (3) the process is easy to use and can be automated, (4) the cost for adding the methane injection capability is relatively low and easily recovered, (5) gaseous nutrient injection represents a significant new delivery technique for in situ bioremediation, and (6) combined with in situ air stripping this technology represents a significant improvement in terms of cost and efficiency over conventional baseline technologies used for remediation of chlorinated solvents.

LANL (21) has completed a history-match model of the SRS demonstration and has run a simulation model with the biodegradation component as well as without this component. Approximately 41% more TCE is destroyed and removed when bioremediation is active. The simulation ran for 475 days and is a close approximation of the actual field test.

4.0 CONSIDERATIONS FOR LOW PERMEABILITY MEDIA

Biological treatment of NAPLs in low permeability media is impacted by the ability of microorganisms and stimulatory nutrients to reach the contamination. Microorganisms can move at a rate of ca. 4 m/day, which is faster than typical groundwater velocities. Some studies report that microorganisms can move through porous media at the same rate as groundwater flow (25).

The active movement of microorganisms towards a chemical concentration gradient is a phenomenon known as chemotaxis. Rapid microbial penetration into porous media has been observed when the chemical attractant is upgradient. The practical result of this phenomenon is that microorganisms will "go after" increasing concentrations of contaminants and penetrate cracks, pores and fissures in the absence of fluid flow as long as a chemical attractant lies at an increasing concentration within the pores, cracks or fractures. While dense, chlorinated solvents may seem unlikely candidates as chemical attractants to microorganisms, an evaluation of subsurface microbes at SRS has identified strong chemotactic response to TCE, even at concentrations toxic to microorganisms. Trichloroethylene was found to increase bacterial soil migration rates by a factor of 100 in the direction of increasing TCE concentrations (26). The discovery that chlorinated solvents invoke a chemotactic response in bacteria means that the penetration may underestimate their transport potential. Microorganisms have been observed to move in the absence of a hydraulic gradient through sandstone cores with a permeability of 0.2 to 0.4 um^2. Penetration rates of organisms vary from between ca. 0.1-3 cm/hr (23, 24). This rate of penetration corresponds to between 2.5-80 cm/day.

In addition to rapid rates of penetration, microorganisms can also degrade chlorinated hydrocarbons very efficiently. The degradation rates of selected chlorinated hydrocarbons by anaerobic microorganisms can be extrapolated from data obtained during a recent field trial: in an aquifer area of 12.2 x 18.3 x 4.6 m and assuming 20% porosity, degradation amounts were 28.6 gm PCE/day, 15 gm DCE/day and 5.7 gm VC/day (27).

If the majority of the TCE (Fig. 1) exists as fingers or free-product pools at the bottom of the aquifer, the indigenous bacteria could deplete the chlorinated hydrocarbon in the soluble phase if all nutrient and electron acceptor and donor requirements were met. Aqueous hydrocarbon concentrations would rapidly decline to below detection limits and remain low as long as biological activity was maintained. The rate of contaminant removal would then be dependent on the rate of dissolution from fingers and pools into the solution phase. Also, the rate of dissolution would be significantly increased due to the increased concentration gradient (29). Once this had occurred, essentially all degradative activity would take place at the interface between the dense nonaqueous phase and the overlying aqueous phase.

Mathematical models evaluate the kinetics of dense solvents dissolving into groundwater for both plumes with fingers and pools of solvent (30) and predict long dissolution times for large pools. These models predict relatively rapid dissolution of NAPL, such as PCE and TCE. Free-product fingers (0.2 and 1.5 L) have lifetime dissolution values of 0.4 - 1.1 yr, assuming standard groundwater flow around the fingers, while large contaminant pools have much longer dissolution lifetimes. Assuming the solution is controlled by standard chemical equilibrium, pools (200 L) at the bottom of aquifers have dissolution lifetimes of ca. 100 - 300 yr. Thus, if microbial degradation is driven by contaminant dissolution this approach would not be practical; however, microbial effects that change this conclusion are neglected in this analysis.

Current (abiotic) dissolution models do not consider the biological effects of microbial degradation. These effects could be profound (29) but have not been evaluated in the field. Since microorganisms are extremely small and widely dispersed, their degradative activity prevents aqueous phase concentrations from approaching equilibrium even a short distance away from the nonaqueous phase contaminant. Extremely sharp concentration gradients would exist soon after biological activity commenced. The contaminant concentration could drop from saturation to less than a few parts per billion within millimeters or centimeters from the DNAPL pool. The effect of this sharp concentration gradient would accelerate the dissolution rate by a presently unknown amount. The surfactant and hydrophobic partitioning effects of microorganisms will also serve to increase the rate of dissolution into the aqueous phase. According to the model cited above, a two-order of magnitude increase in the dissolution rate would be required to reduce the pool lifetime from 300 years to 3 years.

The small microbial size infers an extremely short diffusion path length for dissolved contaminants. Dissolved chlorinated hydrocarbons would travel only a few centimeters before being oxidized by microorganisms. This short diffusion path length and high concentration gradient would not depend on bulk water flow (32). Contaminant degradation can only take place at the interface between free-product and aqueous phase (Fig 2). The small size and penetrative ability of microorganisms means that contaminant interfaces as (1) free product pooled on top of clay, (2) separate phase product trapped in fractures, and (3) dissolved product diffused into matrix blocks would all be degraded by microorganisms. The small interface surface area characteristic of contaminants in fractures or pores would probably limit the degradation due to low rates of diffusion. But as the contaminant was degraded, the microbial activity could "follow" the contaminant through fissures or fractures even in the absence of hydraulic flow until all of the contaminant was removed.

One method of increasing dissolution is to increase groundwater flow (31), however, a 25-fold increase in groundwater velocity is required to achieve a 5-fold decrease in the time required to dissolve the contaminant. Within the zone of degradation microorganisms can maintain extremely low contaminant levels. This concentration reduction in the vicinity of the contaminant pool is equivalent to extremely high groundwater velocities. Groundwater flows of tens or hundreds of meters per day would be required to achieve the same concentration gradient above a pool of contaminant that is equivalent to the concentration surrounding a population of degradative microorganisms. An additional important factor in these models is the effect of contaminant pool length on the required dissolution time. Models measure aqueous contaminant concentrations as the water moves across the DNAPL pool. A 2-fold increase in the DNAPL pool length triples the time necessary for complete dissolution. However, if the microbial population is uniformly distributed over the pool, the length of the pool has no effect on the dissolution rates. That is, the dissolution rate is the same at any point along the pool surface since the solution concentration would be uniformly low.

A second method for increasing dissolution is to add surfactant-like compounds. The desorption rates will be linked to the surfactant concentrations used with the fastest solubilization rates obtained with relatively high surfactant concentrations. However, depending on the surfactant type, these high soil washing concentrations can inversely affect the degradation rates.

Dissolution models predict that significant amounts of time are required for the removal of products diffused into the bulk matrix. If the matrix is left undisturbed, the time required for sorbed contaminant removal is approximately equivalent to the time the contaminant has been in contact with the matrix. A TCE pool contacting and diffusing into an aquitard (30 yr), would still contain significant TCE concentrations in the aqueous phase 30 years after the TCE pool was removed. Without fracturing or other intrusive methods movement of TCE out of the matrix would be slow.

Diffusion of dissolved phase product from matrix blocks into the overlying aquifer could be the largest stumbling block in any approach to degradation. If the pore sizes are too small and the matrix too tight to permit rapid penetration by microorganisms, then diffusion out of the blocks is the only natural mechanism controlling the kinetics of contaminant removal. In this case treatment must be maintained for decades in the aquifer if it is necessary to remove the residual contaminant diffusing out of the matrix. However, it may only be necessary to maintain biological degradation after the bulk pool has been removed for the first one or two years to treat material diffusing out of the solid matrix.

Microorganisms are sensitive to high concentrations of organic solvents, and chlorinated hydrocarbons can be toxic. This toxic effect could limit the microbial activity in the vicinity of a pool or finger when the concentrations in the aqueous phase approach saturation. This toxicity could limit contaminant degradation in the region where degradation is most critical, but degradation could also reduce the zone of high concentrations to very near the pool if degradation rates are high. At increasing distances from the pool, microbial degradation rates would increase as toxicity declined.

Select microorganisms are highly resistant to the toxic effects of organic solvents. Bacteria have been isolated that grow in the presence of saturating concentrations of organic solvents such as toluene (33, 34), while certain *Pseudomonas putida* strains grow in the presence of a two phase water-styrene system. A microorganism that uses styrene as a sole carbon and energy source could grow rapidly in the presence of free-phase styrene at 1% volume to volume (35). Hydrocarbon degradative microorganisms have been isolated that can use xylene, trimethylbenzene and ethyltoluene as sole carbon and energy sources for growth in a two-phase system (36). While organisms that degrade chlorinated solvents under saturated conditions have not been isolated to date (except PCE which has a very low solubility), it is likely that chlorinated hydrocarbon-resistant microorganisms will be isolated or engineered which can be used to reduce the effects of solvent toxicity in an aquifer-free product system.

5.0 COST AND RELIABILITY

Costs for this remediation approach are unknown but are likely to be low relative to other methods. The addition of nutrients and microorganisms is inexpensive and may, when used in combination with other technologies, result in significantly shorter treatment times. The major capital and operating costs would involve drilling wells and pumping to introduce organisms and nutrients into the aquifer which may be activities common to other approaches.

The reliability and performance of this technology at present are unknown and research and development are required to establish a reliable application of bioremediation of DNAPLs. Equally important, however, it is highly unlikely that bioremediation would negatively impact the site. Operating costs would be approximately the same per cubic meter of aquifer treated. The number of wells would increase proportionately to the size of the site.

6.0 COMMERCIAL AVAILABILITY

Bioremediation of DNAPLs is primarily at the bench scale level (at the time of this communication) and many critical experiments have yet to be performed. Likely future efforts include demonstrating the feasibility of the approach and evaluating the effectiveness of organisms in degrading contaminants at or near the interface of a nonaqueous pool. However, a significant data base exists for the successful use of bioremediation in fuel spills.

The key to this approach is linking bioremediation with other technologies. Complimentary technologies that would enhance the clean up include approaches such as soil vapor extraction to remove contaminants from the unsaturated zone and possibly biosparging or air sparging below the water table to increase the rates of aerobic oxidation, delivery of nutrients, and enhanced volatilization. The use of hydraulic and pneumatic fracturing in low permeability media to increase the distribution and penetration of degradative microorganisms and nutrients into the low permeability matrix may also be effective. Microorganisms are particularly well suited to hydraulic or pneumatic fracturing since they are able to withstand high pressures and rapid changes in pressure.

7.0 CASE HISTORIES

Two case histories of the use of degradative microorganisms in situ to degrade chlorinated contaminants are presented below. One attempt involved the addition of an aerobic degradative microorganism to an aquifer contaminated with TCE. Another approach demonstrated the in situ stimulation of anaerobic microorganisms in the reductive dehalogenation of PCE and daughter products.

7.1 Case History 1

An aquifer consisting of silty sand interbedded with sand and sandy clay over a clay aquitard was contaminated with TCE at concentrations ranging from 500 to 2,000 ppb (µg/liter). The saturated zone was at a depth of 14 ft, had a porosity of 25%, and a flow velocity of 10 m/day. An aerobic TCE degradative microorganism was injected, along with nutrients and oxygen, into the plume of contamination. Within 24 hours, the concentrations of TCE began to decline in a monitoring well 10 ft downgradient from the injection well. TCE concentrations declined from a high of 2,500 to 3,000 ppb to a mean value of 78 ppb over a 20-day period. This field test only measured the concentration of TCE dissolved in the water and no attempts were made to measure the total mass of TCE or any degradation of nonaqueous liquids. Nutrients and oxygen were added continuously for 6 days, and the test was continued for a total of 22 days (28).

7.2 Case History 2

The second field test of in situ PCE biodegradation was an anaerobic treatment carried out over a period of two years by workers from DuPont (27). This sand aquifer averaged 12.2 to 18.3 m in thickness with total organic content of 0.08 to 0.72 and a natural groundwater movement of approximately 0.3 m/day. A 12.2 x 18.3 meter test site was established consisting of recovery, monitoring and recharge wells screened in the top 4.6 meters of the aquifer.

Anaerobic microorganisms in this aquifer were stimulated by the addition of benzoic acid and sulfate in a series of three injection wells. Three recovery and several monitoring wells were used to measure the concentrations of PCE and daughter products in the aquifer during the treatment and to recover water for nutrient addition and recharge. During anaerobic treatment interval, PCE concentrations decreased from 1,700 ppb to below the limits of detection. Trichloroethylene levels declined to below detection limits as well. In the early stages of the test, both DCE and VC concentrations increased; however, by the end of the second phase of this anaerobic treatment process, DCE and VC concentrations had declined to near or below detection levels. This field trial demonstrated that reductive dehalogenation could be stimulated in situ to treat PCE and other chlorinated organic contaminants dissolved in groundwater over a fairly large area. The test effectively removed PCE and its daughter products, resulting in the site meeting or exceeding regulatory standards. This is the first example of a field test using reductive dehalogenation processes. The mass amount of PCE removed during this test was 8.4 kg over 2 years.

8.0 SUMMARY

Dense organic liquids such as chlorinated solvents can be biodegraded and removed from the environment by aerobic and anaerobic microorganisms. The use of this technology for in situ treatment of either dissolved or nonaqueous phase organics is still in its infancy. Positive results have been obtained, but more empirical data is required to improve existing dissolution and migration models, allowing predictions of the efficacy and practicality of biological treatment. This is particularly important in low permeability medium containing dead-end pores, pools and other areas of high solvent concentrations. The toxic effect of the solvents has not been adequately assessed but may prove to be a minor concern. Although the potentially large impact of degradative microorganisms on the dissolution rates of organic solvents from pools underlying aquifers is a critical unknown parameter, it may significantly reduce treatment times. The time required may range from as little as 2 to 3 years to up to 300 years, depending on what assumptions are made regarding dissolution, migration and degradation rates and how well the bioremediation technology is linked with other approaches.

Microorganisms that aggressively move towards the source of contamination and show a resistance to high concentrations of organic solvent have already been identified. Degradation rates in the laboratory are sufficiently high that environmentally and economically viable removal rates can be projected based on these data. Bioremediation based approaches are likely to be easily integrated with many other technologies to provide a complete and low cost solution. Certainly microorganisms can be used with soil vapor extraction, air sparging, and bioventing. Furthermore, techniques such as pneumatic or hydraulic fracturing coupled with microorganisms can be used to accelerate the distribution of degradative organisms or stimulatory nutrients into low permeability areas.

While the current state of the technology does not permit predictions of reliable or easily controlled biological degradation of nonaqueous phase liquids, a research effort designed to empirically answer essential questions for predictive modeling would significantly address the viability of in situ remediation. At the field scale the relatively low cost of bioremediation when linked to other primary technologies make experimentation and testing feasible. In any case, microorganisms may be an important part of an integrated method to treat dissolved phase contaminants either directly over a pool of nonaqueous phase liquid or down gradient from the pool. Organisms used as filters or zones of degradation to halt migration of contaminated water can be very low cost and highly effective. It is not unreasonable to also hypothesize that a dense population of active degradative microorganisms in the proximity of a pool of chloro-organics such as PCE or TCE will cause the rapid disappearance of the pool through accelerated solubilization, dissolution and degradation.

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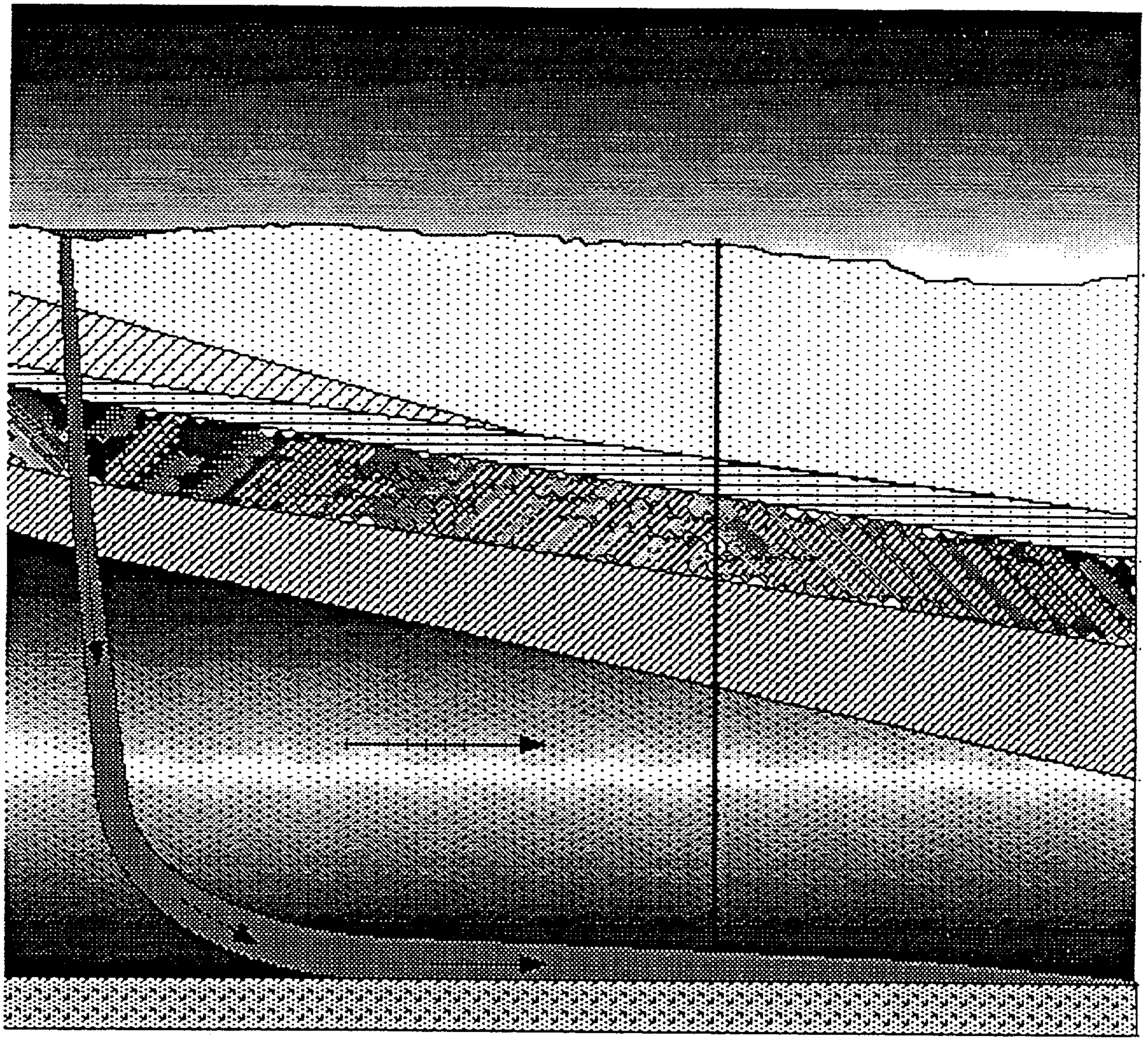

Figure 1. Formation of a subsurface pool of a dense nonaqueous phase liquid from a spill.

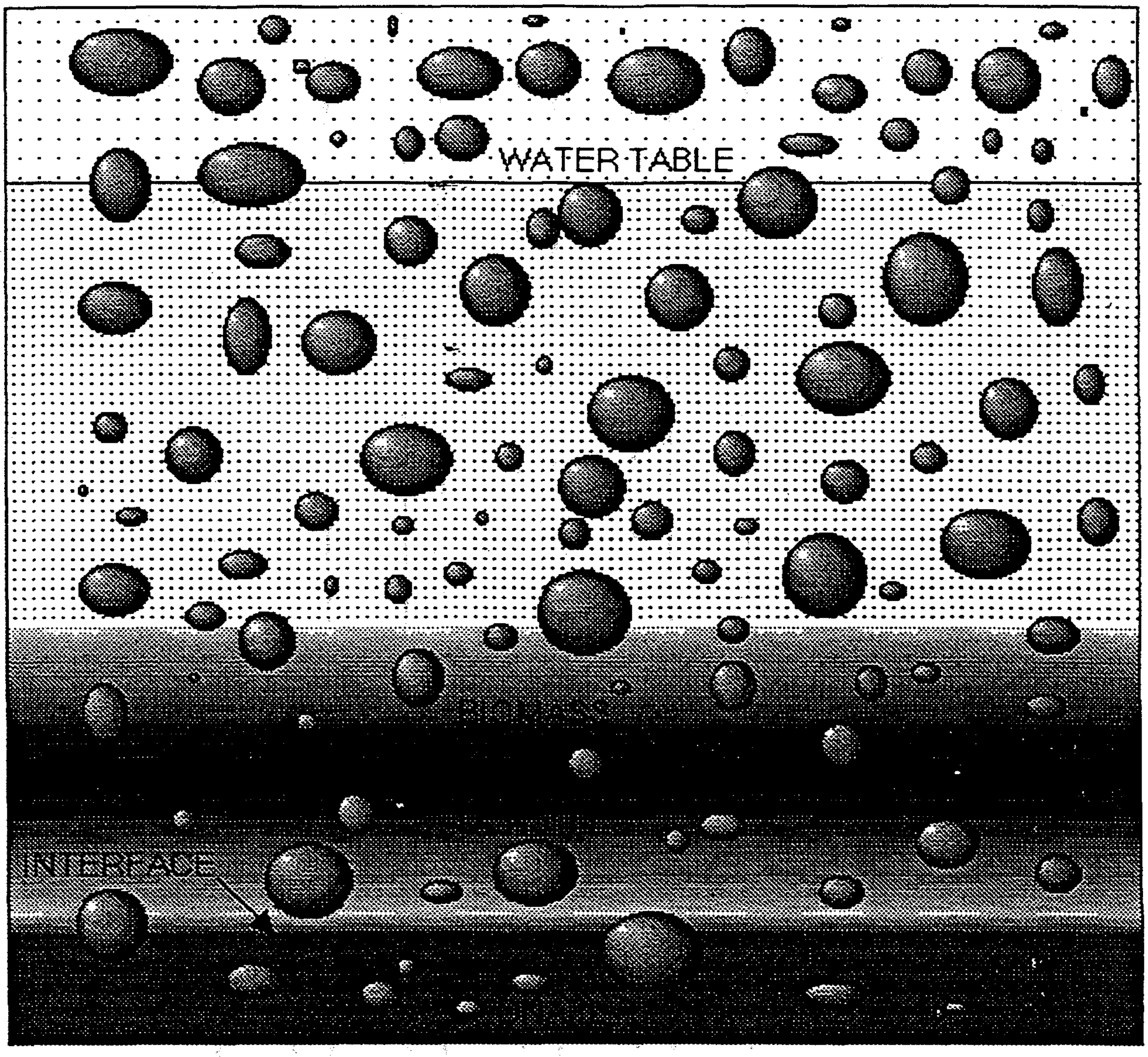

Figure 2. Proposed anaerobic biomass density distribution above a DNAPL pool in an aquifer.

IN SITU CHEMICAL DEGRADATION OF DNAPLS IN CONTAMINATED SOILS AND SEDIMENTS

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

An emerging approach to in situ treatment of organic contaminants is chemical degradation. The specific processes discussed in this chapter are in situ chemical oxidation using either hydrogen peroxide (H_2O_2) or potassium permanganate ($KMnO_4$) and in situ dechlorination of halogenated hydrocarbons using zero-valence base metals such as iron. These technologies are primaryly chemical treatment processes, where the treatment goal is to manipulate the chemistry of the subsurface environment in such a manner that the contaminants of interest are destroyed and/or rendered non-toxic. Chemical properties that can be altered include pH, ionic strength, oxidation and reduction potential, and chemical equilibria. In situ contaminant destruction processes alter or destroy contaminants in place and are typically applied to compounds that can be either converted to innocuous species such as CO_2 and water, or can be degraded to species that are non-toxic or amenable to other in situ processes (i.e., bioremediation). With in situ chemical oxidation, the delivery and distribution of chemical reagents are critical to process effectiveness. In contrast, published approaches for the use of zero valence base metals suggest passive approaches in which the metals are used in a permeable reaction wall installed in situ in the saturated zone. Both types of processes are receiving increasing attention and are being applied both in technology demonstration and as final solutions to subsurface contaminant problems.

2.0 CHEMICAL OXIDATION

2.1 Technology Description

Chemical oxidation processes involving a variety of liquid (e.g., peroxides, permanganates) or gaseous oxidants (e.g., ozone) can be coupled with a variety of oxidant delivery technologies for in situ treatment of DNAPL contaminated media. Due to its widespread availability, use, and acceptance in the waste treatment field, hydrogen peroxide (H_2O_2) has emerged as an attractive oxidant for contaminated soils (Tyre et al. 1991; Gates and Siegrist 1993a; Gates and Siegrist 1993b). Hydrogen peroxide reacts with iron (both ferrous and ferric) in natural soils or amendments in a variety of competing reactions (Tyre et al. 1991):

$$H_2O_2 + Fe^{2+} \rightarrow OH\cdot + OH^- + Fe^{3+} \quad [1]$$

$$H_2O_2 + Fe^{3+} \rightarrow HO_2\cdot + H^+ + Fe^{2+} \quad [2]$$

$$OH\cdot + Fe^{2+} \rightarrow OH\cdot + Fe^{3+} \quad [3]$$

$$HO_2\cdot + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+} \quad [4]$$

$$H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot \quad [5]$$

The free radicals ($OH\cdot$ = hydroxyl and $HO_2\cdot$ = perhydroxyl) formed during iron-catalyzed decomposition of hydrogen peroxide in acidic soils ($pH<\sim 6$) are the primary oxidizing species:

$$RH + OH\cdot \rightarrow R\cdot + H_2O \quad [6]$$

$$R\cdot + Fe^{3+} \rightarrow Fe^{2+} + \text{products} \quad [7]$$

where $R\cdot$ = organic radicals. This reaction of hydrogen peroxide with iron to yield free radicals is commonly referred to as Fenton's process.

Weber (1972) reviewed the application of $KMnO_4$ in water treatment and noted that $KMnO_4$ is useful as a water treatment oxidant because it is a powerful oxidizer of many water impurities including phenols, Fe_2, S_2, and taste and odor producing compounds (typically unspecified organic compounds). Permanganate's attack on organic compounds is described as an oxidative attack of the functional groups and multiple bonds of organics, with the possibility of some cleavage of benzene rings.

Vella et al. (1990) demonstrated the ability of $KMnO_4$ to oxidize phenols in an industrial waste-water to levels below regulatory limits (< 19 µg/L) in laboratory and field scale studies. Vella observed the formation of manganese dioxide (MnO_2) as a reaction by-product and noted the impact of MnO_2 formation on effluent turbidity. Vella et al. (1990) compared $KMnO_4$ and H_2O_2 oxidation of phenolic wastewaters and observed that $KMnO_4$ was as effective an oxidant as H_2O_2 and easier to handle than H_2O_2.

The primary drawback to the treatment of water and wastewater with $KMnO_4$ is the formation of MnO_2, which contributes to the turbidity of the treated water and imparts a pink color to water treated with low $KMnO_4$ overdoses (0.05 mg/L residual $KMnO_4$) (Montgomery 1985). Neither of these should be of concern during the treatment of contaminated soils and sediments with $KMnO_4$, where the formation of MnO_2 may in fact be of some benefit (as a metal sorbent). Since MnO_2 is found naturally, and Mn is the 12th most abundant compound in Earth's crust, (Greenwood and Earnshaw 1984) no problems with the introduction of $KMnO_4$ and its oxidation by-products into the environment are anticipated.

The extent of chemical oxidation reactions may be affected by several parameters including the concentration of reactants, temperature, pH, and the presence of impurities. A comparison of the VOC reduction observed in clay soils treated with either H_2O_2, H_2O_2 + Fe, or $KMnO_4$ is given in Fig. 1. Trichloroethylene (TCE) concentrations after chemical oxidation of clay soils with varied initial TCE concentrations are shown in Fig. 2

In situ chemical oxidation involves the delivery of oxidant solutions (and potentially additives) into and throughout a contaminated region using delivery techniques such as soil mixing or fracturing in combination with oxidant solution injection (see Figs. 3-5). Treatment efficiency appears to be principally a function of media properties (e.g., natural soil organic matter content, pH), oxidant concentration and mass loading rate, and oxidant delivery and distribution. A comparison of treatment efficiency at three different modes of oxidant delivery revealed that as the thoroughness of oxidant delivery and distribution decreased the process efficiency decreased. Hydrogen peroxide solutions of 0.01-10% by wt. in volumetric additions of 5-10% v/v (liquid volume per volume of treated media) have been used to provide oxidant mass at $>10^3$ times stoichiometric requirements for contaminant destruction. At these loadings sufficient fluid volume is available to disperse the oxidant without slurrifying the soil system and yielding free water (Gates and Siegrist 1993a). To enhance distribution of oxidant throughout the mixed region, treatment solutions can be injected into an air stream (air velocity=0.15 m^3/s) such that it enters the mixed region as a fine mist (Siegrist et al. 1993). In this approach some organic compounds can be volatilized and advectively removed concurrently with the in situ oxidation processes. Any off-gas organics are captured in a shroud or hood covering the ground surface and managed as required by a variety of off-gas treatment techniques (e.g., carbon adsorption, catalytic oxidation).

When applied to low permeability media (e.g., silts and clays), hydrogen peroxide can modify the pore size and continuity within the media to dramatically reduce permeability

(Hargett et al. 1985). Reducing matrix and bulk deposit permeability should be beneficial as it inhibits post-treatment leaching of any untreated contaminants (e.g., heavier organics, heavy metals).

2.2 General Technology Considerations

Is the technology primarily geared to soil or groundwater contamination? This technology can be applied to both soil and/or groundwater contamination. High soil water content may enhance in situ chemical oxidation treatment by increasing the amount of soluble contaminant available for treatment and by increasing the efficiency of mixing and distribution of chemical oxidant solution throughout the region of interest.

To what extent is the technology suited to remediating petroleum as well as chlorinated hydrocarbons? Hydrogen peroxide and potassium permanganate oxidation in aqueous and soil matrices has been shown to be an effective treatment technique for a variety of organic contaminants (Table 1). Hydrogen peroxide has also been shown to degrade certain chlorinated solvents and petroleum hydrocarbons in soil systems (Tyre et al. 1991; Gates and Siegrist 1993a; Gates and Siegrist 1993b). Recent studies have demonstrated the effectiveness of $KMnO_4$ as a soil contaminant oxidant (Gates et al. 1995). The effectiveness of these oxidants on heavier petroleum fractions in soil has not been demonstrated extensively, nor has there been much experience with in situ applications for DNAPLs in low permeability media.

How well is the technology able to access under buildings and pavement? In situ chemical oxidation may be feasible under obstructed sites, but data supporting its implementation in these situations are lacking. Remediation under concrete pavements and buildings should be possible as long as the treatment does not adversely affect the stability of the structures (e.g., by disturbing building foundations). Most currently available mixing and reagent delivery technologies employ near-vertical penetration and treatment under surface obstructions and could entail considerable disruption of surface features. To overcome this, implementation of in situ chemical oxidation using directional drilling or auguring equipment would be desirable. However, any treatment process implemented in this manner would require further developments in off-gas capture and treatment techniques. In addition to potential surface physical disruption, the effects of media volume expansion and increases in soil/sediment water content on the structural integrity of the zone of interest needs to be considered.

What is the maximum depth of remediation? The maximum depth of treatment is limited by oxidant delivery methods. Equipment utilized for soil mixing has been adapted from the construction industry to accommodate a combination of deep soil mixing and reagent injection. With this type of equipment, drilling has occurred to depths well over 30.5 m. In situ chemical oxidation (with H_2O_2) of silt/clay soils to 4.6 m depth has been demonstrated at a land treatment site located on a dense fluvio-lacustrine deposit in southern Ohio (Siegrist et al. 1993). Greater depths may be possible, although limits exist due to geotechnical and treatment considerations. The maximum depth to which this technology can be applied is dependent on the mixed region diameter, the media properties (e.g., density, water content, air permeability), and the power and geometry of the mixing equipment (e.g., maximum torque). The injection of chemical-oxidant solutions may reduce power requirements for mixing. Regarding the chemical oxidation treatment process itself, process efficiency should not be negatively affected by increasing depth. However, monitoring of process effectiveness may be more difficult at greater depths.

Mixing of deeper and denser soil regions (e.g., >6 m) may also increase absolute volume expansion (i.e., more soil will be lifted above the original ground surface). The volume expansion observed during in situ chemical oxidation using hydrogen peroxide to 4.6 m depth in a dense silt/clay deposit was observed to be ~15% (1.1 m^3 of soil displaced above ground per 7.6 m^3 of media treated in situ) (Siegrist et al. 1993).

What are the utility, operation and maintenance requirements? The utility requirements associated with in situ chemical oxidation are either related to the on-site preparation of oxidant solutions, the delivery of the chemical oxidant to the contaminated region, or the above ground treatment of off-gases. The equipment required for the application of this technology is mobile and can be operated in the absence of permanent power using portable generators. The only maintenance requirements are those needed to keep heavy equipment operating properly and most likely would be performed on a routine basis.

Are secondary waste streams produced? If in situ chemical oxidation results in complete oxidation of organic contaminants, no secondary waste streams will be produced. More research is needed in this area, since data are not available to determine the contaminant and oxidant combinations and treatment conditions that will result in complete oxidation or the characteristics of the by-products formed by incomplete oxidation.

Are there potential environmental impact or safety risks associated with the use of the technology? With hydrogen peroxide addition, the environmental impact is minimal if contaminants are completely oxidized. The safety risks associated with hydrogen peroxide addition are related to the safe handling and storage of strong peroxide solutions. These safety risks can be minimized by purchasing weak hydrogen peroxide solutions in bulk from manufacturers instead of preparing the weaker solutions from more concentrated H_2O_2 stock on site. There are no handling problems associated with the use of $KMnO_4$.

Are models available to predict performance in porous media and to what extent are they developed? There are no models currently available that predict the performance of in situ chemical oxidation. Reaction rate data coupled with transport and fate models could be used to model in situ chemical oxidation.

2.3 Low Permeability Media Considerations

Describe the ability of the technology to remove: free product pooled on top of a clay layer, separate phase product trapped in continuous clay fractures, separate phase product trapped in 'dead end' fractures, and dissolved phase product diffused in the matrix blocks. If in situ chemical oxidation is combined with soil mixing, the mixing process will disrupt and homogenize to some degree subsurface heterogeneities, and oxidants will be delivered throughout the mixed region. As a result, degradation of DNAPLs should occur, whether they are present as residual product or diffused into matrix blocks. This will potentially mitigate any adverse affects associated with the model site's described heterogeneity. Oxidation of various types and concentrations of organic compounds including soil organic matter have been demonstrated (Table 1). The extent of degradation is a function of oxidant concentration and mass loading. With the degradation of natural soil organic matter, it is possible that sorbed product would be released from the soil matrix and made more available for treatment.

2.4 Cost and Reliability

Assume a 40 × 40 m area with a 3 m thick clay layer. The TCE concentration in the clay is 2000 mg/kg and the target cleanup level is 200 mg/kg (90% removal). Estimate the time and cost to remediate to target levels, economies of scale and the confidence or expected reliability of in situ chemical oxidation.

The principal costs associated with in situ chemical oxidation are reagent cost and equipment and utility expenses related to the delivery of the chemical oxidant to the zone of interest. Based on a limited amount of full-scale data for in situ chemical oxidation of chlorinated solvents (such as TCE with hydrogen peroxide), the cost for 80% removal efficiency using soil mixing as a delivery method is estimated at approximately \$130-\$200/m^3. This assumes that off-gas treatment constraints are nominal. These costs are not significantly different than those associated with vapor stripping, since the major costs are associated with mobilization and demobilization and operation of the mixing equipment (Siegrist et al. 1993). Coupling chemical oxidation with secondary processes might reduce the treatment costs.

The treatment time is believed to be controlled by delivery and distribution of chemical oxidant throughout the contaminated region. The reaction rates are rapid (e.g., 10^7 to 10^{10} $M^{-1}s^{-1}$) and most chemical oxidation will occur within hours if not minutes of injection (Tyre et al. 1991; Gates and Siegrist 1993b). Using commercially available equipment, soil columns 3 m diameter by 4.6 m deep can by mixed and injected with chemical oxidant in approximately 75 min. Based on limited full-scale data, the treatment time for the site is conservatively estimated at 30 to 60 days based on a processing rate of 75-150 m^3/d (Siegrist et al. 1993).

2.5 Commercial Availability

The use of in situ chemical oxidation to remediate contaminated soils and sediments is at the pilot-scale for most organic contaminants with the exception of TCE, which has been treated at the field-scale with hydrogen peroxide. In situ chemical oxidation using potassium permanganate is at the bench-scale for all contaminants. Soil mixing and reagent delivery technology is commercially available. Other delivery techniques, such as those employing land tilling or fracturing, are at the pilot-scale.

Because of the rapid nature of this technology, it can be used to pretreat contaminated soils to an intermediate level prior to using more time intensive technologies capable of reaching lower residual concentrations. In situ chemical oxidation may partially degrade refractory or inhibitory compounds to the extent that they become amenable to biotreatment. Biotreatment could also be enhanced by oxygen released during hydrogen peroxide decomposition. Processes that are dependent on contaminants being in a free or aqueous state could benefit from in situ chemical oxidation due to its anticipated soil organic matter degradation capabilities.

Providing thermophysical enhancements such as soil heating could enhance degradation rates in some settings. Also, coupling in situ chemical oxidation approaches with horizontal fracturing could provide benefits by distributing oxidants into zones beyond the boundaries of the mixed region.

2.6 Case Histories

Hydrogen peroxide has a long history of application in the waste management industry, particularly for wastewater treatment. It has been used for removal of organic clogging materials from the infiltration surfaces of wastewater land treatment units. More recently, it has seen application for removal of organic contaminants from soils (e.g., Khan 1990; Tyre et al. 1991; Gates and Siegrist 1993b). Much of this work has been conducted ex situ in laboratory or field experiments. Full-scale applications of ex situ hydrogen peroxide oxidation have also been completed involving repeated additions of peroxide solutions to fuel contaminated soil stockpiles. An alternative process involves placing contaminated soil into a hopper and mixing it under vacuum while hydrogen peroxide is added. The off-gas is passed through carbon filters to remove volatile organic compounds (VOCs). Approximately one hundred sites containing TCE and other VOCs have reportedly been treated by this latter method with VOC levels reduced below 1 mg/kg at typical processing rates of ~75 m^3/d (Khan 1990).

Experiences with ex situ peroxidation of petroleum contaminated soil have also been reported (Watts 1992). In this work, waste oil and diesel fuel contaminated soil was excavated and treated on a batch basis. The soil was an arid western soil, with low organic carbon and low manganese oxide concentrations. Studies were conducted at pH 3 with no iron addition and 2 or 7% peroxide solution added at a volume equal to 4 times the field capacity of the soil. Soil was added to pH adjusted peroxide solutions and reacted for 1 to 3 days. Soils with an initial TPH (total petroleum hydrocarbons) greater than regulatory limits (between 200 and > 2000 mg/kg) were effectively treated to less than regulatory required concentrations (<100 mg/kg). Also some preliminary indication of a positive temperature effect was noted (destruction increases as temperature increases). Watts reported a peroxide cost of \$0.34 per lb. of 50% peroxide.

Application of in situ chemical oxidation has been studied at Oak Ridge National Laboratory (ORNL) as part of a program on in situ treatment of contaminated soil, including various oxidants, contaminant and media systems, and implementation techniques (e.g., Gates and Siegrist 1993a; Hurst et al. 1993; Gates and Siegrist 1993b; Siegrist et al. 1993). As part of a major field demonstration project at the X-231B land treatment site located at the DOE Portsmouth Gaseous Diffusion Plant in Ohio, an evaluation was made of chemical oxidation coupled with soil mixing. Prior to the field demonstration, oxidation of VOCs with hydrogen peroxide was studied in bench- and pilot-scale experiments using clay soil material from the DOE site. Initial experiments were conducted with clean clay soil contaminated with an aqueous solution of TCE (~1-35 mg/kg). Results of bench-scale experiments with soil slurries and intimate contact between the soil and H_2O_2 solution revealed that destruction efficiencies of 95% could be achieved with dilute solutions of hydrogen peroxide (e.g., <5% by wt.). Destruction efficiency in this soil appeared to be independent of VOC concentration and reaction time (Fig. 3). Pilot-scale experiments with contaminated soil cores revealed similarly high destruction efficiencies at H_2O_2 volumetric loading rates of 10% v/v, but with markedly lower efficiencies at lower volumetric loadings (Gates and Siegrist 1993a). Peroxide distribution and intimate contact throughout the contaminated soil appear important to achieving high destruction efficiencies. A subsequent full-scale field demonstration of in situ chemical oxidation with hydrogen peroxide was completed in 1992 at the X-231B site (Siegrist et al. 1993). A dilute solution of hydrogen peroxide (5 wt.%, 7% v/v) was injected into the air delivery line from an ambient air compressor system. The treatment operation was conducted for approximately 60-75 min. During injection of a hydrogen peroxide mist into the mixed soil region, concentrations of VOCs in the off-gas from the system initially rose and then slowly declined. The treatment performance achieved as a result of 75 min. of operation with treatment to a depth of 15-ft appeared to average ~70%.

3.0 REDUCTION OF HALOGENATED HYDROCARBONS WITH ZERO-VALENCE BASE METALS

3.1 Technology Description

The exposure of solutions of some halogenated hydrocarbons to certain zero-valence base metals results in the dechlorination of the hydrocarbon. Use of this reaction for remediation of contaminated groundwater was originally proposed by O'Hannesin and Gillham (1992). The reaction is believed to be abiotic, reductive dechlorination. The research published to date has focused on use of iron because it is readily available, inexpensive, and more acceptable environmentally than metals such as zinc or manganese. The evaluation of other metals and metal combinations, however, is an active area of additional research.

As proposed by Gillham and O'Hannesin (1994), iron filings could be used in a permeable reaction wall (Fig. 6) that degrades the halogenated organic compounds in situ. The contaminants are degraded as they pass through the iron-impregnated wall. The wall can be left in place for an extended period of time providing passive containment and treatment of the contaminants. It should be recognized, however, that with this funnel and gate approach, zero-valence base metal reduction can only be considered a containment method because treatment of the entire aquifer, particularly in fine-grained zones, would require too much time to be practical (Chehata 1993).

Novel applications for zero-valence base metal reduction could involve coupling this emerging technology with others such as in situ soil mixing or fracturing. The in situ soil mixing technology could be used to mix zero-valence metals into the subsurface as a means of providing treatment throughout a large soil zone. This approach would most likely be coupled with vapor stripping as recently demonstrated at a fine-grained site in southern Ohio (Siegrist et al. 1993). Alternately, iron filings or powder could be incorporated into the proppant when a fine-grained zone is fractured. The iron would then react with chlorinated hydrocarbons that were pumped through this zone. Successful coupling of these technologies, however, may be complicated by the need to establish and maintain reducing conditions.

At present, the use of zero-valence metals for remedial action is being studied by a number of universities, corporate research groups, and national laboratories. Interest is high because the materials used in the process (e.g., iron filings) are inexpensive and because treatment is passive. Furthermore, in a funnel and gate approach, the installation of the impermeable wall or funnel is standard practice, accomplished with conventional slurry wall technology or by means of inter-locking sheet-pilings. Once the permeable reaction "gate" is in place, operational costs would presumably be limited to monitoring and occasionally replacing the reaction wall if or when clogging occurs.

There are, however, a number of uncertainties. Notable is the lack of agreement regarding the mechanism. One research group (Hassan et al. 1993) has suggested that sulfur impurities are responsible for the reaction. Surface analysis by proton induced x-ray emission (PIXE) performed at the University of Arizona for ORNL, however, demonstrated that the reaction occurs when the Fe is free of sulfur (Korte et al. 1995a).

Other researchers believe that the reaction is a direct electrolytic reduction (Matheson and Tratnyek 1994) as depicted in Fig. 6. This reaction is believed to occur by means of the formation of a free radical (Fig. 7), but this has not been confirmed. In fact, recent evidence from a similar system suggests that the reaction occurs by a 2 electron transfer and not a free radical (Totten and Roberts 1995). Other uncertainties that various investigators have reported are that the reaction is either slow or ineffective for less-chlorinated compounds such as dichloromethane (Matheson and Tratnyek 1993), the dichloroethenes (DCEs) and vinyl chloride. For example, Fig. 8 shows the reaction of carbon tetrachloride with iron. Chloroform reacts slowly, and dichloromethane accumulates. This is a potentially significant shortcoming for low permeablility soils because anaerobic biodegradation, which commonly occurs in such systems, may cause the formation of significant concentrations of the less-chlorinated species (e.g., formation of DCE from TCE). The mixed or uncertain results with the less chlorinated species presents an interesting problem because calculations suggest that complete dechlorination is thermodynamically feasible.

A related approach is the use of bimetallic systems. Zero-valence iron with a small amount (nominally 0.05%) of palladium plated on it has been shown to increase the reaction rate by several orders of magnitude as well as to accomplish complete dechlorination of dichloromethane (Fig 9), PCBs and chlorophenols (Muftikian et al. 1995, Korte et al. 1995a). This work is preliminary, and additional studies are needed to determine whether the material is cost-effective for below ground use. One potential approach is to use a series of gates. The initial gate could be a coarse iron which can be replaced as clogging occurs. A subsequent gate of pallidized iron could be used for the final treatment.

3.2 General Technology Considerations

Is the technology primarily geared to soil or groundwater contamination? Thus far, this technology has been proposed primarily for the treatment of groundwater. Both in situ treatment, with a reactive wall, and aboveground use in pump and treat systems have been proposed. As previously mentioned, other potential applications are to employ the method with fracturing or with in situ soil mixing. When soil is fractured hydraulically, a proppant, usually a sand, is forced into the newly formed fractures. Iron filings could be mixed with this sand. Then when groundwater is pumped through the fracture, some treatment would occur in situ. Such a process could also be used in the vadose zone with electroosmosis used as a driving force to move the soil water through the treatment zone. Treatment could also be induced by mixing the zero-valence metal through soil when performing in situ soil mixing. Such an approach may be most applicable in the saturated zone because of the need to establish and maintain reducing conditions. Recently, preliminary experiments have been performed by ORNL in which iron particles were successfully injected at a clean test site with a multi-point injection system (Korte et al. 1995b, Siegrist et al. 1995). Preliminary laboratory studies have also suggested that soil contaminants may be degraded when sand is mixed with zero-valence iron (O.R. West, ESD-ORNL, Oak Ridge, TN, personal communication to N. Korte, ESD-ORNL, Grand Junction, CO, September, 1994).

To what extent is the technology suited to remediating petroleum as well as chlorinated hydrocarbons? The available data suggest that the technique has little application for petroleum spills. Zero-valence metals dechlorinate compounds such as TCE and perchloroethene (PCE) (Cipollone et al. 1993) forming ethene or ethane as the final products. These results and the nature of the reaction mechanism, so far as it is understood, suggest that straight-chain petroleum hydrocarbons do not react with iron filings under the conditions studied. Investigators have also noted that aromatic compounds such as those found in fuels (e.g., benzene, toluene) do not react, although substituent groups in some nitroaromatic compounds are degraded (Agrawal and Tratnyek 1994).

How well is the technology able to access under buildings or pavement? The funnel and gate technique is suitable at locations where subsurface walls could be installed. Limitations for other potential applications are those inherent in the specific permeability enhancement technique. For example, in situ soil mixing is difficult to perform underneath buildings and pavement. Likewise, if the iron were emplaced in induced fractures, the access would be limited to that of the fracturing method. One additional possibility is to use a horizontal well that could be keyed into a reaction wall or, perhaps, the iron filings could even be emplaced within the well.

What is the maximum depth of remediation? There are no inherent limitations regarding the depth at which this reaction might be utilized. The limitations are all due to the method by which the iron is introduced: slurry wall excavation, caisson drilling, fracturing, or in situ soil mixing.

What are the utility, operation, and maintenance requirements? The funnel and gate technique requires no utilities because, following installation, the driving force is the natural flow of groundwater through the wall. Operation and maintenance requirements are unknown at present except that monitoring would be required. More data and field studies are needed to determine how often, or if, the wall will have to be replaced. For example, the reaction may slow or stop when the pH rises to about 9.2. This phenomena is probably due to coating of the surface with iron oxides or other precipitates such as iron carbonate. The time at which high pH conditions is reached, however, might be several years or not at all depending on the natural buffering capacity of the water being treated and the amount of iron used in the treatment system. Thus, the longevity of the wall will be related to the initial oxygen content of the groundwater, the initial pH, and the effect of other constituents in the water. For example, precipitation of iron, manganese, and carbonates that are naturally present may result in clogging and more frequent maintenance (Mackenzie et al. 1995). If iron powder is used in conjunction with fracturing, deep-soil mixing or electroosmosis, no additional utility requirements would be needed other than those already inherent with the introduction method.

Are secondary waste streams produced? Secondary waste streams containing organic contaminants are theoretically not a problem for TCE or PCE because these compounds are reportedly completely dechlorinated by the reaction. However, the reaction wall must be sufficient in width to ensure complete dechlorination. Two pilot studies have demonstrated significant removal but some chlorinated compounds remained in the treated water (Mackenzie et al. 1995, Puls et al. 1995). Also, as previously noted, dichloromethane is not degraded by zero-valence iron. In addition, the two studies mentioned above reported significant production of soluble iron. This iron may cause a problem as an aquifer contaminant itself, when present at a concentration greater than the secondary standard or by causing undesirable staining or harmful environmental effects if the effluent from the treatment well discharges to an adjacent surface water.

Are there potential environmental impacts or safety risks associated with the use of the technology? Perhaps the most attractive aspect of using iron filings is that there are few potential environmental impacts or safety risks. Following installation of the funnel and gate, or emplacement of the iron in fractures, the environmental impacts and safety risks would be no different than for groundwater monitoring. Similarly, if a treatment wall has to be replaced, it could be rinsed and disposed of as solid waste in most instances. It should be noted, however, that iron and its oxides are excellent sorbents for many inorganic species. Consequently, if the site had significant quantities of radionuclide (e.g., Tc) or metal (e.g., Cr) contaminants (Puls et al. 1995, Clausen et al. 1995), the wall might scavenge sufficient quantities to be considered a hazardous waste. On the other hand, this property might be a benefit because the technique would offer treatment for both inorganic and organic wastes.

Are models available to predict performance in porous media and to what extent are they developed? Modeling the use of the "funnel and gate" technology is being performed at the University of Waterloo (Starr and Cherry 1993, 1994). A theoretical treatment for using cutoff walls and a treatment gate has been published (Pankow et al. 1993). The extension of this type of theoretical treatment specifically to a zero-valence metal reactive wall is straightforward. Groundwater from the site would be used in a pilot test with a column of the zero-valence metal. The resulting site-specific kinetic data could be used in conjunction with hydraulic data from the field to predict the wall's performance.

3.3 Low Permeability Media Considerations

Describe the ability of the technology to remove:

- Free product pooled on top of a clay layer
- Separate-phase product trapped in continuous clay fractures
- Separate-phase product trapped in discontinuous or "dead end" fractures
- Dissolved-phase product diffused into the matrix blocks)

The "funnel and gate" approach is a containment technology, not a source treatment technology, and would not be applicable to free product removal.

What is the effect of soil water content on contaminant removal? A high soil water content is desirable to the use of the method because dissolved species are treated and reducing conditions favor application of the method. If the iron metal were introduced into a zone with low moisture and high oxygen content, it would react with the oxygen, become coated with iron oxides, and be less efficient for reaction with the hydrocarbons.

Is hydraulic control of the water table critical to success? If the iron is exposed to air for a sufficient period of time, it will oxidize and form ferric oxides and hydroxides. Thus, the portion of a permeable reaction wall that is at the top of a fluctuating water table could lose effectiveness much more rapidly than those portions that remain saturated. This potential effect has not been evaluated at the present time.

Can the porous media models (if available) be reliably adapted to predict performance in low permeability media? As described previously, theoretical treatments of the "funnel and gate" technology have already been published (Pankow et al. 1993; Starr and Cherry 1994). Modeling other remedial applications that employ zero-valence base metals should be straightforward so long as accurate kinetic data are obtained.

3.4 Cost and Reliability

(Assume a 40 × 40 m area with a 3 m thick clay layer. The TCE concentration in the clay is 2000 mg/kg and the target cleanup level is 200 mg/kg (90% removal). Estimate:

- Cost to remediate to the target cleanup level
- Time to reach cleanup target
- Economies of scale
- Confidence or expected reliability
- Cost and time to remediate 1000 mg/kg

The above scenario is focused on cleanup of contaminated soil. As noted, the only published approach proposed for zero-valence base metals is for an in situ treatment gate. That technique is not suitable for this scenario. On the other hand, the treatment gate would be an effective and inexpensive method for containing contaminated groundwater flowing from the site. The time for cleaning the aquifer in this way, however, would be exceedingly long (Chehata 1993).

Novel approaches that employ fracturing and in situ soil mixing technology have not been thoroughly investigated to date. However, it is believed that including use of zero-valence base metals with those technologies would add only modestly to their costs. The focus papers on those methods in this volume may be consulted for additional information.

3.5 Commercial Availability

3.5.1 Stage of Development

The zero-valence base metal remediation technology is at the pilot stage. Column experiments have either been performed (Johnson and Tratnyek 1994, Mackenzie et al. 1995) or are planned at a number of sites (e.g., Clausen and Richards 1994). As data from such experiments become available, additional field scale tests will be performed.

Other approaches for the use of zero-valence base metals, such as in situ soil mixing or in conjunction with fracturing, are at the conceptual stage or pilot stage (Korte et al. 1995b).

3.5.2 Commercial Availability

Environmetal Technologies Inc. provides commercial support for applying the zero-valence iron technology. They are currently performing a field study with Geomatrix Inc. at a site in California (Yamare et al. 1995) and are involved with several potential applications at federal sites in the United States. A patent has also been filed for use of palladized iron. This technique is being commercialized on behalf of the University of Arizona by Research Corporation Technologies of Tucson, Arizona.

3.5.3 Likely Future Enhancements/Complementary Technologies

Basic research is focusing on kinetic enhancements and application to a wider variety of compounds. For example, nitro-aromatic compounds have been successfully reduced (Agrawal and Tratnyek 1994), and a recent report noted that the reaction rate is faster at 50°C (Schreier and Reinhard 1994). Heating a reactive wall, in situ, is not likely to be practical. For other applications (e.g., aboveground treatment), however, increasing temperature might be relatively uncomplicated and inexpensive.

Indeed, as knowledge of this reaction continues to grow, incorporation into or coupling with complementary technologies is a likely area of future research. Some specific suggestions for use with other technologies have already been presented in this paper (Sect. 2.2.1 and 2.2.3).

3.6 Case Histories

The first field installation that was reported was a pilot study at the Canadian Bases Borden site (O'Hannesin and Gillham 1993). A contaminant plume was located about 4 m below ground surface and 1 m below the water table. The plume was about 2 m wide and 1 m thick with maximum concentrations of approximately 250 mg/L of TCE and 43 mg/L of

PCE. The reactive wall was installed approximately 5 m downgradient from this source. The plume and its migration through the wall were monitored for over 500 days. TCE concentrations were reduced by 95% and PCE by 91%. No vinyl chloride was detected and only traces of DCE were reported.

A field application of the technique at a contaminated site has recently been installed at a site in California (Yamane et al. 1995). At this site, chlorinated solvent contamination in a clay aquifer is being contained. The installation was completed in February 1995, thus, operational data were not available at the time this report was prepared.

An aboveground system has been installed at a site in New Jersey (Vogan et al. 1995). Only 0.5 gpm is being treated, but in order to have sufficient iron, a reactor that is 5.5 ft high and 8 ft in diameter is required. Specific cost information has not been published for these projects, but in both instances both capital and long-term costs are believed to be less than with conventional treatment methods.

4.0 SUMMARY

In situ chemical oxidation appears to be a viable remediation technology that is applicable to a wide range of contaminants and site conditions. The reagents needed for this process are readily available and inexpensive. The primary area of concern with in situ chemical oxidation is the delivery and distribution of the chemical oxidant solutions to the contaminated zones. It is anticipated that this process will be acceptable to regulators, since the characteristics of any secondary products formed can be determined with laboratory studies, and previous field applications of this technology did not encounter any difficulty with regulators.

The use of zero-valence base metals to reduce halogenated hydrocarbons to non-hazardous compounds is an area of active research. Bench and pilot studies indicate the possibility of several remedial applications. The use of an inexpensive, environmentally friendly material such as iron filings in a passive treatment system is attractive. At present, however, the theoretical understanding of the chemical mechanism is incomplete with contradictory information reported by various investigators. For instance, kinetic information that has been published does not present a consistent view either with respect to the compounds that are affected or the rate of reaction. Additional laboratory, bench, and field studies must be completed to determine the ultimate long-term value of this technique.

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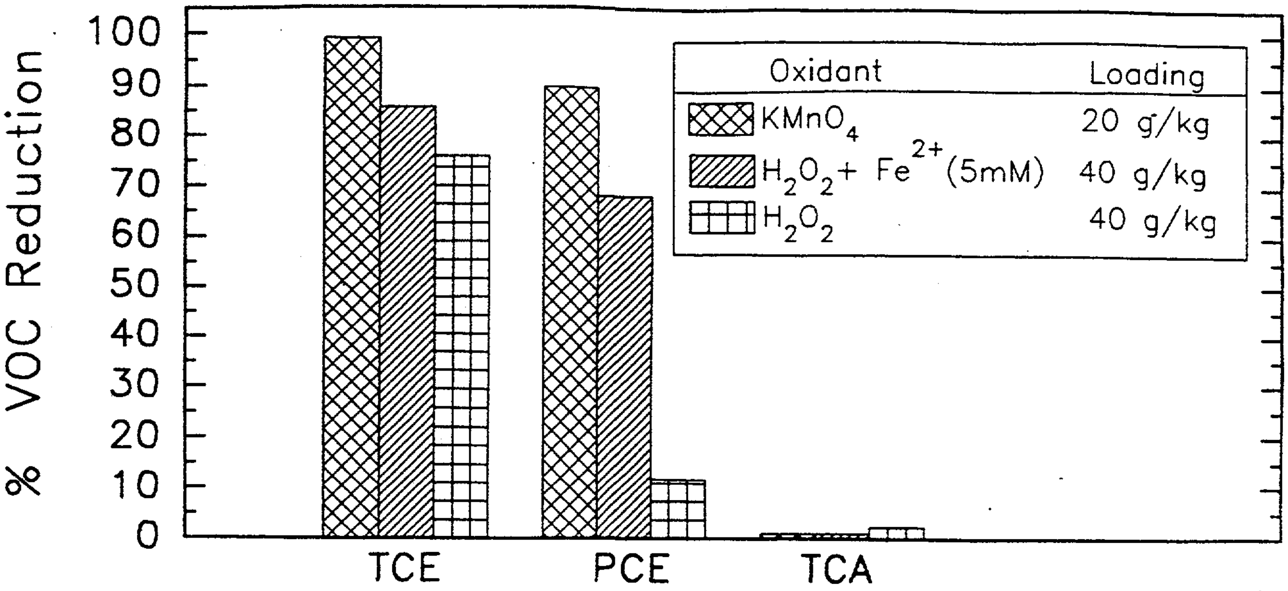


Figure 1. VOC reduction observed in clay soil treated with $KMnO_4$, H_2O_2, or H_2O_2 + iron. Initial contaminant concentrations (mg/kg): TCE=130, PCE=30, TCA= 130.

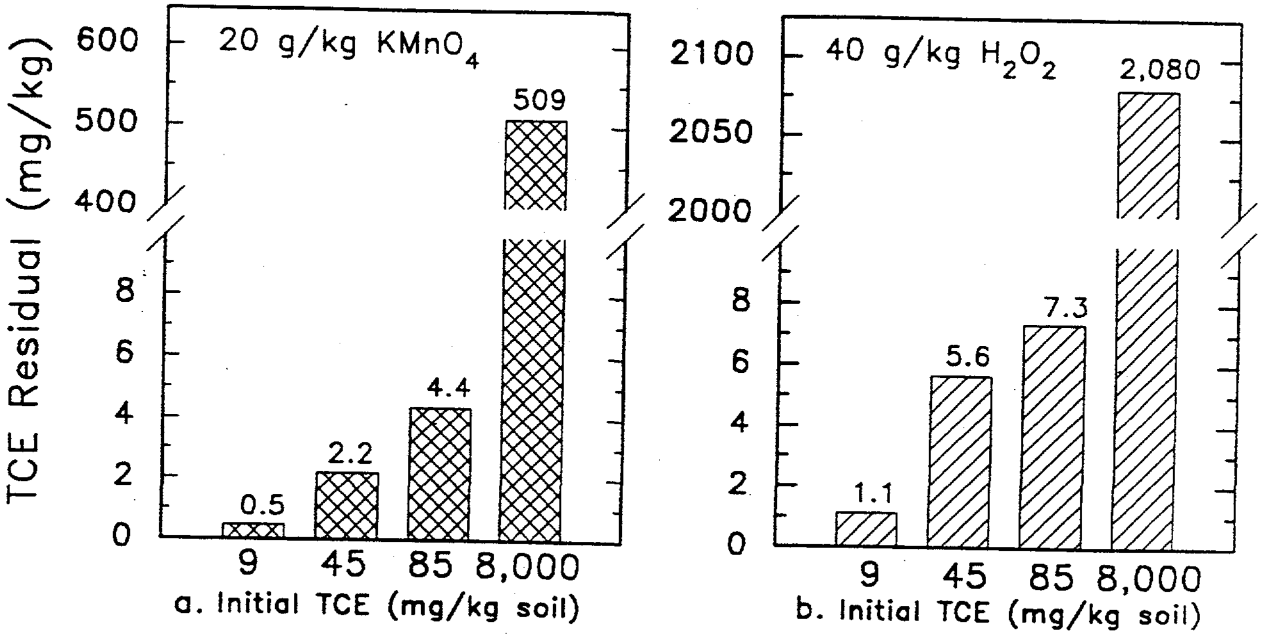


Figure 2. TCE concentration in clay soil after chemical oxidation.

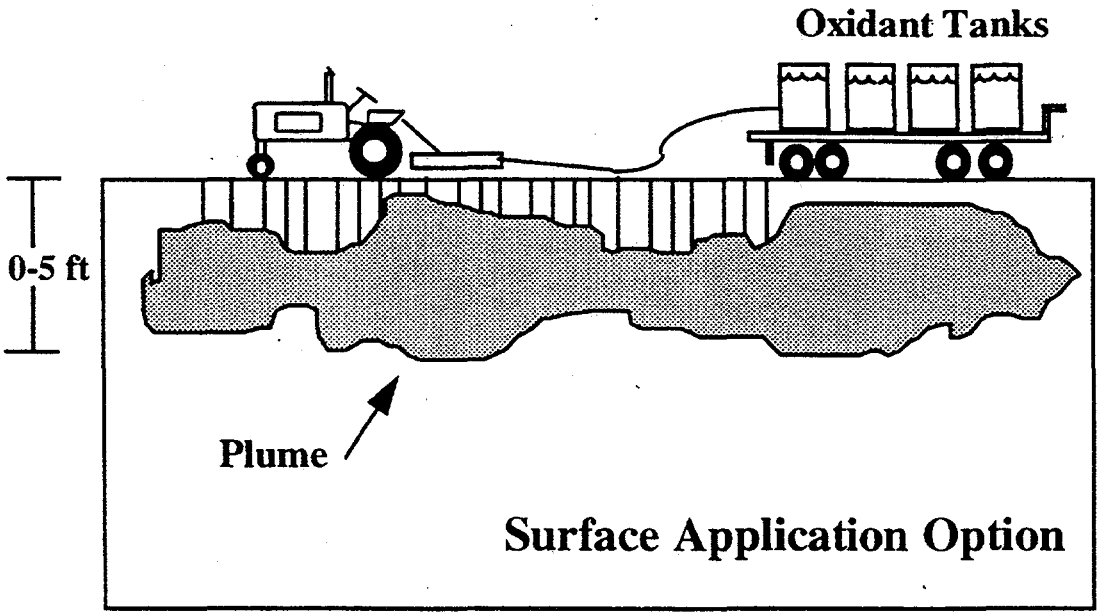


Figure 3. Potential oxidant delivery method I. Shallow tilling with spray application of oxidant.

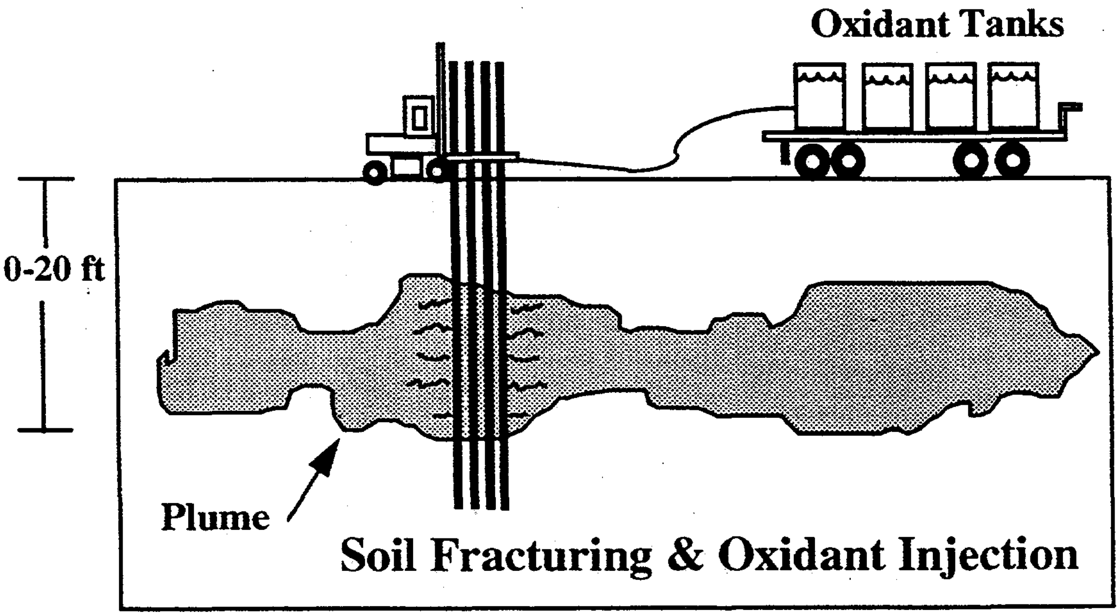


Figure 4. Potential oxidant delivery method II. Soil fracturing and oxidant injection.

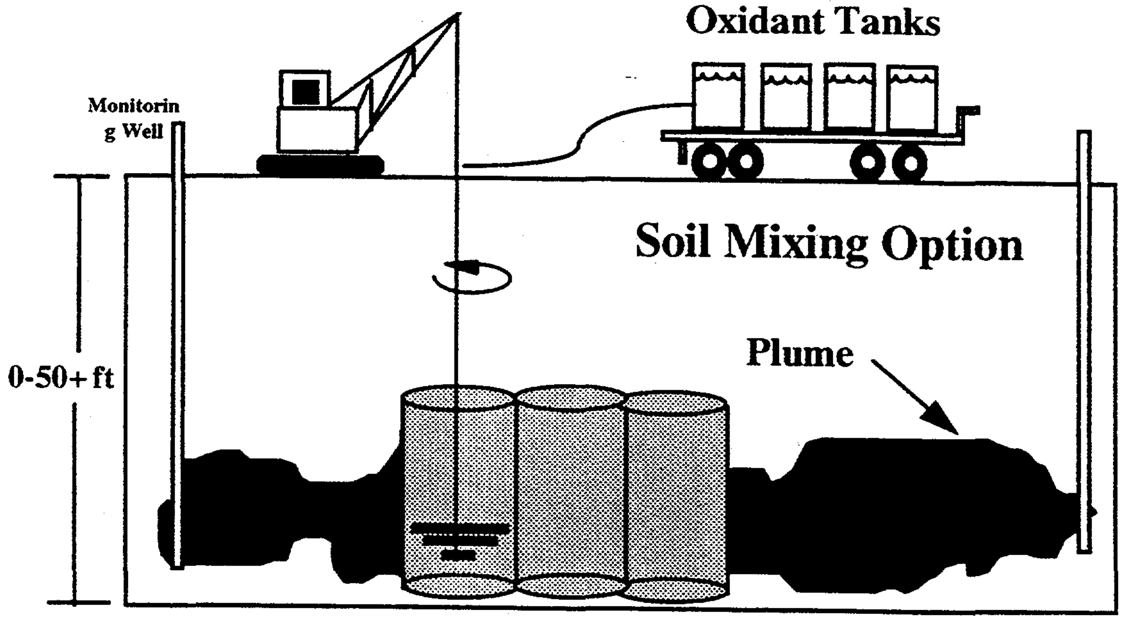


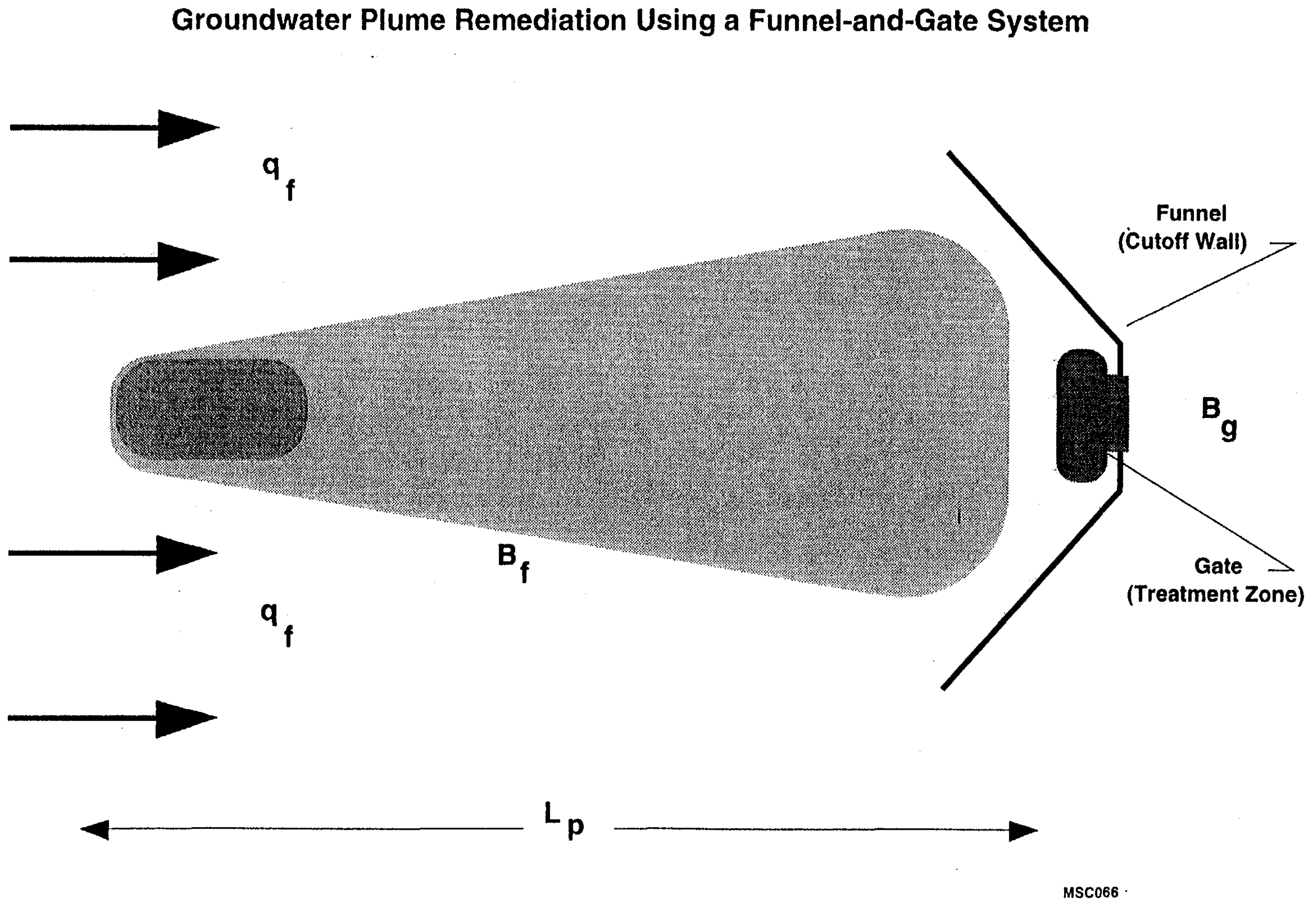
Figure 5. Potential oxidant delivery method III. Mixed region injection of oxidant.

Table 1. Compounds successfully treated by chemical oxidation.

Contaminant	Matrix	Oxidant	Reference
Tetrachloroethylene	silica sand	H_2O_2	Leung et al., 1992
	water	H_2O_2	Bellamy et al., 1991
	clay soil	H_2O_2	Gates, Siegrist and Cline, 1995
	sandy soil	H_2O_2	Gates, Siegrist and Cline, 1995
	clay soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
	sandy soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
Trichloroethylene	silica sand	H_2O_2	Gurol and Rivikumar, 1991
	water	H_2O_2	Bellamy et al., 1991
	silt and clay soil	H_2O_2	Gates and Siegrist, 1993a
	silt loam soil	H_2O_2	Hurst et al., 1993
	clay soil	H_2O_2	Gates, Siegrist and Cline, 1995
	sandy soil	H_2O_2	Gates, Siegrist and Cline, 1995
	clay soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
	sandy soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
Carbon tetrachloride	water	H_2O_2	Bellamy et al., 1991
Trans-1,2-dichloroethylene	water	H_2O_2	Bellamy et al., 1991
Pentachlorophenol	silica sand	H_2O_2	Gurol and Rivikumar, 1991

Table 1. (continued)

Contaminant	Matrix	Oxidant	Reference
	natural soil	H_2O_2	Watts et al., 1990; Tyre et al., 1991
2,4-dichlorophenol	water	H_2O_2	Bowers et al., 1989
Dinitro-ortho-cresol	water	H_2O_2	Bowers et al., 1989
Formaldehyde	water	H_2O_2	Murphy et al., 1989
Trifluralin	natural soil	H_2O_2	Tyre et al., 1991
Hexadecane	natural soil	H_2O_2	Tyre et al., 1991
Dieldrin	natural soil	H_2O_2	Tyre et al., 1991
Motor oil and diesel fuel	naturally contaminated soil	H_2O_2	Watts, 1992
Naphthalene	clay soil sandy soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
Phenanthrene	clay soil sandy soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
Pyrene	clay soil sandy soil	$KMnO_4$	Gates, Siegrist and Cline, 1995
Naphthalene	clay soil sandy soil	H_2O_2	Gates, Siegrist and Cline, 1995
Phenanthrene	clay soil sandy soil	H_2O_2	Gates, Siegrist and Cline, 1995
Pyrene	clay soil sandy soil	H_2O_2	Gates, Siegrist and Cline, 1995
Octachloro-dibenzo-p-dioxin	natural soil	H_2O_2	Watts et al., 1991



Groundwater Plume Remediation Using a Funnel-and-Gate System

Figure 6. Groundwater plume remediation using a funnel-and-gate system (Chehata 1993).

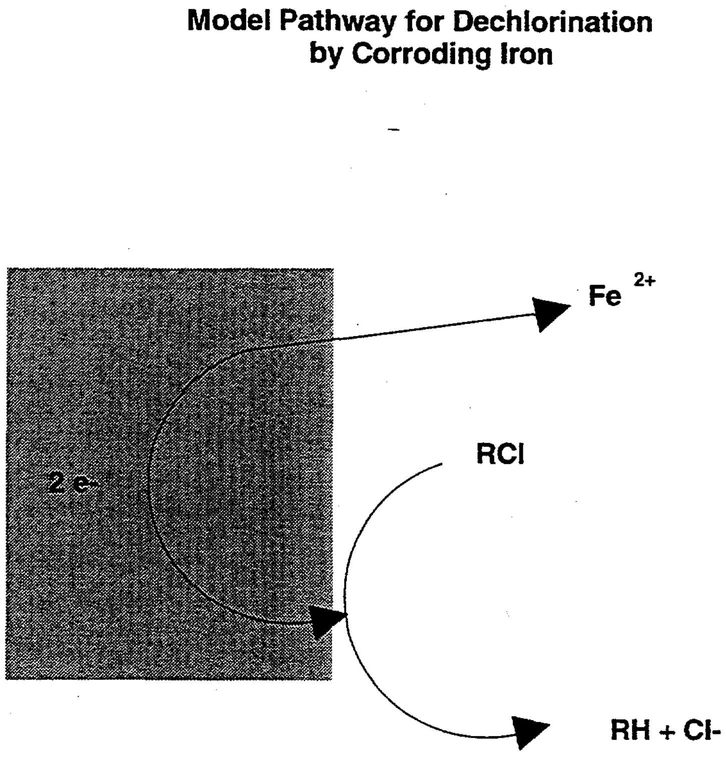


Figure 7. Model Pathway for Dechlorination by Corroding Iron (Matheson 1994).

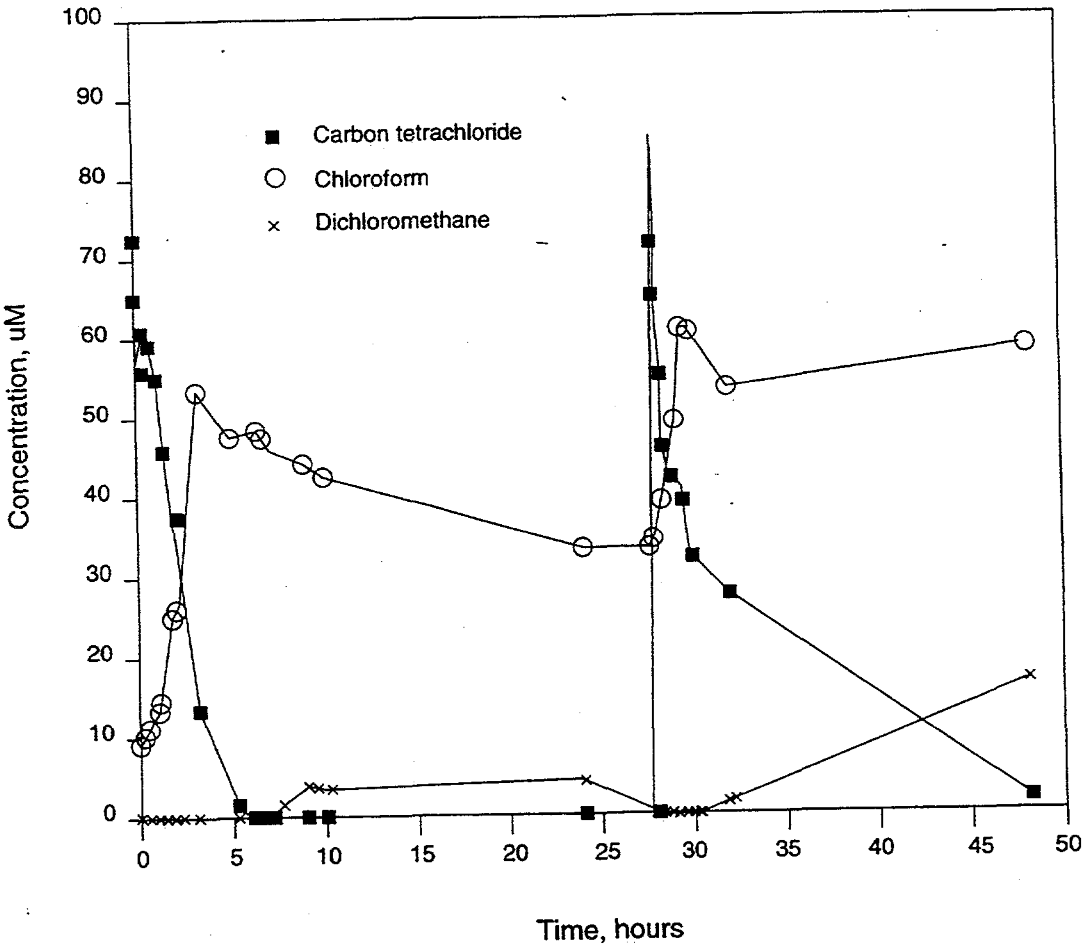


Figure 8. Carbon tetrachloride (closed squares) is dechlorinated to chloroform (open squares) and dichloromethane (asterisks) in laboratory model experiments. Arrow indicates second carbon tetrachloride addition. (from Matherson and Tratnyck 1993).

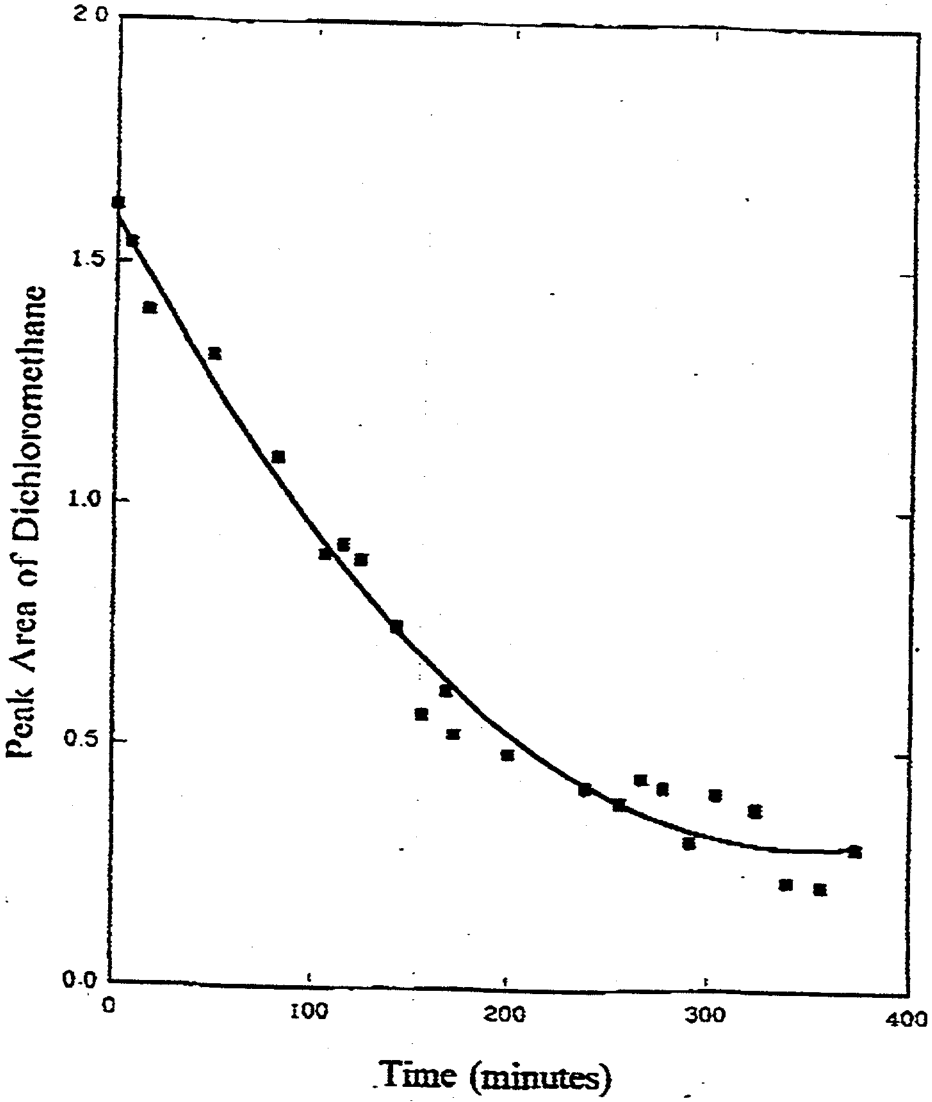


Figure 9. Reaction of dichloromethane with palladized iron.

ELECTROOSMOSIS REMEDIATION OF DNAPLS IN LOW PERMEABILITY SOILS

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Electroosmosis is the movement of water through a soil matrix induced by a direct current (DC) electric field. The technique has been used since the 1930s for dewatering and stabilizing fine-grained soils. More recently, electroosmosis has been considered as an in-situ method for soil remediation in which water is injected into the soil at the anode region to flush the contaminants to the cathode side for further treatment or disposal. The major advantage of electroosmosis is its inherent ability to move water uniformly through clayey, silty soils at 100 to 1000 times faster than attainable by hydraulic means, and with very low energy usage. Drawbacks of electroosmosis as a stand-alone technology include slow speed, reliance on solubilizing the contaminants into the groundwater for removal, potentially an unstable process for long term operation, and necessary additional treatment and disposal of the collected liquid.

Possible remediation applications of electroosmosis for DNAPLs would be primarily in the removal of residual DNAPLs in the soil pores by electroosmotic flushing. The future of electroosmosis as a broad remedial method lies in how well it can be coupled with complementary technologies. Examples include combining electroosmosis with vacuum extraction, with surfactant usage to deal with non-aqueous phase liquids (NAPLs) through enhanced solubilization or mobilization, with permeability enhancing methods (hydrofracturing, pneumatic fracturing, etc.) to create recovery zones, and with in-situ degradation zones to eliminate aboveground treatment.

2.0 DESCRIPTION OF THE TECHNOLOGY

Electrokinetics is a general term used to describe a number of phenomena that occur due to coupling between electrical and hydraulic flows and gradients in the soil-water-electrolyte system (1). Within the context of remediation, two relevant electrokinetic phenomena are **electroosmosis** and **electrophoresis**. Electroosmosis is the movement of ion-containing liquid (e.g. water) relative to a stationary charged surface (e.g. soil pores) due to an applied electric field. Electro phoresis, the opposite of electroosmosis, refers to the movement of charged particles through a stationary liquid. The transport of soluble ions in solution in the presence of an electric field has also been called **electromigration** (2). The following describes in more detail electroosmosis and its potential applications in waste site remediation.

When a DC electric field is applied between two electrodes immersed in a wet soil mass, water in the soil matrix will move from one electrode to the other electrode. This occurs because of the movement of a thin layer of charged fluid near the pore wall that drags the bulk fluid in the pore along with it. Most soils are negatively charged, which causes cations in the pore water to accumulate near the surface of the soil particles. The thin layer of fluid (called double layer) near the pore wall is thus positively charged, which moves toward the negative electrode (cathode), resulting in a net water flow from the anode (positive electrode) to the cathode (Figure 1).

Bulk electroosmotic flow through soil is normally described empirically by:

$$Q = k_e i_e A \tag{1}$$

where Q: volumetric flow rate by electroosmosis (cm^3/sec)
k_e: coefficient of electroosmotic conductivity (cm^2/volt-sec)
i_e: voltage gradient applied across the soil mass (volt/cm)
A: cross-sectional area perpendicular to the direction of flow (cm^2)

Note that the electroosmotic flow is proportional to the applied voltage gradient, and that the electroosmotic conductivity has the units of velocity over field strength (cm/sec over volt/cm).

Based on the Helmholtz-Smoluchowski theory, which assumes thin double layer with respect to pore size, k_e is given by the following relationship (1):

$$k_e = \varepsilon \, \zeta \, \theta / \mu \qquad (2)$$

where ε: permittivity of solution; $\varepsilon = \varepsilon_0 D$
ε_0: permittivity of vacuum ($\varepsilon_0 = 8.854 \times 10^{-12}$ farad/m)
D: dielectric constant of solution (no units)
ζ: zeta potential of the soil (volt)
θ: soil porosity
μ: liquid viscosity (Newton-sec/m^2)
and k_e in units of m^2/V-sec (or m/sec per V/cm)

The model thus predicts that electroosmotic flow is independent of pore size of the soil matrix. Experimental data obtained for various soil types present a consistent picture with the model. Table 1 shows that electroosmotic conductivities vary only a few-fold for soils with hydraulic conductivities ranging over five orders of magnitude due to the large differences in particle size (1). Electroosmotic conductivity typically ranges from 10^{-5} to 10^{-4} cm^2/V-sec and is relatively independent of soil type. It is because of this characteristic that electroosmosis is effective for moving liquid through fine-grained soils (such as clayey, silty soils) or heterogeneous soil matrices.

Electroosmosis has been used since the 1930s for removing water from clays, silts, and fine sands (3,4). More recently, electroosmosis has been investigated as an in-situ method for soil remediation (5-10). Water injected into the soil at the anode region flows under electroosmosis through the contaminated soil, flushing the contaminants to the cathode for further treatment or disposal. Major advantages of electroosmosis as an in-situ remediation method for low-permeability soils include fairly uniform flow distribution in the soil matrix, controllable flow direction by the placement of the electrodes and the voltages applied, relatively low power consumption, and electroosmotic permeability being 100 to 1000 fold higher than the hydraulic conductivity (9,11). For metal removal, ionic migration is usually several times faster than the convection velocity, which enables a very high degree of removal by collecting only a fraction of the saturating liquid (11). There is evidence that electro migration can be effective in unsaturated soils (27).

During electroosmosis, however, there are a large number of chemical and electrochemical processes occurring that can negatively affect the electroosmotic process and the effectiveness of the intended remediation. These include ion diffusion, ion exchange, development of osmotic and pH gradients, soil drying, mineral decomposition, precipitation of salts and secondary minerals, electrolysis, physical and chemical adsorption, fabric changes, etc. (12).

At the current state of knowledge, the electroosmosis method appears to suffer from two key limitations that complicate its implementation in the field. First, the liquid flow induced by electroosmosis is very slow, about 1 inch per day for clayey soils, which could result in a very long-term operation for large-scale applications. Second, it has been found in several laboratory studies (7-10) that extended operation of electroosmosis could lead to soil drying and cracking, pH change in the soil bed, and precipitation of metals and minerals near the cathode, which results in high electrical resistance and reduced flow, and could eventually stop the process.

The prevailing approach for stabilizing the electroosmosis process is to condition the electrode solutions with respect to solution electrical conductivity and pH, which can be accomplished either with aboveground liquid handling systems (14,19,20) or with composite electrodes containing solid reagents such as ion-exchange resins (32). Another interesting approach is the Lasagna™ process in which electrokinetics is coupled with in-situ treatment. This coupling allows the utilization of water recycling between the electrodes and periodic polarity reversal to stabilize the electroosmosis. The process appears to hold great promise for enhancing the remedial utility of electrokinetics, especially as an in-situ treatment method (29-30).

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

Following are some key characteristics of electroosmosis as a remediation technology:

a) The technology is geared primarily to soil remediation. Since electroosmosis is basically an electrically-induced movement of water in the soil pores, it works best in saturated zones, but could be partially effective in unsaturated zones.
b) The technology is suited to remediating chemicals that can be solubilized in the sweeping water, including petroleum and chlorinated hydrocarbons to the extent of their solubility in the water. Reagents such as surfactants (15-16, 28) and solvents such as isopropanol (17) can be incorporated into the flushing water to enhance the removal efficiency.
c) How well the technology is able to access under buildings and pavement depends primarily on how well electrodes can be installed in these physical settings. Various established geotechnical methods exist for electrode installation, e.g. hydraulic fracturing, impulse fracturing, and directional drilling (18), that could operate well under buildings and pavement.
d) The maximum depth of remediation is very high with hydraulic fracturing, an established technology for enhanced oil recovery, as a method for electrode installation.
e) Electroosmosis is a mechanically passive process. The utility, operation and maintenance requirements have to do primarily with construction equipment for installing electrodes, power supply and electrical connections, and monitoring equipment (parameters: voltage, current, soil moisture, pH, temperature, etc.)
f) Secondary waste streams produced: water exiting the cathode side will contain the contaminants and needs to be further processed.
g) There is little potential environmental impact and few safety risks associated with electroosmosis since power consumption is very low and is not expected to alter the physical and chemical nature of the soil to any significant extent. Significant temperature rise (to about 60^0C), however, has been reported in one field test (19).
h) Key transport models taking into account electrode reactions and liquid-soil interactions have been under development by Probstein et al. at MIT and Acar et al. at LSU (14,20). These models appear successful in predicting pH gradient and chemical transport by electrokinetics in homogeneous model clay soils.

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

a) Effects of soil water content on contaminant removal: Electroosmosis works best in saturated zones; its effectiveness is partially reduced when the soil is not saturated.
b) Hydraulic control of the water table is not critical to success as long as the contamination is saturated or partially saturated.
c) Electroosmotic permeability has been found to be fairly insensitive to the heterogeneity of the soil media; electroosmotic permeability only varies a few fold from sandy soil to clayey soil (see Table 1). This is a major strength of electroosmosis for remediation. Since electroosmotic permeability for most soils is on the order of 10^{-4} to 10^{-5} cm^2/volt-sec (or 10^{-4} to 10^{-5} cm/sec for a typical applied voltage of 1 volt/cm), flow induced by electroosmosis will be insignificant in media with hydraulic conductivities higher than 10^{-3} cm/sec.

Consider the scenario where the soil is stratified with layers ranging from a medium sand (permeability of 10^{-3} cm/sec) to a clay (permeability ranging from 10^{-6} to 10^{-8} cm/sec). The clay layer contains natural desiccation fractures that are spaced a few cm apart and have apertures of 10-40 microns. The effective soil porosity of the clay is <1%. Assume an underground storage tank of TCE and PCE leaked slowly over many years and the hydrocarbon entered a sand layer overlying this clay aquitard, into which it has diffused. The clay layer is 3 m thick and it in turn overlies a sand aquifer. Assume the water table is at the top of the clay layer and the natural fractures in the clay can be dewatered by pumping the aquifer (if needed to enhance contaminant removal). The following statements can be made about the capability of electroosmosis in this case:

- Electroosmosis with unmodified groundwater will not be able to remove free product pooled on top of the clay.
- The technology may or may not be able to flush separate phase product trapped in the continuous clay fractures. This is an aspect of electroosmosis that requires further study.
- For separate product trapped in discontinuous or 'dead end' fractures, the main removal mechanism will be the diffusion of the dissolved portion of the trapped organic liquid into the passing electroosmotic flow.
- Due to its ability to effectively penetrate low permeability media, electroosmosis will be most effective in removing the dissolved portion of the trapped organic liquid product that has diffused into the matrix blocks.

5.0 COST AND RELIABILITY

Information on cost to clean up contaminated soils using electrokinetics is very sketchy at this time. The literature suggests a range from about $30 (14) to about $85 per m^3 of soil treated (25), but these figures appear to come from either crude estimates or are based on specific cases. As with any remediation method, the actual cost of electroosmosis treatment will depend very much on the site characteristics, the nature of contamination (type of contaminant, concentration, contaminant-soil interaction, etc.), and the cleanup target. Geokinetics, an electro-remediation company in the Netherlands with fairly extensive field experience, gave a range of $150 to $500 per ton of soil depending upon the energy used, with electricity taking up to 20 to 25% of total cost (26).

For the scenario described in the previous section, assume that the contamination covers a plane area of 40 x 40 m and the clay layer is 3 m thick. The TCE concentration in the clay is 2000 mg/kg (DNAPL situation) and the target cleanup level is 200 mg/kg (90% removal). For the conventional application of electroosmosis (electroosmotic flushing), the overall treatment cost will consist of the costs associated with the electroosmosis operation for flushing TCE out of the soil, and the cost for additional treatment of TCE-containing effluent collected at the cathode area. Since electroosmosis is unlikely to be used as a single technology in this case, the following analysis is intended only to provide a framework for cost estimates, and will focus primarily on the electroosmosis part. The TCE-containing water collected from the cathode can be treated above ground with various methods such as activated carbon adsorption, stripping, or biodegradation. This part will need to be considered separately.

For the electroosmosis operation, key cost factors are the capital cost associated with the electrical system and materials (electrodes, rectifier, power control, fluid handling system, etc.), power consumption (electricity), and fixed costs such as equipment mobilization, maintenance, supervision. Assume the clay soil has a porosity of 40% with a bulk density of 2 g/cc. The actual TCE concentration in the soil pore water is thus about 10,000 mg/L, which is about ten times the TCE solubility in water at 25°C (about 1100 mg/L). This is consistent with the fact that TCE is present as residual TCE droplets in the soil matrix. For an *ideal case* the water moving through the soil can be assumed to be saturated with TCE at about 1000 mg/L. (This is probably unlikely unless some surfactants are introduced, which could potentially lead to higher concentrations than the solubility in water). It will take about 9 pore volumes of water through the contaminated soil for 90% removal. The major part of the operating cost is then the cost of electricity required to move those 9 pore volumes of water electroosmotically through the soil. Note that this is a fairly ineffective way to utilize electroosmosis due to the large volume of liquid that has to be moved through the soil, resulting in high power consumption as shown below.

The electrode configuration adopted is most critical to the energy cost of electroosmosis. Key considerations include vertical vs horizontal electrodes, anode-cathode spacing, like-electrode spacing if vertical wells are used for electrodes. The costs associated with vertical and horizontal electrode configurations are considered below.

Vertical Electrodes:

With vertical electrodes, the setup can consist of alternating rows of vertical anodes and cathodes. Using the following values,

k_e (electroosmotic permeability) = 10^{-5} cm^2/volt-sec
soil porosity = 0.4
anode - cathode spacing = 1 m; 41 electrodes needed at 120 m^2 each
voltage applied between anode-cathode pair = 100 V (1 V/cm)
total current = 180 Amp (at 1.5 Amp/m^2 electrode),

one can obtain the following:

pore volume of each soil section = 40 x 3 x 1 x 0.4 = 48 m^3
average electroosmotic flow would be about 43 L/hr
time needed for one pore volume of electroosmotic flow = 46.5 days
remediation time for 5 pore volumes (50% removal) = 233 days
cost of electricity (at $0.05/kWh) = $42/m^3 treated soil
remediation time for 9 pore volumes (90% removal) = 419 days
cost of electricity (at $0.05/kWh) = $75/m^3 treated soil

One vertical electrode system that has been considered uses wickdrains with incorporated galvanized steel chicken wire for cathodes and incorporated IrO_2-coated expanded titanium mesh for anodes (25). The wickdrain configuration allows fluid circulation through the electrodes. The material cost and installation cost for this type of electrode is about $\$100/m^2$ electrode, resulting in a total cost of almost \$500,000 for the electrodes, or over $\$100/m^3$ soil. This is clearly a major cost item, probably due to the special design and materials, thus a potential area for significant cost improvement. Larger electrode spacing would reduce the number of electrodes required and the associated cost accordingly, but would increase the power cost due to the longer distance the water has to travel.

Fixed cost and cost of post-collection contaminant treatment have been estimated to be about $\$20/m^3$ soil (25) for an organic contaminant at subsaturation level. However, for DNAPLs, if carbon adsorption were used for aboveground treatment, it would take about 18 kg of granular carbon to remove 90% of the initial TCE in a cubic meter of soil (assuming carbon capacity of 0.2 g TCE/g carbon), or $\$40/m^3$ soil at a carbon cost of \$1/lb (\$2.2/kg). The total treatment cost using the composite wickdrain electrodes would be about $\$230/m^3$ for 90% TCE removal, and $\$180/m^3$ for 50% removal. Note that these figures did not take into account the cost of surfactants to get TCE concentration in the pore water up to 1000 mg/L.

Horizontal Electrodes:

For the relatively thin clay layer under consideration (3m), horizontal electrodes that could be installed with emplacement methods like hydraulic fracturing could be more cost-effective than vertical electrodes. Significant progress in this area is described in the focus paper entitled "Hydraulic Fracturing To Enhance The Remediation of DNAPL in Low Permeability Soils" by Larry Murdoch and Bill Slack.

If hydrofracturing is applicable in this case, the following can be considered:

- dimensions of each fracture: 9.14 m (30 ft) in diameter and 2 cm thick,
- 4 fractures spaced 1 m apart and stacked vertically,
- covering the 40 m x 40 m area requires a total of 120 fractures (30 wells with 4 fractures per well) assuming 20% overlap of the hydrofractured zones.

According to Golder Associates (31), the cost per fracture is about \$575, or \$69,000 for 120 fractures. The cost of granular graphite needed to be injected into each fracture to form a horizontal electrode is about \$1400 (at 50 cents/lb carbon), or \$168,000 for 120 electrodes. The total cost of installing horizontal electrodes with hydraulic fracturing is thus about \$240,000 or \$50 per m^3 of contaminated soil, which is about half of the cost for vertical electrodes mentioned above. The overall cost for 90% TCE removal in this case would be \$50 (electrodes system) + \$75 (electricity) + \$55 (fixed cost + carbon adsorption) = \$180 per m^3 of contaminated soil, and \$130 per m^3 of contaminated soil for 50% removal.

The above rather approximate analysis shows that the cost of using electroosmosis to remove 90% of TCE for the hypothetical case (40 m x 40 m x 3 m thick clay soil containing 2000 mg TCE/ kg soil) ranges from \$180 to \$230 per m^3 of contaminated soil. The range for 50% TCE removal is \$130 to \$180 per m^3 of contaminated soil. It is important to note that these costs did not take into account the cost of surfactants needed to get TCE concentration in the pore water up to 1000 mg/L. If one uses the Geokinetics guideline (26), i.e. electricity making up about 25% of the total cost, the total cost would be $\$300/m^3$ of soil for the 90% TCE removal, and about $\$170/m^3$ soil for the 50% TCE removal.

It should be pointed out that recent developments in coupling electroosmosis with in-situ treatment zones (Lasagna™ process) indicate that this innovative approach can significantly reduce the overall cost of treatment. A detailed discussion of the Lasagna™ process is, however, outside the scope of this focus paper.

6.0 COMMERCIAL AVAILABILITY

- Stage of development of technology: Electroosmosis is well established for dewatering and stabilizing fine-grained soil deposits, but it is in research stage for remedial applications.
- Commercial availability of the technology: There are a small number of outfits that offer the technology at field scale, such as Electro-Petroleum and others for dewatering and consolidation applications and Geokinetics, Inc., in the Netherlands for metal removal. Remediation of soils contaminated with organics is still in the research stage, but is undergoing rapid development.
- Likely future enhancements with respect to electroosmosis will involve electrode-related issues (material, design, and emplacement method) as well as novel ways to control key parameters (e.g. pH and conductivity) of the solutions in the electrode compartments.
- With electroosmosis providing fairly uniform movement of water through low-permeability soils, there are many complementary technologies that would enhance cleanup if incorporated in a treatment train. Following are some ideas that have been proposed:
  - coupled with surfactant flushing to enhance removal of non-polar organic contaminants, thus significantly reducing the number of pore volumes of water required;
  - coupled with permeability enhancing methods (e.g. hydraulic fracturing, pneumatic fracturing, directional drilling) to shorten liquid movement distance, hence reducing treatment time and facilitating DNAPL removal and recovery;
  - utilizing membranes to recover TCE from collected effluent and recycle the water, with or without surfactant, back to the anode side;
  - aboveground chemical or biodegradation of TCE and recycle the water;
  - coupled with pump and treat: Electroosmosis is utilized to move organics out of the low-permeability zone into the hydraulic flow path to cut down on treatment time;
  - coupled with vacuum extraction;
  - coupled with in-situ treatment zones (e.g. Lasagna™ process).

7.0 CASE HISTORIES

All field applications of electroosmosis, or more generally electrokinetics, have been with low permeability media due to the unique applicability of the technology for fine-grained soils. Earlier implementations primarily focused on soil dewatering and stabilization. More recent field applications have aimed at removing heavy metals from contaminated soils. There have been no documented cases in which soils contaminated with organic compounds were remediated at field scale using electroosmosis. At the time of writing, a small field test (15 ft by 10 ft by 15 ft deep) is being conducted at a DOE site in Paducah, KY., using the Lasagna™ process (33) to remove TCE from clay soil. The objective of the test is to demonstrate the removal of TCE from the contaminated soil using electroosmosis with simultaneous adsorption of the TCE by activated carbon in the in-situ treatment zones.

Following is a brief summary of three field implementations of the technology, the first case for dewatering, the other two for remediation.

1) **Electroosmotic treatment at Monsanto Tennessee phosphate mine operation for tailings consolidation:** This is one of the largest applications of osmosis for dewatering clay soils. Monsanto's contribution lies in scaling up electroosmosis to the size needed for clarifying a settling pond in a cost-effective manner. Settling ponds represent a very slow process of phosphate mining in the eastern U.S. Most eastern phosphate rock contains phosphate nodules in a matrix of clay. Such ores are crushed then washed with water. The heavier phosphate sinks down and the clay slurry is sent to a settling pond. The larger clay particles sink to the bottom of the settling pond at a reasonable rate, but the finer particles can stay in suspension for years. Setting of the clay is necessary to reclaim the lake.

   The electroosmosis process was implemented to accelerate the settling and consolidation of the fine clay particles. There were 20 electrode stations installed in a large 400 acre lake (4,22,24). Each electrode station consisted of 8 anodes (sacrificial iron rods, 2.5 in diameter, 40 ft long) placed equidistantly around a 290-foot-diameter circle, suspended about 100-150 ft down in the mud, and one cathode at the center of circle but *near the surface*. The cathode was an iron cross, made from 1 in pipe, and was 18 feet in diameter. For the site, total voltage applied between the anodes and the cathodes was about 300-400 V with a current of 40 amp, corresponding to only 12-15 kW power consumption. The station was designed to have close to linear potential gradient from the anode to the cathode, at about 3 V/m. During operation, large potential drops near both electrode areas were observed. Hydrogen was liberated at the cathode due to water electrolysis, raising the pH there. Cathodes tended to become encrusted with lime deposits, but this never caused serious problems.

   The clay acted as a negative membrane causing water to migrate by electroosmosis from the clay into the water surrounding the cathode. This condensed the clay and lowered the elevation of the mud line while stabilizing the muds. After the clay settled, electroosmosis moved the water out and up to the top of the pond, where it could be decanted. The electroosmosis unit performed well throughout the life of the impoundment (about 22 years). The unit was kept in operation for almost two years after no fresh tailings were delivered to the pond. It was largely responsible for the method chosen to retire the pond. The system increased the density of the muds in the pond. When the impoundment was decommissioned, aa probe torpedo would not penetrate more than 25 m at any point in the impoundment. More than 1,000,000 cyprus trees have been planted to stabilize and compact the clays. This could never have been accomplished without electroosmosis, since the bottom would have remained too deep to have been reached by tree roots.

2) **Electrokinetic Applications in The Netherlands for Heavy Metals Removal:** The following two cases were chosen from several field tests described by Lageman (19) in which he documented successful remediation and listed some practical concerns encountered during the implementation of electro-reclamation projects.

a) Copper and Lead Removal: This case was conducted in 1987 at the site of a former paint factory in Groningen, The Netherlands. The field test took place in the peat soil along a ditch, bordered on one side by the factory and on the other side by open grassland. Contamination in this area consisted of heavy metals, such as lead and copper, that had leached down into the soil from sludge that had been dredged from the ditch and dumped onto the grassland. The sludge was heavily contaminated with metals in the form of paint residues (solid particles). The lead concentration ranged from 300 to over 5000 ppm, and copper from 500 to 1000 ppm. The treated area was 70 m long and 3 m wide. Electrode set up consisted of one horizontal cathode at 0.5 m below ground surface and a row of vertical anodes installed at a depth of up to 1 m and spaced 1 m apart. Changes in lead and copper concentrations were monitored at 26 sampling locations, spaced at regular intervals and at several depths (10, 20, 30, 40, and 50 cm below ground surface). Current was applied 10 hr per day for 43 days. The lead level was reduced by up to 70%, and copper about 80%. Energy consumption was about 65 kWh/m^3 of treated soil. In the layer just underneath the sludge, metal concentrations were found to increase as a result of some dissolution of the paint particles.

This test showed that the relatively low pH of the peat soil (pH 4) facilitated the mobilization of the heavy metals greatly, resulting in low power consumption. The already acidic environment was further acidified through the electrokinetic generation of H+ at the anode, causing the unexpected dissolution of the paint particles. In order to successfully remediate the site by electrokinetics, the sludge layer containing the solid paint particles would have to be removed. The energy consumption needed to meet the Dutch regulated levels for lead and copper was estimated to be 85 kWh/m^3 soil.

b) Arsenic Removal: This case was an actual cleanup at the site of a former timber impregnation plant in Loppersum in the Netherlands in 1989. The site was underlain by heavy clay soil containing arsenic level up to 400-500 ppm to a maximum depth of 2 m. The source of arsenic was attributed to $Na_2HAsO_7.7H_2O$, or "Superwolman salt D", used for impregnation. The contamination was confined to an area 10 m x 10 m x 2 m deep and an adjoining area 10 m x 5 m x 1 m deep (total of 250 m^3 soil). In this application, arsenic was present as a anion, hence it would migrate towards the anode. Electrode solutions were circulated through conditioning systems for control of pH and conductivity.

After 3 to 4 weeks of operation the soil temperature rose to an average of 50^0C from the initial 7^0C, and the resistivity dropped from 10 to 5 ohm/m. The initial voltage gradient of 40 V/m decreased to 20 V/m with an average current $\underline{4}$ amp/m^2. The total cross sectional area was 110 m^2.

Arsenic concentrations were monitored at 10 fixed sampling locations and many randomly selected points. After 65 days roughly three quarters of the area showed arsenic concentration below the remediation objective of 30 ppm. There were complications at the remaining quarter of the area: the arsenic concentration decreased much more slowly than at other locations and the temperature rose to 60^0C. The remediation was terminated and this part of the soil was excavated. Many metal objects such as tins, barrels, and reinforcing rods were found at the location; they were shiny, without any rust and most were partly dissolved. These metallic objects apparently functioned as preferential flow paths for the electrical current. About 40 m^3 of soil had to be excavated because of this. Periodic treatment of the electrode solutions yielded 800 kg of filtrate. The site has become a residential area.

A main conclusion from this case was that metallic objects larger than 10 cm should be removed if possible since they interfere with the electric current. Insulating objects such as wooden beams, plastic sheets, and concrete blocks also interfere with the process. The presence and location of subsurface pipes and cables should be identified and properly protected.

3) **Field-scale electrokinetic treatment of a Superfund site contaminated with chrome-plating wastes -- Combined electrokinetics with hydraulic flow.** This case was conducted to treat hexavalent chromium-contaminated soil on the United Chrome Products, Inc. premises by Banerjee (21). The site covered approximately 0.6 hectares of level ground. The hydrogeologic conditions at the site and the hydraulic conductivity of the subsurface soils were judged suitable for electrokinetic treatment. The goundwater table at the site varies in depth depending upon the season. During wet winters, the water table is from 0 to 2.5 cm below ground surface. There is very little groundwater flow through the site and the average hydraulic gradient is approximately 0.008 m/m. The contaminated soils near surface have hydraulic conductivity ranging from 5×10^{-4} to 5×10^{-6} cm/sec. The contaminants at the site are inorganics, mostly hexavalent chromium (CrVI) which exists in anionic form as CrO_4^{-2}, $HCrO_4$- or $Cr_2O_7^{-2}$ depending upon pH and concentration of the chromium ion in the soil-water system. Chromate concentration ranged from 100 to 10,000 mg/L and is a major ionic constituent of the solution.

A hexagonal arrangement of electrodes was chosen for electrokinetic treatment: a central 20-foot deep, 2-inch diameter stainless steel well was used as the anode; hexagonal surrounding wells (15-foot deep, 4-inch diameter slotted PVC wells) were used as the cathodes. The voltage gradient applied was 1 V/cm, and current density was 2 amp/m^2. Electrokinetics combined with continuous or occasional pumping as well as alternating electrokinetics and pumping were investigated. A hydraulic gradient in the direction of the anode was obtained by pumping groundwater from the anode region. The alternating electrokinetics/pumping approach was found to be more practical for treatment of contaminated soil: the concentrations of anions at the anode rose steadily throughout the experiment, and a much higher rate of chromium removal was obtained. The coupling of electrokinetics with hydraulic pumping (Pump & Treat) appears quite attractive conceptually and could have wide applications.

8.0 SUMMARY

Electroosmosis is the phenomenon in which movement of water in soil pores is induced by an applied DC electric field. Used since the 1930s for dewatering and stabilizing fine-grained soils, electroosmosis has recently gained increasing attention as an in-situ remediation technology. Important strengths of electroosmosis include uniform flow distribution in a heterogeneous soil, controllable flow direction, relatively low power consumption, and electroosmotic flow possibly 100 to 1000 fold higher than attainable by hydraulic means in clayey soils. As a stand-alone method, however, electroosmosis is a slow process, does not destroy the waste, requires controlling electrode solutions as well as additional above ground treatment. Remedial field applications of the technology have been mainly in the removal of heavy metals (Pd, Cr, Cu, As, etc.) from soils and sludges, which have shown a fair degree of success. While cleanup feasibility has been reported at laboratory scale for acetic acid, phenolic compounds, gasoline, and chlorinated solvents from clay soils, no field-scale remediation of soils contaminated with organic compounds has been reported. At the time of writing, a small field test is under way at a DOE site in Paducah, KY, investigating the coupling of electroosmotic removal of TCE from clay soil with in-situ carbon adsorption (Lasagna™ process).

Remediation applications of electroosmosis for DNAPLs will be primarily in the removal of residual DNAPLs in soil pores by electroosmotic flushing. The future of electroosmosis as a broad remedial tool lies in the possibility of coupling it with complementary technologies. Examples include combining electroosmosis with vacuum extraction, with surfactant usage to deal with DNAPLs through enhanced solubilization or mobilization, with permeability enhancing methods (hydrofracturing, pneumatic fracturing, etc.) to create DNAPL recovery zones, and with in-situ degradation to eliminate above-surface treatment.

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TABLE 1. Comparison of Electroosmotic Permeability and Hydraulic Conductivity for Various Soils

(Adapted from J. Mitchell, Ref. 1)

Material	**Water Content** %	k_e in 10^{-5} cm/sec Volt/cm	Approximate k_h (cm/sec)
Na-Montmorillonite	170	2.0	10^{-9}
Boston blue clay	50.8	5.1	10^{-8}
Kaolin	67.7	5.7	10^{-7}
Rock Flour	27.2	4.5	10^{-7}
Clayey silt	31.7	5.0	10^{-6}
Mica powder	49.7	6.9	10^{-5}
Fine sand	26.0	4.1	10^{-4}
Quartz powder	23.5	4.3	10^{-4}

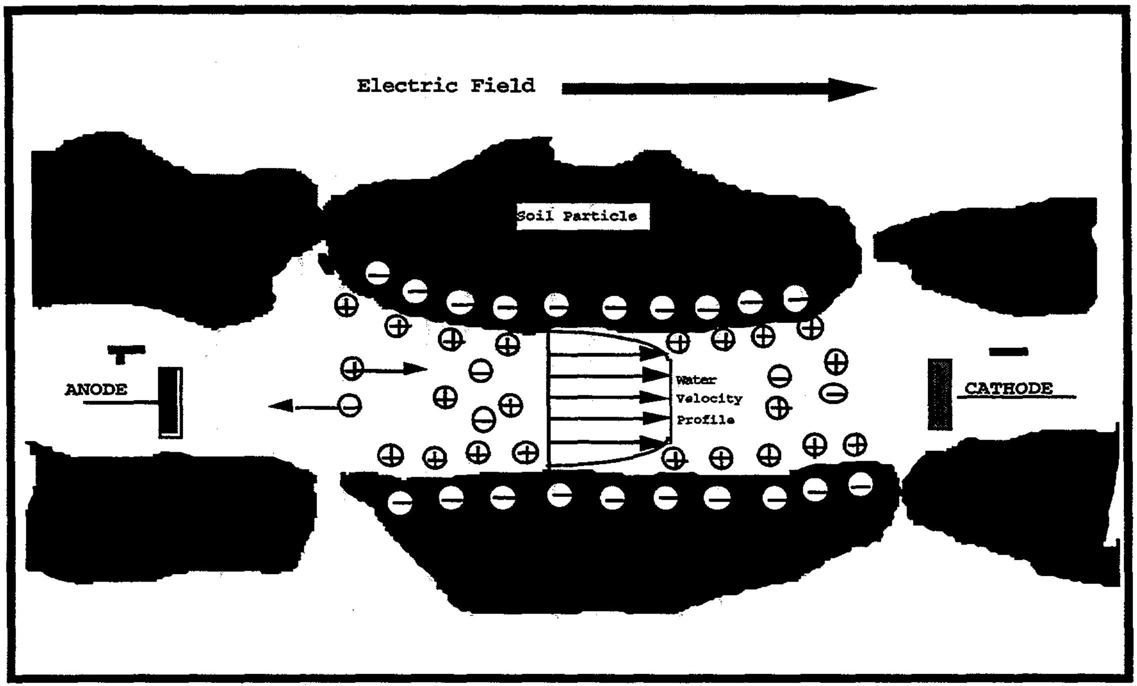

Figure 1. Principle of Electroosmosis through Soil (adapted from Probstein).

RADIO FREQUENCY HEATING FOR IN-SITU REMEDIATION OF DNAPL

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and
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Remediation of DNAPL in Low Permeability Media Project

1.0 DESCRIPTION OF TECHNOLOGY

Overview

In-situ radio frequency (RF) heating technology imparts heat to non-conducting materials through the application of carefully controlled RF transmissions. The technology can be used for controlled in-situ heating of a variety of contaminants thereby improving contaminant flow characteristics and facilitating subsequent separation and removal of the contaminants from subsurface soils. In essence, the technology is applied by inserting a flexible coaxial transmission line and applicator (antenna) system into one or more vertical or horizontal boreholes in the area to be treated. RF generators supply energy through coaxial transmission lines to a multiple of electromagnetically-coupled down-hole antennas or applicators, and the subsurface material between the antennas increases in temperature as it absorbs electromagnetic energy radiating from the antennas. This energy weakens chemical bonds between soil particles and contaminant molecules and enhances soil permeability in tight soils for ease of recovery. Properly configured, the system provides a "steerable" heating pattern that can be controlled by varying the operating frequency, electrical phasings, and antenna length and position. Pumpable liquids or vapors created as a result of in-situ heat absorption may be extracted through the same boreholes used to apply the electromagnetic energy or other optimally arranged recovery boreholes. Figure 1 below outlines the component groups of a typical RF single applicator borehole heating system. The critical design element for the system is the RF HEATING APPLICATOR (l) or "antenna". The RF GENERATOR supplies power through the TRANSMISSION LINEs and the MATCHING NETWORK to the RF HEATING APPLICATOR which radiates over 90% of the energy into the surrounding medium (soil, rock, oil). The medium is heated volumetrically through an RF dielectric heating process.

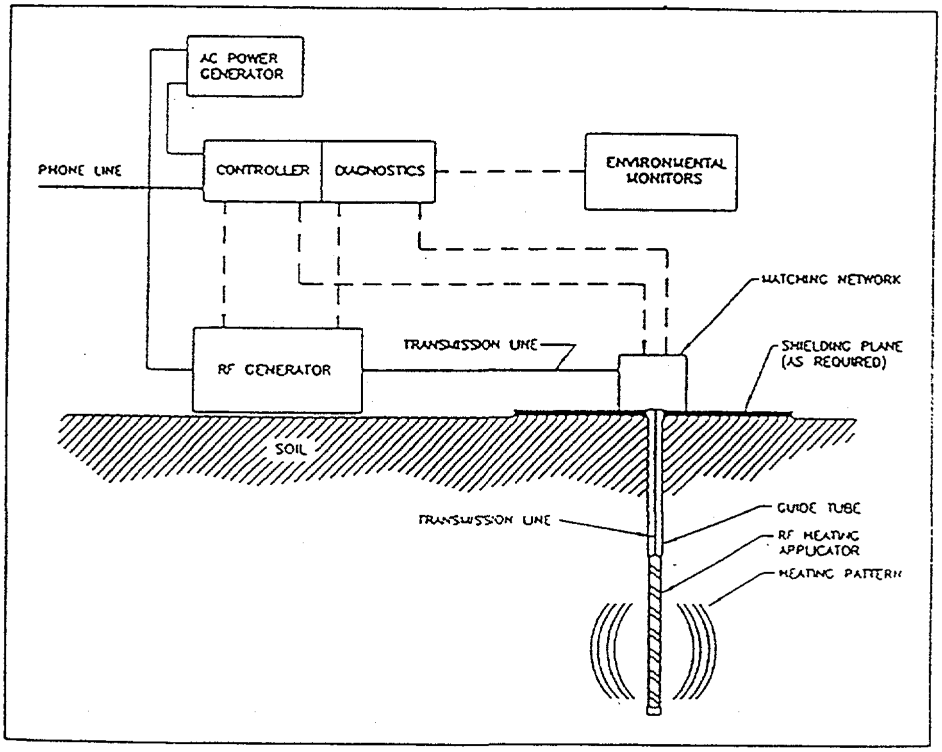

Figure 1. KAI Radio Frequency Heating-Basic System Diagram.

The system Controller is interfaced to all elements of the system. The figure above outlines components, energy leakage and component tampering. The CONTROLLER is capable of transferring the complete monitoring of the system to a remote location through a PHONE LINE. On-site Diagnostics can periodically measure the system's performance and recommend or make adjustments to it. The complete system is powered by a portable AC POWER GENERATOR or from power supplied by the local power grid (2).

Advantages and Limitations

RF heating offers numerous advantages over other heating mechanisms for environmental applications. In particular, the remote antenna system offers significant advantages to heating in-situ over other RF heating deployment mechanisms. The advantages of RF heating include, but are not limited to:

- Applicators can be placed beneath structures to treat soils without demolition.
- Process rates can shorten remedial time-frame.
- Mobile systems with remote applicators are compatible with horizontal or vertical wells.
- Systems can be combined with other remedial technologies.
- Remote applicators can be deployed in vapor recovery wells.
- Field systems can be operated by remote control and have on-site low maintenance requirements.

By impedance matching to site conditions and employing dynamic power and frequency control throughout the process, applicators can achieve energy efficiencies of 95 to 99%. Multiple applicators can deliver and focus RF energy where the heating is needed, thus making the system more effective.

RF heating is commercially advantageous for in-situ treatment of hydrocarbon or volatile organic contaminated soils. The in-situ treatment process eliminates the need for costly bulk excavation. Arrays of high power generators and applicators can be used to treat large areas of contaminated soils at a significant economic advantage.

The capacity to place remote applicators under buildings or structures enables remediation of soils without demolition of the overlying structures. RF heating applicators placed in horizontal wells located beneath industrial buildings, landfills, or storage tanks may be the only way to treat soils without site demolition, excavation, and extensive soil processing. A schematic of an RF system layout for beneath a building application is shown in Figure 2. Relatively small diameter boreholes (4.0 inch) are employed for applicator placement several feet below the building foundation.

Thermal enhancement of established remedial techniques such as soil vapor extraction and biological treatment are applications where RF heating offers synergistic advantages. RF heating can be used to enhance bioremediation by significantly speeding process times. Chemical treatment temperatures can be maintained for optimizing reaction kinetics. Soil or rock permeability can be increased by thermal expansion of water as it is converted to steam.

Since the technology provides heat at the molecular level and does not rely on thermal conduction, the approach provides an advantage of efficiency over other forms of industrial heating. Mobilization and set-up activities for in-situ applications require less labor and equipment than other approaches to heating. Automated systems allow minimal monitoring personnel for many applications. The use of the technology is primarily limited by the power requirements and temperature constraints of the technique. However, waste materials or conditions which do not benefit from heating are not candidates for this process.

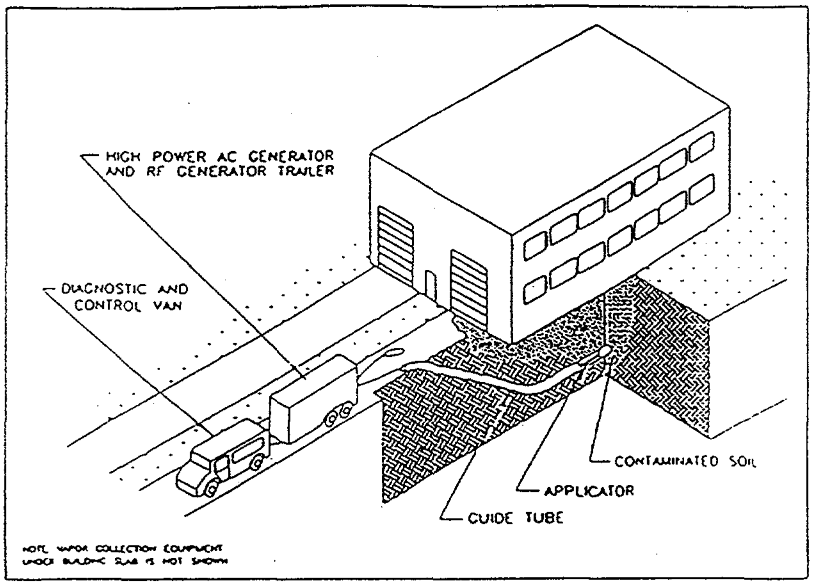

Figure 2. KAI Radio Frequency Heating System for Soil Decontamination.

RF heating technology can be applied in-situ to a variety of soil contamination problems. The thermal field created by the volume heating effect of RF applicators is used to drive volatile materials from the soil. On the soil surface, the volatile vapors are collected or safely vented. When the thermal processing is concluded, the decontaminated soil is left intact.

Process Operations

Antennas and transmission lines are the basic means of conveying and radiating electromagnetic wave energy for communications, radar, dielectric heating, and other electronic systems. Generally speaking, energy in the form of time and space varying electric and magnetic field components couple together to give a propagating electromagnetic wave. This special form of energy is generated by electronic equipment and fed to an antenna system by means of transmission lines. The transmission line conveys the wave energy in a shielded structure and delivers it to an antenna system with high efficiency. The antenna system may be as simple in structure as a wire connected to the transmission line in such a way as to cause radiation fields to exist in either free space or a lossy dielectric medium. The lossy dielectric medium may be contaminated soil or rock, water, etc. Such a dielectric has the ability to absorb electromagnetic wave energy and convert it to heat as the electromagnetic wave propagates through the material or a standing wave pattern is established within the material.

Suffice it to say, the electric field component of the electromagnetic wave acts at the molecular level to dampen the wave energy effectively as the wave propagates through the material. The microscopic dipoles of the material experience forces from the electric field to cause them to rotate and generate heat by "molecular friction" thereby converting wave energy to heat. The resultant vibration of the contaminant molecules helps to weaken the chemical bonding between them and soil particles.

Although required equipment and operating conditions are site-specific, implementation activities generally require:

1. Bench studies to determine the extent of thermal desorption of contaminants during RF heating and the dielectric properties of the soil with contaminants.
2. Pilot studies using one or more applicator boreholes to assess treatment time, contaminant recovery rates, energy requirements, and requirements for an on-site production facility.
3. Full-scale commercial implementation.

Equipment used to generate the electromagnetic energy is housed in an on-site trailer, and may include portable diesel-fueled generators for 3-phase, 240V power to on-board RF transmitters. Rigid or flexible 1 5/8-inch flexible coaxial cable with a corrugated copper jacket typically is used to transmit RF energy from a trailer to the down-hole antenna. The number of boreholes required depends upon the particular site. Typical borehole diameters range from 4 to 6 inches. Effective borehole depths may range up to 1,500 feet. Individual holes may be spaced as far as 25 feet apart. The radial extent of heating from a single borehole varies with the operating frequency, antenna length, and dielectric properties of the soil. The surface system RF equipments are completely shielded for operator safety.

Physical Process

The physical process involved consists of the initial heatup period where the soil temperature rises rapidly toward the vaporization temperature of water. Thereafter the temperature rise is reduced until the latent heat of vaporization of water is supplied by the RF energy. In regions where steaming occurs, a much slower heating rate develops based on a lower dielectric loss or electrical conductivity. Chemically bound water will continue to absorb RF energy as well as other high boiling point liquids or soil particles with dielectric loss. When the temperature of the wet soil approaches the boiling point of the liquid, internal evaporation and an increase in the total pressure can occur within the pores. Mass transfer is now primarily governed by the total pressure gradients. When the soil contains high proportions of water, some moisture may be removed as liquid, due to filtrational flow driven by the total pressure gradient.

When the soil is heated to the boiling point of the liquid phase, the pores are filled with vapor and moisture flow is governed by the total pressure. The excess pressure can cause the material to expand thereby increasing pore size and the pressure diffusivity. (In conventional convective heating, there is no internal pressure generated and the volumetric heat sources are zero.)

Because water is a very polar molecule, the RF energy is rapidly absorbed and converted to heat. The nature of the water absorbed in the contaminated soil matrix has a marked effect upon its dielectric properties and consequently upon the interaction of the RF field with that of the material (3). Absorbed water in wet soil can exist in two states. Free water which resides in capillaries, pore spaces etc., and bound water which is chemically combined to other molecules or physically adsorbed to the soil particles. Figure 3 indicates how the absorption of RF energy in soil varies with moisture content for a typical wet solid.

The two states 1 and 3 relate to two distinct slopes of the energy-moisture curve. The state 1, negligible slope region, is the bound water condition whereas state 3 relates to the presence of free water. The water molecules in state 1 are less rotationally free to interact with the RF energy than the free water residing in pore spaces, cavities, etc. The width of the transition region 2 varies with soil chemistry, type of soil, etc. As a rule of thumb, the transition region for highly hygroscopic materials occurs in the 10-40% by volume moisture whereas for non-hygroscopic sand, it is about 1% (4).

Measurements of soil properties show high electrical losses in the iron ores hematite and magnetite and soils with some small salt content indicating RF absorption mechanisms at high temperatures even when all the water has been removed. RF temperatures in the range of 250°C have been achieved in field testing of RF systems for soil remediation.

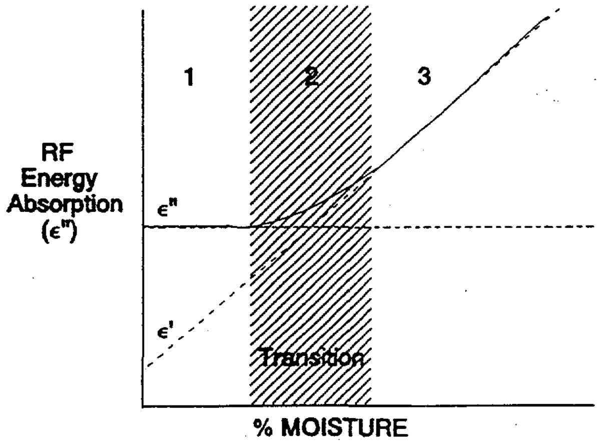

Figure 3. RF Absorption Variation With Moisture Content.

The action of RF energy on wet soil is as follows. Initially, the RF frequency energy penetrating the soil is rapidly absorbed near the RF energy source. Upon evaporation of the state 2 water, the remaining bound water and iron ores will act as an energy absorber but at a much lower absorption rate. This dry zone will expand with time away from the source as more moisture is removed. Heating in the dry zone is continued above the vaporization point of the water. In some soils, full dehydration will not occur until temperatures well above 100°C have been created. For example, in normal circumstances, clay particles are never completely dry. Even after being heated at 105°C for 24 hr, which is the standard for drying soil material, clay particles still retain appreciable amounts of adsorbed water. The strong affinity of clay surfaces for water is demonstrated by the hygroscopic nature of clay soils.

Decontamination mechanisms operative with RF may involve: (1) evaporation, (2) steam distillation, (3) super-heated steam distillation, (4) distillation, (5) thermal decomposition, and (6) pyrolysis. The particular mechanism will depend on temperature residence time, soil chemistry and type of contaminant.

Many compounds on the CERCLA Hazardous Substance List are hydrocarbons (HC) with boiling temperatures between 80°C and 420°C. Heating these compounds to 300°C to 400°C would recover a large fraction of these components by vaporization and distillation (5). Steam distillation may be included provided the vapor pressure of the HC is of the same order of magnitude as that of water. Components boiling above 100°C may be distilled in the presence of super-heated steams. In the RF process, the steam front may propagate back toward the source of RF thereby experiencing higher temperatures than 100°C. As it propagates, this super-heated steam front may cause distilling of high boiling point liquid contaminants. PCB mixtures are such an example.

Temperature and residence time requirements for the thermal decomposition of chlorinated hydrocarbons were estimated by Dev, Bridges and Sresky using Duvalls' data (5). They calculate for 344°C, a residence time of 7 days for 99.98 percent thermal decomposition of hexachlorobenzene (HCB).

Windgasse and Daurerman have studied microwave steam distillation processes in contaminated sand, and soil containing volatile and semi-volatile organic contaminants (paraxylene and naphthalene) (6). These results apply to RF heating as well. As noted previously, such compounds distill at temperatures much lower than their boiling points where the sum of the vapor pressures of the immiscible condensed phase compound is equal to the ambient pressure. Therefore, high vapor pressure compounds require less water to steam distill than low vapor pressure compounds. They concluded that single stage steam distillation is sufficient for removal of highly volatile pollutants in soils. For compounds of low volatility, repeated application of water (multiple steam distillation) may clean contaminated soil to the desired level.

General Electric has carried out laboratory transport and kinetics studies on a variety of contaminants in different soils (7). They have heated PCBs with conventional heating methods and have demonstrated that heat increases the desorption rate by orders of magnitude and can dramatically decrease the time necessary to achieve low residual levels of contamination. At 250°C and 300°C, desorption by heat decreases PCB concentrations to below detection limits of gas chromatography.

2.0 GENERAL TECHNOLOGY CONSIDERATIONS

RF heating for soil remediation is most economical when applied to the vadose zone of soils. Where moisture contents are high it is best to consider dewatering of the soil to minimize energy costs involved in supplying the latent heat of vaporization of free water. A practical moisture level for RF applications is based on the type of soil, environmental conditions and amount of dewatering necessary to ensure a range of moisture in the treatment volume that will not compromise the treatment cost and power requirements. Five to ten percent moisture levels are reasonable amounts for RF heating applications. Low moisture content soils provide additional benefits for the emplacement of RF electrodes or antenna elements. The spacing between electrodes or antennas of the in-situ RF applicator system depends on the electrical properties of the soil for a specific ISM (Industrial, Scientific, Medical) operating frequency. For wet soils the spacing is small to ensure relatively uniform heating among antenna elements in boreholes spaced on a square grid pattern. The spacing is considerably larger for drier soils. RF heating in saturated zones therefore requires closely spaced antenna elements with significant amounts of energy used for conversion of water to steam.

Groundwater contamination in the form of layers of free product on the water surface may be directly heated with RF energy by proper choice of frequency and applicator positioning relative to the free product layer. However, significant heat loss to the water mass could make such applications of RF uneconomical.

RF energy application to the remediation of chlorinated petroleum hydrocarbon in soils is related to the overall ability of soils containing these materials to absorb RF energy through dielectric loss mechanisms. Measured values of the dielectric properties of TCE and creosote show significant differences in the ability of these individual molecules to absorb RF energy. For example, TCE with a dielectric constant of 3.374 and a loss tangent ($\varepsilon'' \varepsilon''$) of 0.00014 is essentially transparent to RF at 1 MHz whereas creosote at 1 MHz has a dielectric constant of 10 and a loss tangent of 4.1. Creosote therefore is a significant absorber of RF energy. In soil, TCE would be steam distilled and have a temperature of 100°C through its association with pore water which is the principal absorber of RF energy. Temperatures above 100°C would be achievable if the soil matrix contained bound water or inorganics such as iron ores.

The creosote molecule readily absorbs RF energy without the need for moisture or bound water. Creosote deposits or individual particles will vaporize in the presence of RF fields because of its significant ability to absorb RF through dielectric heating at the molecular level.

The maximum depth of remediation is limited only by transmission loss in conducting RF energy by means of coaxial transmission lines to the applicator. With commercially available materials, depths exceeding 2000' start to become impractical unless engineering design steps are taken to minimize resistive losses in the transmission line. It is therefore reasonable from cost and efficiency of power transmission viewpoints to consider a depth of 1500' as practical for RF remediation applications. At a particular depth, the volumetric extent of the heating pattern will depend on the number of applicators and spacings employed, applicator length and operating frequency. Using four applicators in four separate boreholes operating at 13.56 MHz would provide heatup of about 150 cubic yards of soil. Each applicator is about 18 ft in length and provides an ellipsoidal heating volume where the major axis of the ellipsoid is equal to the antenna length.

RF heating systems can be configured to adapt to a wide range of utility and field power sources. A typical 25 kilowatt master heating module is configured to be supported by 3-phase power sources with a nominal capability of 60 KVA. Typical utility supply voltages of 208, 240 and 480 VAC are adaptable to all heating system applications. When power is not available from the utility power grid the systems can be powered from diesel generators. The control and monitoring instrumentation of the master heating module is supported by an uninterruptable power system (UPS) with a battery pack that allows stable data logging and remote control restart of the heating systems after they have been shut down by a utility failure or the maintenance cycle of a diesel generator.

The RF heating systems are designed to be robust to lighting strikes, power line transients and "brown outs". In special cases of highly unstable power sources such as remote oil field sites with "COGEN" power, motor-generator sets can be used to provide the necessary voltage stability for reliable system operation.

Operating costs are kept to a minimum by the use of a dedicated control computer for each system. The system will control and track system performance and allow for remote control and data transfer to the central office computer or the lap top computer of a field engineer linked by a cellular phone.

Commercial RF heating systems will take advantage of design features that are common for commercial broadcast stations and mobile military communications vans.

Maintenance costs and equipment down time are minimized by the use of modular systems with Built In Test Equipment (BITE).

RF heating zones can be shielded to contain the RF emissions within the health and safety guidelines of OSHA and the electromagnetic interference standards of the FCC. A typical 25,000 watt applicator installation can be shielded to limit its emissions to a level of a similar magnitude to that produced by a common 5 watt Citizens Band transceiver (8).

3.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

Soil moisture plays a fundamental role in the contaminant removal process. Water, as the principal RF energy absorber will rapidly reach boiling temperatures throughout the treatment volume through the $SAR=\sigma E^2/\rho$ (watts/kg) mechanism occurring at the molecular level. Excessive moisture will prolong the timing for the full treatment volume to reach water boiling temperatures and therefore the overall cost of application may be adversely effected. The hydraulic control of the water table in some applications of RF may be important. Specifically, in situations where the capillary fringe is intruding into the RF heated volume, it may be necessary to reduce the water level to avoid the continuous injection of water into the treatment volume.

An experimental and theoretical study of remediation of multi-component organic contaminants in unsaturated soil has been recently developed by Lingineni and Dhir (9). They have recently provided a theoretical model to predict the evaporation rates of contaminants with enhancement provided by in-situ heating techniques. This model is being explored to predict RF heating performance with SVE in low permeability soils.

The method-of-moments Numerical Electromagnetics Code (NEC-3I) developed by Lawrence Livermore National Laboratories (10) and the finite element analysis (FEA) heat transfer code, COSMOS developed by Structural Research and Analysis Corporation (11) can be used to model RF heating of soils which have both isotropic and isothermal physical and electrical properties. The process of modeling the RF heating of soils involves three steps: 1) creating a finite element model of the soil volume, 2) running NEC-3I to determine the heat flux produced by the RF energy within each element of the soil volume, and 3) running a transient COSMOS heat transfer analysis to generate temperature profile data at specific intervals of time throughout the soil volume.

Input to NEC-3I consists of the physical dimensions of the antenna and its environment, the electrical properties of the soil, the operating frequency, and the power radiated by the antenna. The parameters of the antenna are its burial depth, length, conductor radius and the thickness and electrical properties of its insulation. Finally, the location of the points are specified within the soil where the heat flux will be calculated using the RMS electric field. NEC-3I generates a file consisting of the position of the centroid of each soil volume element and its associated heat flux formatted for input to COSMOS.

Temperature profiles are generated by COSMOS using the heat flux data and by providing values for the specific heat, density, and thermal conductivity of the soil. Currently, COSMOS assumes that the soil volume is well insulated. After the run is initiated, COSMOS generates data consisting of the temperature of each of the volumetric elements of the soil at specified time periods.

Scenario

Problem

Consider a scenario where the soil is stratified with layers ranging from a medium sand (permeability of 10^{-3} cm/s) to a clay (permeability ranging from 10^{-6} to 10^{-8} cm/s). The clay layer contains natural desiccation fractures that are spaced a few cm apart and have apertures of 10-40 microns. The effective soil porosity of clay is < 1 %. Assume an underground storage tank of TCE and PCE leaked slowly over many years, and the hydrocarbon liquid entered a sand layer overlying this clay aquitard, into which it diffused. The clay layer is 3 m thick and it in turn overlies a sand aquifer. Assume the water table is at the top of the clay layer and the natural fractures in the clay can be dewatered by pumping the aquifer (if needed to enhance contaminant removal). Describe the ability of the technology to remove:

- Free product pooled on top of the clay
- Separate phase product trapped in the continuous clay fractures
- Separate phase product trapped in discontinuous or "dead end" fractures
- Dissolved phase product diffused into the matrix blocks

The depth of the clay layer is not indicated in this scenario. However, the application of RF energy by means of widely spaced vertical or horizontal boreholes can be accomplished over a wide range of depths to as much as 1500 feet. Applicators or antenna elements can be positioned within the 3-m thick clay layer as was recently performed at the Savannah River Integrated Demonstration Site by KAI Technologies. A horizontal borehole was employed that achieved coupling of the RF energy primarily within the clay layer. The RF fields did not distinguish between free product on top of the clay layer, separate phase product trapped in the continuous clay fractures or dead end fractures or dissolved phase product diffused into the matrix blocks. The basic RF power absorption mechanism is related to the electrical conductivity of the free and bound waters in the matrix. Radio frequencies because of their wavelength are not sensitive to fractures in the clay as far as the power absorption ability of the matrix is concerned. The steam and pressure generated in the pores effect the TCE and PCE throughout the matrix. If pressure gradients exist, the RF induced permeability of the clay matrix will permit recovery of the contaminant. The same phenomena exists in the RF heating of oil shale rock. Oil shale is a very tight matrix with primarily chemically bound water and organic kerogen. The application of RF heat literally microfractures this type of rock and allows recovery of oil vapor and steam and other gaseous by-products through a system of minute fractures created by gas pressure buildup and water movement in the rock matrix along an established hydraulic gradient. Despite significant overburden pressures, experimental results have demonstrated this effect in Colorado oil shales.

Free product pooled on top of the clay will be steam heated by RF energy and by indirect thermal conduction from adjacent layers. The loss factor of TCE is extremely small and therefore its molecular ability to directly absorb RF energy is small by comparison to moisture.

Problem: 40m x 40m x 3m TCE Contaminated Clay (Dewatered 5% Moisture) depth unspecified.

Horizontal Wells Solution: The TCE contamination can be remediated by bringing the soil up to 130°C and then extracting the contaminant with a vapor recovery system. To do this, 13 horizontal, 130 ft-long boreholes spaced 10 feet apart could be used to house four applicators (one per borehole) through which 100 kW of RF power would be delivered to the clay soil at 85 % RF generator to soil efficiency (25 kilowatts per applicator). Each applicator can effectively treat a 1000-cubic-foot volume of this soil in 5.7 days which includes a 20% heat loss.

Using four applicators simultaneously, the soil RF heat treatment would proceed at a rate of 180 cubic yards per week which would result in the completion of RF heating operations in 35 weeks for cleanup to target cleanup levels of 2000 mg/kg.

Vertical Wells Solution: This option requires a total of 169 vertical boreholes (13 rows and 13 columns) to be drilled into the clay. Each borehole would be spaced 10 feet from the adjacent borehole. RF energy would be applied with four applicators operating simultaneously as in the horizontal case and would result in the same treatment time.

The commercial RF system to effect this cleanup would be entirely computer controlled. Target costs for this type of remediation would be below $100 per ton for the RF system and its operation.

4.0 COMMERCIAL AVAILABILITY

A commercial-like two antenna, vertical borehole RF heating system is currently undergoing evaluation at Kelly Air Force Base. Under sponsorship by the U.S. Air Force and EPA, high power testing began in mid-April 1994 and lasted for approximately 45 days. The system is completely mobile and computer controlled through specially developed software. A picture of the mobile system and its 25 kilowatt transmitter with control electronics and applicator is depicted in Figures 4, 5, 6, and 7 respectively.

RF heating development efforts currently rely on the adaptation of components and equipment designed for the commercial radio and television broadcast industry, military communications systems and the semiconductor materials industry. It is important to note that the vendors in these markets typically produce a wide range of components and

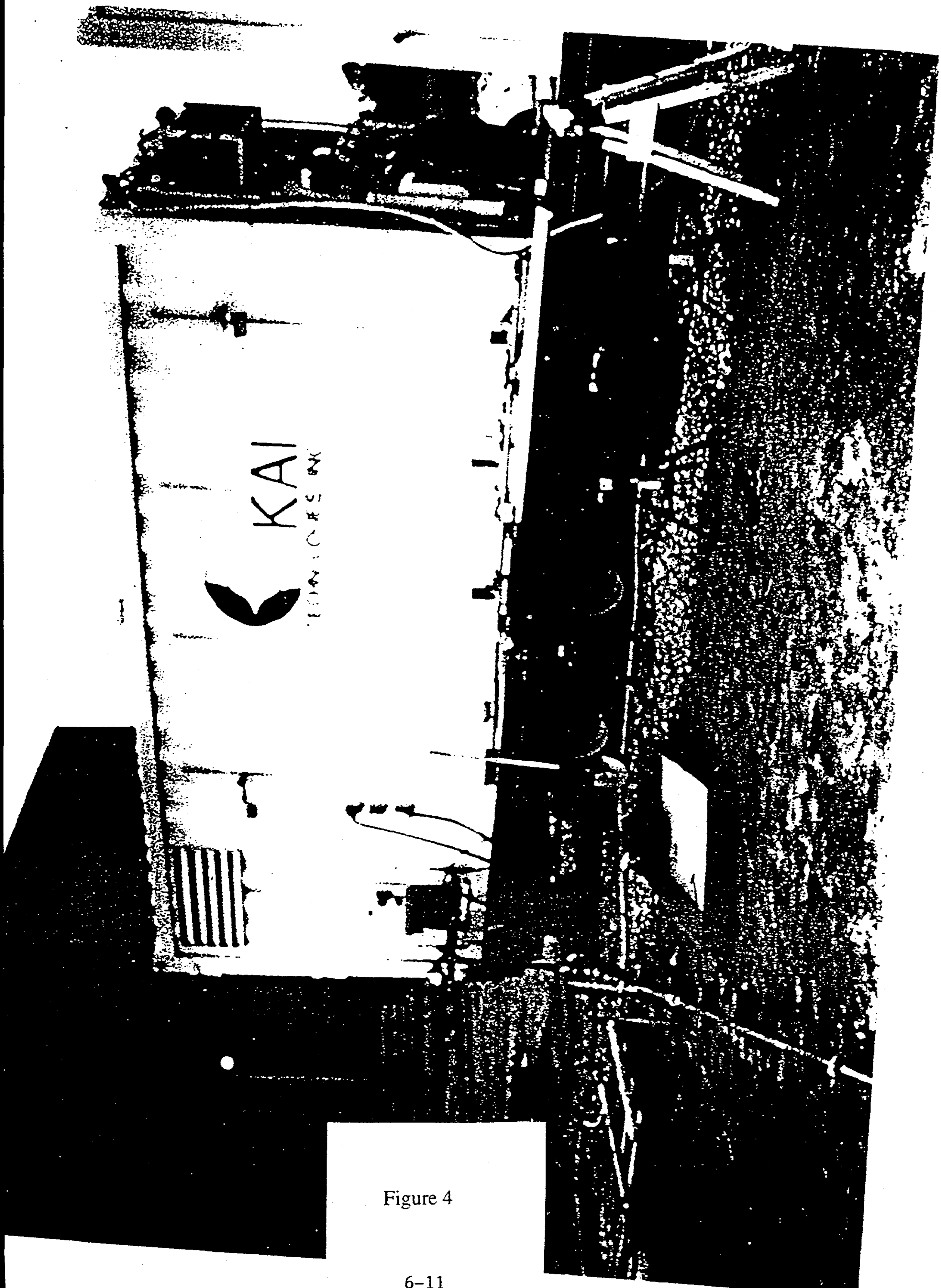

Figure 4

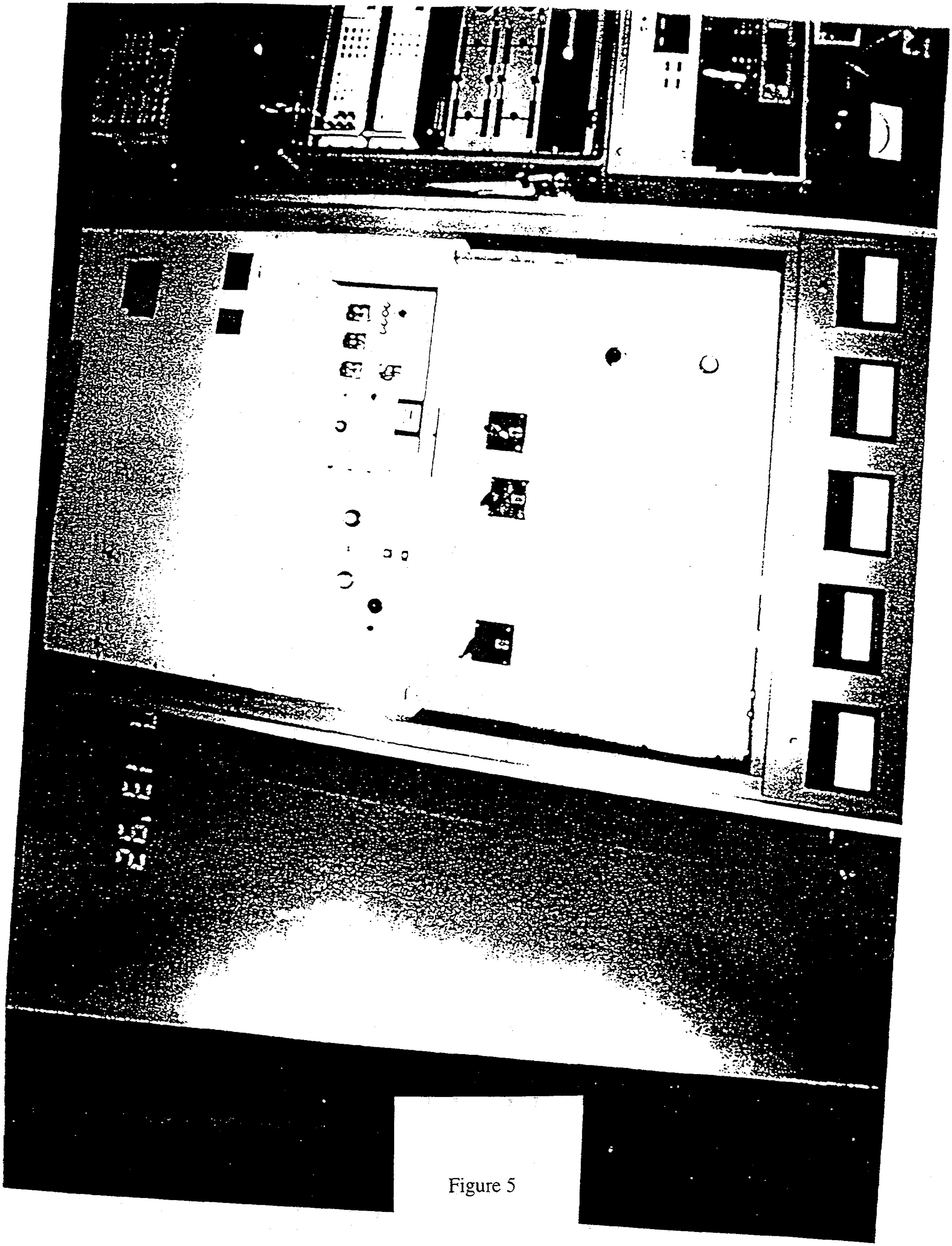

Figure 5

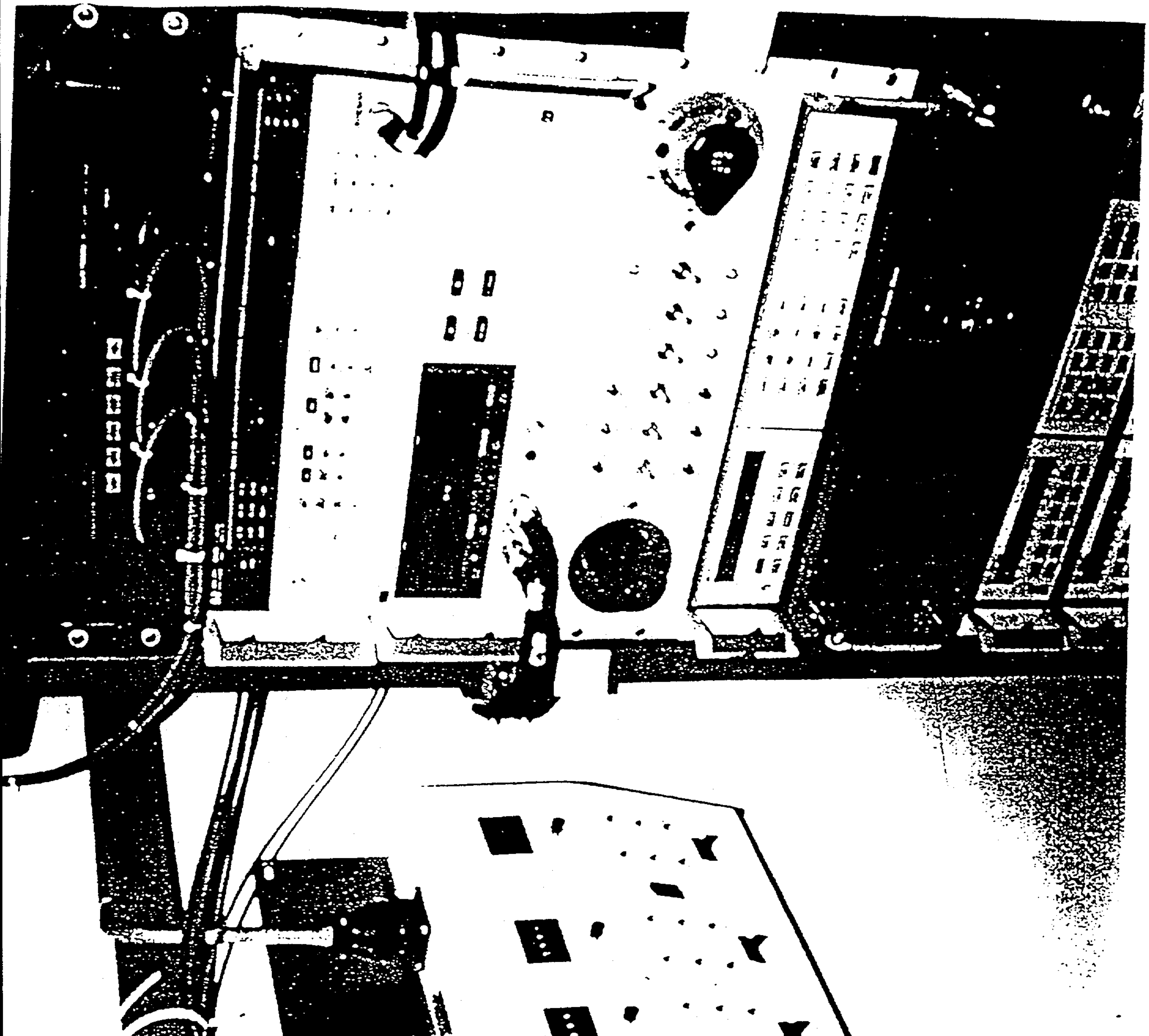

Figure 6

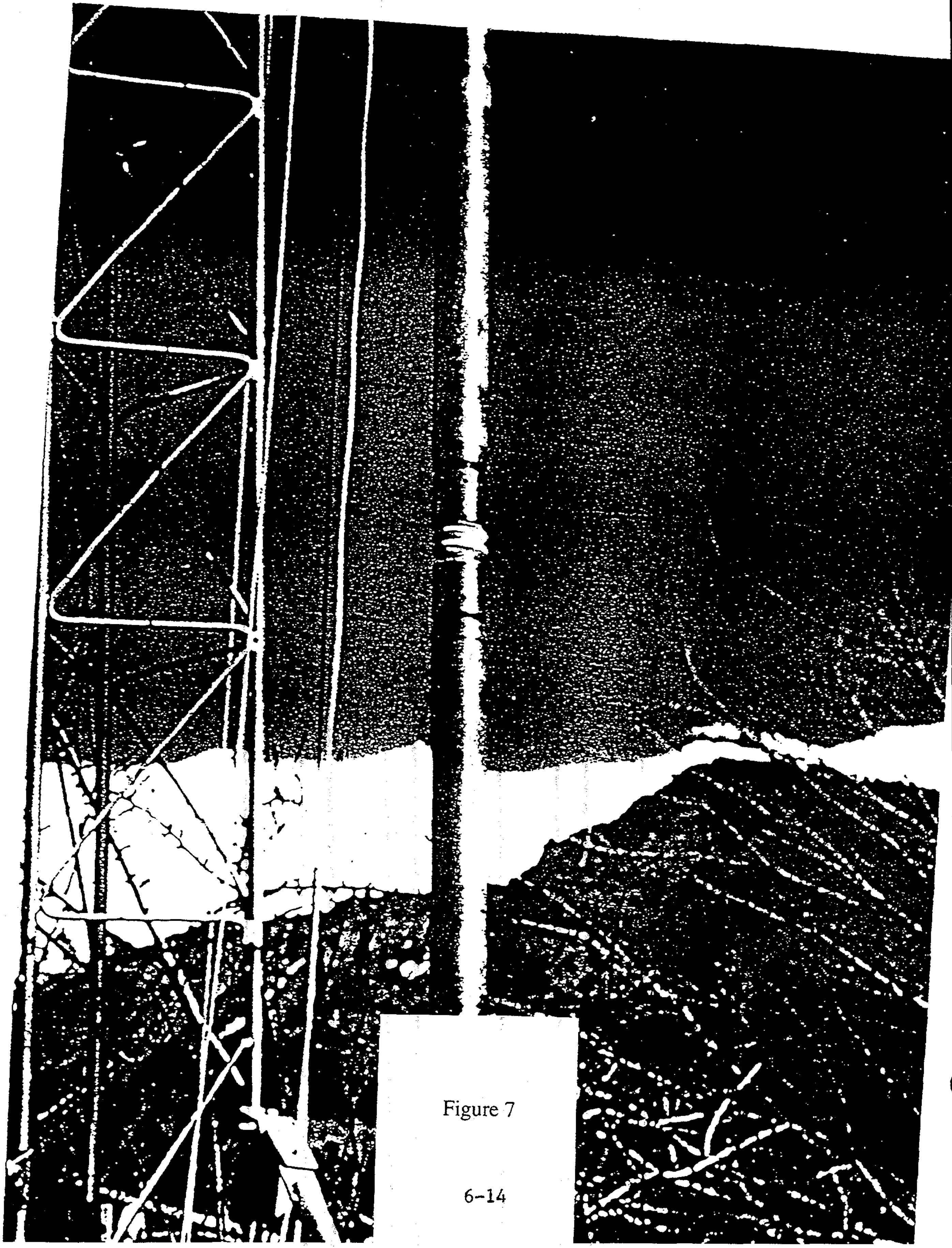

Figure 7

products in low volumes, with limited product stocking. Major components such as RF generators, tuners and high power coaxial switches are typically delivered between 90 and 240 days from receipt of order.

The environmental and industrial application of RF based heating systems are likely to justify development of a number of devices and components that will significantly reduce system costs and increase system versatility. The most significant savings are projected in the following areas:

1. Modular multi-frequency RF generator systems with integer computer control, wide singe tuning and multi-line switching capability.
2. High strength, high temperature flexible RF transmission lines capable of efficient operation at 27.12 MHz at the 25,000 watt level.
3. Development of dual swivel joint transmission line couplings with fast attach and release connections as well as rigid line stress relief capability.
4. Development of a high-temperature ceramic housing and well liner strategies.

A near-future commercial configuration of the in-situ RF heating system would employ either multiple antenna elements in widely spaced vertical or horizontal boreholes.

Figure 8 shows a commercial RF system layout. At an RF of approximately 27.12 MHz, this system consists of 36 antenna elements disposed in boreholes drilled in a square grid pattern, the grids being approximately 10 to 15 feet apart. Each antenna is approximately four inches in diameter and 9 feet in length (see Figure 7). The heating interval is therefore 9 feet at the applicator depth assumed to be greater than several feet from the surface. All antennas are powered by RF generators (for example, approximately 25 kilowatts of power per borehole) that may be operated in either a cw or pulsed mode. Both the borehole temperature and feed-line VSWR (VSWR is the voltage standing wave ratio and is a measure of system efficiency) are monitored in real time. This information is supplied to and used by a central computer for power and phase control adjustment (throughout the heating period) to insure maximum remediation rates with time. The entire system is computer controlled from a remote location. The soil vacuum extraction system is not shown.

This commercial phased array system is capable of providing a near-uniform distribution of electromagnetic power in the contaminated region by proper antenna design, borehole spacing and choice of frequency and phase modulation. A three-dimensional temperature distribution profile shown in Figure 9 represents the temperatures generated by a four applicator system (the boreholes being at the corners of a square) when all four input currents to the antennas are in time phase. In this example, the energy from one applicator at the selected frequency will arrive at a second applicator out of phase and will cancel a portion of the radiating field gradient. Thus, the heating effect in the areas immediately adjacent to the respective applicator will be reduced while the radiating fields will have an additive effect in the central areas of the contaminated region. Thus, when multiple systems are properly spaced with different current phasings, that may vary in time, a volumetric heating pattern is generated that produces a nearly uniform temperature distribution throughout the contaminated volume.

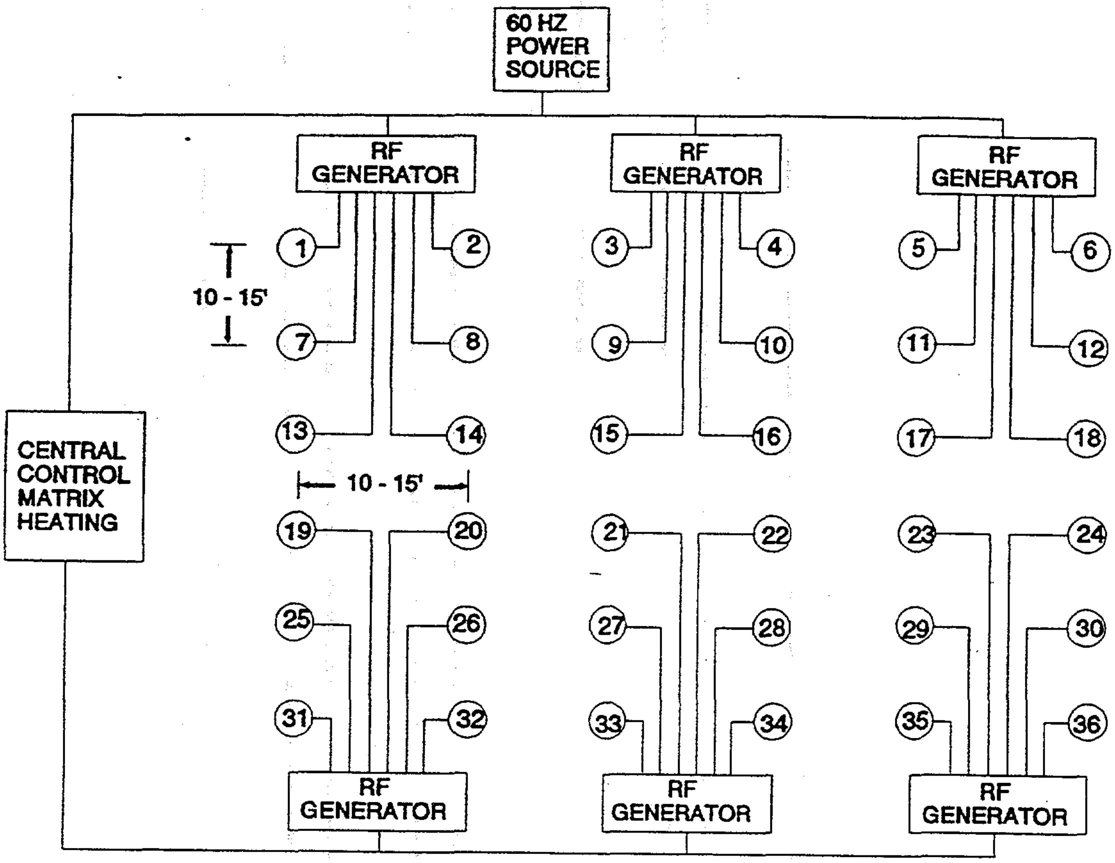

Figure 8. Commercial RF System Layout.

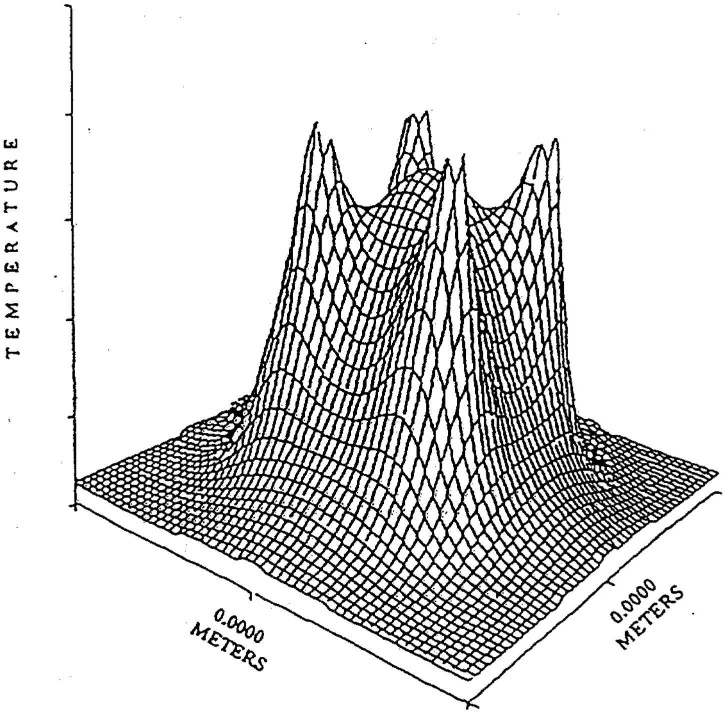

Figure 9. Four Coupled Antennas - Subsurface Heating Pattern.

5.0 COST ELEMENTS OF RF HEATING SYSTEMS

Capital Costs

The cost for a generic system is divided into the following categories with a typical range of assembled equipment costs for each grouping of system components. The grouping descriptions are:

- **Heating applicator** for a vertical emplacement borehole with a light weight 30-ft emplacement tower and 100 ft of flexible 1-5/8 in. transmission line and rigid line components to connect the applicator to the RF heating module to a maximum depth of 30 ft with the RF generator located 50 ft from the borehole. The applicator and transmission lines employ Teflon components and therefore the operation of this system is limited to a maximum of 200°C.

- **RF heating module** capable of delivering 25,000 Watts of RF power from a ceramic vacuum tube (12) through a tuner designed for a single frequency of operation (constructed by the vendor for either 27.12 or 13.56 MHz). The unit typically requires a 50 KVA, 3-phase power source.

- **Control computer** with basic sensors and system interfaces for time and temperature control as well as operation logging. Simple wire line remote control capability is provided along with suitable software. The computer system is transient and surge protected by an uninterruptable power supply.

- **Equipment shelter** for a fixed site installation with a usable interior volume of 7 ft x 7 ft x 15 ft with heating, ventilation and air conditioning for instruments. The unit must also have input and output ducting to provide 600 CFM filtered air for the RF generator. The shelter also contains a 3-phase, 480 VAC, 100 Amp power panel and a l-phase 110/220 VAC power panel with a 10 KVA transformer.

The above items are provided below in terms of low and high range costs for the groupings. The low range sets a boundary for either minimum capability and design margin systems or costs associated with volume discounts for key components. The high range is defined by one-of-a kind construction costs and the use of premium components.

CAPITAL COST SUMMARY

	Low Range	**High Range**
Heating Applicator	$13,050	$ 26,500
RF Heating module	$80,100	$112,200
Control computer	$14,450	$ 75,500
Equipment shelter	$18,000	$ 44,500
TOTAL	**$125,600**	**$258,700**

System Operating Costs

The operating cost of the generic system described under capital costs is based on the following components that are extremely variable due to the labor components involved in complete costing:

- Electrical power costs - Typical utility costs run from \$0.05 to \$0.15/kWh. With a typical total system energy conversion efficiency of 45 % the AC input energy would be 55 kW. The system electrical utility cost would range from \$2.75/hr to \$8.25/hr for each 25 kW of RF energy delivered to the target region.
- Supporting equipment and tools are required for setup, operation and maintenance of one or more systems. The typical value of the instruments and tools ranges from \$75,000 to over \$250,000 for detailed operating and troubleshooting diagnostics. A typical site installation will need approximately one month of this detailed support capability. Therefore support equipment through selective short term rentals or long term leasing or purchases add a cost of \$5,000 to \$20,000 to each site installation budget.
- Scheduled maintenance and repair costs as well as periodically replaceable components (e.g. vacuum tubes). For a ceramic vacuum tube based system, the material costs are typically \$2 to \$5 per heating hour with scheduled outages for replacement after every 3,000 hours of operation. Service of this type can typically be accomplished by one technician in less than one day.
- Environmental monitors can be added to the system controller as required for the site. Typically, the control computer can be interfaced to these devices without adding significant cost to the control system.
- Mobilization of the system summarized here is at the component level with on-site assembly of pre-tested system modules. RF heating system components can be mounted in trailers or on truck bodies to minimize many reoccurring setup costs if the system is to be transported frequently.

6.0 CASE HISTORIES

Demonstration of Enhanced Chlorinated Hydrocarbon Extractions (13)

A demonstration was conducted at the DOE Savannah River Site which featured RF heating as an enhancement to in-situ vacuum extraction of chlorinated, volatile, organic compounds (CVOs, primarily TCE and PCE) from vadose clay deposits. The team assembled for this demonstration included participants from the Westinghouse Savannah River Technology Center; the Westinghouse Science and Technology Center (Pittsburgh, PA); and KAI Technologies, Inc. which provided the RF technology.

The purpose of this demonstration was to integrate within a single horizontal well the application of RF heating and vacuum extraction. The horizontal well was screened and passed through a region containing a layer of contaminated clay. Off-gases from the well were destroyed with a skid mounted, thermal-catalytic oxidation system (CATOX) so that they could be vented directly to the atmosphere and be within permissible guidelines established by the state of South Carolina. For round-the-clock operations the RF heating system employed a remotely controlled 13.56 MHz RF generator.

During the demonstration, RF energy was coupled to the clay layer from the generator with over 95% efficiency by a specially designed RF applicator. Over the 25 days of operation, the RF heating system safely delivered a total of 11,000 kilowatt-hours to the subsurface soil. This energy raised the temperature of approximately 27,000 cubic feet of soil above ambient (i.e. 20°C) and caused the nearest 800 cubic feet to exceed 60°C. Most importantly, off-gas concentrations were in the range of 20 to 30 ppmv for TCE and 150 to 200 ppmv for PCE at the end of RF heating, having risen from initial concentrations of less that 10 ppmv. Over 170 kilograms of VOCs were successfully extracted over the course of the demonstration. During the test, a steam block formed downhole which limited the achievable vacuum and therefore reduced the extraction rates. This problem is solvable by the relocation of the recovery well pattern and adjustments of pressure gradients. Also, the casing material employed for the horizontal well could not be allowed to exceed its temperature rating. Consequently, automatic RF transmitter control based on fiber optic temperature sensing of the borehole material adjacent to the applicator was employed. Future tests will employ a borehole liner of higher temperature ratings. Inexpensive ceramic cements are a reasonable choice for vertical well borehole liners. (See Figure 10 for horizontal borehole system deployment.)

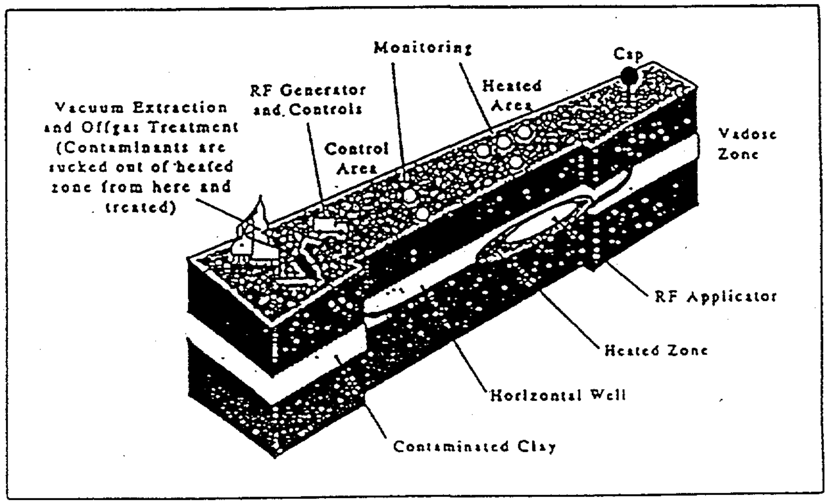

Figure 10. Horizontal Deployment of RF Applicator.

Pilot Test on #2 Fuel Oil Spill

A 25 kW, 13.56 MHz mobile RF heating system was used in a pilot test to enhance remediation by soil vapor extraction (SVE) on a #2 fuel oil plume in soil in Eastern New England. At this site, recovery rates had dropped from thousands of gallons per hour under several feet of product head to the low hundreds of gallons per month. Given this low oil recovery rate it was uncertain how much longer the present gravitational product recovery system would be in operation before shutdown. As a result the client became interested in RF heating combined with a soil vapor recovery system to enhance the product recovery rate.

The pilot study involved three phases: bench-scale tests, low power RF heating and oil vapor recovery tests, and high-power RF heating with vapor recovery tests. The bench-scale laboratory tests determined the rate of recovery of #2 fuel oil from representative site soil samples, during RF heating system. Bench-scale testing also determined that the temperature of the contaminated soil must be 130°C for substantial oil recovery. In-situ low-power RF heating tests were employed to characterize the proposed high-power test area and for gaining knowledge of the electrical properties of the soils. These data were then used in the site-specific design of the applicator so that it would efficiently couple RF energy into the contaminated soil located in a 5-10 foot thick band above the water table.

During the two weeks of high-power testing, a total of 8000 kWh was applied to the contaminated soil region, resulting in surface recovery of oil and water. Heated soil samples (70 to 80°C) collected towards the end of the test from boreholes located at 2 and 4 feet away from the applicator had a jar headspace analysis performed on them which yielded non-detectable readings to within one or two feet from the water table. Measurements of the permeability, porosity, and fluid saturation of the soil samples were made prior to heating and after heating. When compared, they showed significant reductions in the percentages of water and low levels of oil in the pore volume after heating. This water level reduced below its residual saturation value, is a strong indication that this water was converted to steam during the RF heating process.

7.0 SUMMARY

RF heating technology for in-situ thermal desorption is a promising general and cost effective approach to many contamination problems, both in-situ and ex-situ. Vacuum tube RF power amplifiers provide a cost effective approach to the economic realization of an RF system for environmental remediation. Commercially built vacuum tube systems under computer control are highly reliable and field proven. Solid state amplifiers for RF power production are considerably more expensive as compared to vacuum tube systems and perform at higher efficiency. However, commercial, low cost, solid state systems suitable for the environmental market are not presently available.

RF heating combined properly with soil vapor extraction technology is an important technology enhancement for in-situ soil clean-up applications. The employment of remote applicators in horizontal or vertical boreholes provide considerable flexibility in the location and positioning of the heating pattern. RF heating occurs within arbitrary contamination volumes by proper positioning of the applicators and electrical phasing. Very efficient heat treatment within a specified volume is therefore possible without minimum heating outside the volume. RF propagation and antenna behavior can be employed in RF systems for diagnostic work. Such applications are under investigation.

The cost of RF remediation is based on specific site conditions, treatment volume, time duration of treatment, capital equipment cost and temperature requirements. The anticipated commercial cost is targeted below 100 dollars per ton for capital equipment and operation of the system assuming a computer operated system. A vadose zone application is desirable and if moisture content is high; some dewatering by non-RF means will be necessary for economy. Transmitter and RF hardware modifications are future trends in the application of this energy for low cost remediation. RF heating integrated with soil vapor extraction is commercially cost effective and provides a unique technology approach to DNAPL recovery in low permeability media.

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Pump and Treat in Low Permeability Media

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Pump and Treat (P&T) is a commonly applied technology whose primary promise for the low permeability environments of interest to these technology reviews is almost certainly containment of the problem. Conventional P&T would be expected to offer little promise of complete restoration in such environments, unless very long time frames (decades or centuries) are considered. A variety of approaches have been proposed to enhance the efficiency of P&T; some appear to offer little promise in low or mixed permeability environments, while others may offer more promise (e.g. hydro- or pneumatic-fracturing, which are described elsewhere in this document, and application of vacuum to the extraction well(s), which is a proprietary technology whose promise is currently difficult to assess objectively). Understanding the potential advantages and means of optimizing these enhancement approaches requires more understanding of the basic processes limiting P&T performance in low or mixed permeability media. These efforts are probably also necessary to understand the advantages and means of optimizing many of the very different remedial technologies that may be applicable to low or mixed permeability environments. Finally, since a reasonably certain capability of P&T is containment (i.e. prevention of further migration of contaminants), P&T may generally be required as a sort of safety net around sites at which the alternative technologies are being tested or applied.

2.0 DESCRIPTION OF THE TECHNOLOGY

P&T is classified for the purposes of these focus area papers as a physical remediation option applicable to management or removal of contaminant mass present in the saturated zone. In P&T, groundwater is extracted by pumping on one or more wells; the extracted groundwater is treated in above-ground facilities and either discharged off-site or reinjected into the aquifer. P&T in essence controls the flow directions and rates for the groundwater at the site and uses the groundwater as a fluid for removing contaminant mass from the subsurface, including that originally present in the saturated zone as dissolved, sorbed and nonaqueous phases (Mackay and Cherry, 1989). The number, location, and extraction rate of the wells depends on the extent and nature of contamination, the hydrogeological characteristics of the site and the goals for the remediation program.

The discussion of subsurface contamination and remediation is clearest and most useful if the contamination in the saturated zone is recognized as being in two quite distinct zones (Cherry et al., 1994): 1) the source zone, within which the contaminants are present in concentrated forms such as non-aqueous phase liquids (NAPLs) and 2) the plume, which is produced by the contaminants migrating in the groundwater from the source zone, and thus within which the contaminants are present in dissolved and sorbed phases only.

In assessing the performance of P&T or any other remediation technology, it is necessary to specify the intended goal (Cherry et al., 1994; Mackay et al., 1993). P&T can be used for three distinct goals: 1) containment (risk reduction), i.e. prevention of further migration of the contaminants in the saturated zone (for containment, contaminant mass removal is a consequence, but not a specific subgoal); 2) partial aquifer restoration (mass reduction), i.e. removal of contaminant mass from a portion of the contaminated zone (most commonly this will be directed at remediation of the plume, which will be a reasonable goal only if the source zone is contained); and 3) complete aquifer restoration (nearly complete mass removal), i.e. removal of enough of the contaminant mass so that cleanup criteria are met and will remain met throughout the aquifer (past experience indicates that this will be possible only if the source zone contains insignificant contaminant mass).

The performance of P&T has been the subject of many reviews in the last several years (EPA, 1989, 1992; Mackay and Cherry, 1989; Harman et al., 1993; National Research Council, 1994; among others). Most of the reviews have focused on performance of P&T in relatively permeable subsurface environments. However, the general conclusions of these reviews may apply to any subsurface environment. As summarized by Harman et al. (1993) and supported by additional analyses by the University of Waterloo (Mackay et al., unpublished results) and the National Research Council (1994), past performance of P&T has been found to be:

1) generally successful at containment when conditions permit and technology design is adequate;
2) occasionally successful at partial aquifer restoration (remediating the plume), but only when the source zones were either insignificant or contained; and
3) rarely successful (at least to date) at full aquifer restoration, the most common cause being an uncontained source zone.

The conclusion that can be drawn is that P&T is not capable of remediating significant source zones within reasonable time frames (decades); the mass removal rates by P&T are simply too low, given the relatively large masses that can be present in source zones, the relatively low residual mass that must be achieved to reach typical cleanup criteria, the low solubility of most contaminants of interest, and the limitations of transferring mass into the extractable groundwater (i.e. that can be moved at significant rates by pumping) from the other, relatively immobile, reservoirs of contaminant mass. These other reservoirs of contaminant mass are: 1) contaminants dissolved in immobile groundwater (in low permeability portions of the subsurface), 2) contaminants sorbed to the geologic media, and 3) contaminants present in NAPLs. These important mass transfer processes are all controlled to some degree by diffusion of the contaminants through water, a phenomenon that is inherently slow compared to the typically desired time scales of remediation.

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

As described above, P&T is applicable to management or remediation of groundwater contamination, i.e. that portion of the subsurface within which groundwater flow can be controlled by extraction (and perhaps also injection) wells. When containment is the goal, P&T is applicable to any contaminant that can dissolve into groundwater, i.e., any contaminant that poses a risk via groundwater contamination. However, when either partial or complete aquifer restoration is the goal, it is clear that P&T is most applicable to relatively soluble contaminants (including many petroleum hydrocarbons and halogenated organics).

Because a P&T system consists of nothing more than a number of wells connected with one or more above-ground treatment systems, P&T is relatively easily adapted to surface constraints such as pavement, buildings, etc. Such surface obstructions may necessitate location of wells in what are anticipated to be somewhat nonoptimal locations, but given the uncertainties typically facing the system designer, the optimal locations are probably not very reliably predicted anyway. In principle, P&T systems can be used for contamination at any depth that can be reached by extraction well installation equipment, which indeed are the same constraints affecting depths at which we are currently able to detect contamination via monitoring wells.

In general terms, operation and maintenance of P&T systems focuses on: 1) maintaining flow from the extraction wells (requiring electrical power and occasional pump maintenance and redevelopment of the well/screen/gravel pack); 2) maintaining efficiency of the aboveground treatment facilities (thus depending on the treatment technology); and 3) monitoring of treatment efficiency, extracted concentrations and changes to plume extent or concentration (which requires apparatus and personnel for sample acquisition, which is usually conducted manually, transport of the samples to a laboratory, sample analysis, and recording and interpretation of the analytical data).

In most P&T systems to date, the above-ground treatment system simply transfers the contaminants from the extracted groundwater to another medium. In air-stripping, for example, the contaminants are either discharged to the atmosphere, if conditions and regulatory agencies allow, or extracted from the air flow by an air treatment system. In activated-carbon treatment of groundwater or air from an air stripper, the contaminants are sorbed to the carbon, which has a limited capacity. Thus the carbon must either be disposed or regenerated.

Operation of a P&T system would generally be viewed as having insignificant environmental impacts or safety risks, other than those expected of any operating facility including machinery, electrical lines, etc. However, in areas with limited groundwater resources, P&T can have significant environmental impacts if the treated water is not returned to the hydrologic system from which it was extracted. These impacts can include drying up or significant alteration of surface water bodies, displacement or destruction of habitat for some species, etc. Other impacts, particularly evident in areas prone to subsidence, could in some circumstances include accelerated subsidence and damage to surface structures. In some areas, discharge of contaminants into the air from air stripping treatment units may either pose specific health risks associated with inhalation of the contaminants, or other risks associated with deposition of the contaminants into surface water bodies, contributions to the total organic load to the atmosphere (potentially increasing smog or other more specific atmospheric reactions), etc.

For many years, many applied and academic efforts have been directed to developing computer models to represent the significant processes controlling contaminant behavior in groundwater, including those important under the conditions induced by P&T systems. In the last several years, there seems to have developed a widespread agreement that the modeling capabilities now exceed our ability to satisfy their data requirements. It is quite clear, for example, both from controlled experimental work and from anecdotal information available from analysis of real site data, that the progress of a P&T system designed for partial or complete aquifer restoration is dependent on at least the following:

1) 3D variations in hydraulic conductivity,
2) 3D variations in sorption characteristics of the geologic media for the contaminant,
3) 3D distribution of contaminant mass (NAPL, sorbed and dissolved),
4) 3D variations in rates, extents and products of in-situ transformations (abiotic or microbially-mediated) that may occur,
5) locations of the extraction wells compared to the 3D distributions mentioned above,
6) hydraulic performance of the extraction wells (drawdown vs extraction rate, head loss across screen, capture zone, etc.), and
7) mass transfer limitations, including not only the transfer of contaminant mass from immobile reservoirs (discussed above) to the mobile water that can be extracted via the wells, but also the transfer of mass from the mobile water to immobile reservoirs that may occur inadvertently during P&T operation, for example, concentrations are increased in some portions of the aquifer as the contaminant migration directions and rates are altered by the extraction wells (Haggerty and Gorelick, 1994).

While in principle all of these factors could be accounted for with the existing computational capabilities, there are two major limitations to modeling at this level of detail for real sites: 1) the detailed data necessary to describe the magnitude or rate of the various significant processes would not be available in the foreseeable future, especially if the data must describe the three dimensional variations (e.g. McCarty, 1990; Mackay, 1990; National Research Council, 1994), and 2) if the detailed data were in fact available, the duration and cost of running simulations would be significant, even utilizing supercomputers (see, for example, Rabideau and Miller, 1994). Thus the majority of simulations done in practice currently use relatively simple models based on a large number of simplifying assumptions. There are certainly more complex and presumably complete models available, but some are poorly documented (e.g. models created and used largely in the academic domain) and others are simply not widely used or are proprietary. Thus, it seems fair to conclude that although there are a large number of models available and in use for simulating the progress of P&T, they must be assumed to be inherently inaccurate to unknown degrees and therefore primarily useful for comparing alternative designs for P&T systems (i.e. to determine whether one design might offer advantage(s) over other designs). To the author's knowledge, there has been little success in true predictions of the full range of behavior during P&T, including both the initial, relatively rapid decline in concentrations as well as the more practically important slow decline thereafter, which leads to the "tailing" phenomena that tend to frustrate attempts to achieve cleanup criteria.

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

By definition, a basic P&T system only applies to fully saturated media within which wells can be operated. Certainly in some very low permeability media, such as unfractured clays, claystones, etc., the application of P&T would be absurd but presumably also unnecessary since there would be no significant migration route for contaminants other than by diffusion.

In this series of technology evaluations, the low permeability environment of interest has been defined as a stratified medium consisting of layers ranging from a medium sand to a clay, with the clay containing natural fractures spaced a few centimeters apart. The specific layering for this hypothetical scenario is a sand overlying a 3 m thick clay which in turn overlies a sand aquifer. The water table is assumed to be at the top of the clay layer, and it is assumed that pumping the lower aquifer can dewater some of the fractures in the clay, particularly those that are "continuous" and thus connected to the underlying aquifer. The contamination assumed in this hypothetical scenario is caused by a long-term low-rate leak of TCE and PCE (as NAPLs) from a storage tank into the sand layer overlying the clay. NAPL is assumed to have penetrated some of the fractures in the clay, including those which are "continuous" and "dead-end." Dissolved TCE and PCE are assumed to have diffused into the clay matrix itself.

In this scenario, based on the well-documented experience alluded to previously, the most logical goal for a P&T system would be containment if the dissolved contaminants have not yet formed a significant plume in the underlying aquifer. If such a plume has formed, then partial aquifer restoration might be achievable, meaning that there would be some hope of reducing the plume size or removing the plume altogether from the sand aquifer beyond the area immediately beneath the clay impacted by the spill of TCE and PCE. After that, the goal would most logically return to containment of the rest of the problem. Depending on the rate of groundwater flow through the lower aquifer, the containment might be accomplished with a modest P&T system comprised of a few shallow wells or well points placed appropriately around the downgradient periphery of the contaminated clay.

Implicit in the above discussion is the assumption that complete restoration of the contaminated zone is not a reasonable expectation for a simple P&T system. As implemented, the mass removal by P&T is limited to the mass flux out of the clay into the underlying aquifer in a dissolved phase, either by aqueous diffusion from the matrix into the fractures or the underlying aquifer or by advection of dissolved contaminant into the underlying aquifer via the fractures. Neither of these processes would be expected to yield much mass per unit time to the underlying groundwater, at least compared to the probable total NAPL mass spilled into the subsurface. Although the mass flux might be more than enough to cause a groundwater problem in the aquifer, the mass flux would probably be too low to deplete the source at a rate that would make a P&T system appear to be functioning as an efficient remediation approach.

One of the questions posed for these reviews is whether hydraulic control of the water table is critical to success. For the P&T applications discussed above, control of the head distribution within the lower aquifer is the important issue. How the water table in the clay responds is perhaps less important, especially since its response might be very difficult to measure, depending on the interconnectedness of the fractures.

Another of the posed questions is whether existing models could reliably be adapted to predict performance of P&T in the hypothetical scenario. Given that the models have not been shown to reliably predict performance of P&T in simpler scenarios, it seems unlikely that their adaptation to this scenario could be considered to yield reliable predictions. On the other hand, there is no reason to believe that the existing models could not relatively easily be adapted for comparisons of alternative well spacing, pumping rates, etc., which comparisons do not necessarily rely on accuracy of predictions but rather on inclusion of all important processes in a quantitatively reasonable fashion (implying that the conclusions of the comparison would be the same if the predictions were in fact accurate).

5.0 COST AND RELIABILITY

The author does not have the requisite practical experience to discuss costs of this technology in other than generalities. Costs for the hypothetical scenario would presumably be dominated by the cost of treatment and monitoring, if indeed only a modest system of wells or well points were required. Treatment costs would depend on the allowable method of treatment, while monitoring costs would clearly depend on the type and required intensity of monitoring in space and time. In any case, the costs of P&T would be comparable only to other technologies whose primary goal was containment. Thus the annualized costs would be presumed to be incurred essentially indefinitely.

Assessing the reliability of the method raises a general question applicable to all technologies: can the performance be monitored unambiguously? When restoration is the goal, performance is presumably best measured by the rate or extent of mass reduction in the subsurface. However, rarely are there reliable estimates of the total mass initially present in the subsurface. The available monitoring tools are not able to define contaminant distribution in sufficient detail to yield such estimates; this is especially true in heterogeneous environments containing NAPLs (Mackay, 1990; Cherry et al., 1994). Thus for the hypothetical scenario under consideration, it should be expected that determination of the distribution of contaminant mass in or adjacent to the fractured clay would be difficult and lead to uncertain estimates. For the same reasons, estimates of total mass remaining at any point of the remediation process would be unreliable. This means, of course, that attempts to monitor the progress of remediation by following estimates of total mass remaining in the subsurface are likely to be unproductive or confusing. For related reasons, the total mass removed from the surface by the remediation program, which can be much more reliably estimated, is still an ambiguous measure of progress since the total amount initially present is generally unknown and only very roughly estimated (probably more often underestimated than overestimated).

When containment is the goal for the P&T program, the reliability can generally be presumed to be high, unless there are significant heterogeneities in the aquifer permeability that are not understood or not taken into account in the design of the program. However, even when there is every reason to believe that containment is being or will be achieved, experience at sites with relatively permeable media suggest that proving to regulatory agencies that containment has or will be achieved may not be straightforward (Harman et al., 1993). There are two cases to consider: 1) complete containment in which the wells are placed so that no contamination is allowed to escape, and 2) partial containment, which may be more common, in which well placement is constrained by property boundary, road, etc., and thus the wells are placed across the existing plume so that much, but not all, of the plume is captured (the portion of the plume downgradient of the capture zone is thus allowed to continue to migrate uncontrolled).

The first case is the simpler case from the point of view of regulatory approval, since monitoring wells placed just beyond the downgradient end of the existing plume could presumably provide convincing evidence that further migration was not occurring. Note, however, that the complicated flow fields introduced by the containment wells may make it somewhat tricky to determine where the monitoring wells should be located to test the weakest portion of the capture zone; the uncertainty would arise primarily from uncertainties in the 3D variations in hydraulic conductivity in and around the capture zone. In the second case, the situation is more complicated because the monitoring must actually confirm a separation of the uncontrolled downgradient portion of the plume from the portion controlled by the containment system. This means that the uncontrolled contaminants must migrate beyond the monitoring wells. Because of the complicated flow system introduced by the containment wells, however, the directions and rates of migration of the uncontrolled contaminants will be quite variable in the areas immediately downgradient of the presumed capture zone. Given the inevitable 3D variations in hydraulic conductivity, the rates of migration of uncontrolled contaminants in some strata may be much lower than in others, even within what would generally be described as relatively uniform sand and gravel aquifers (see, for example, Mackay and Thorbjarnarson, 1990; Mackay et al., 1994; Thorbjarnarson and Mackay, 1994a). Adding the potential effects of three-dimensionally variable sorption (e.g. Thorbjarnarson and Mackay, 1994b) in slowing the uncontrolled migration, it may take a very long time for the uncontrolled contaminants to flush downgradient of the monitoring wells. During that time, it will not be clear whether the containment system is working or failing. Practical experience in such situations has suggested that the use of head distributions on their own or in combination with contaminant monitoring data will not be convincing to regulators in part because the typically available 3D resolution on head is not sufficient to conclude that there are no conceivable paths past the containment system (Harman et al., 1993). Thus, in cases where the hydrogeology is somewhat complex, it may be a long time after initiation of the containment efforts before it can be clearly shown that the containment system is successful.

6.0 COMMERCIAL AVAILABILITY

P&T is by far the most commonly applied groundwater remediation approach worldwide. It would thus be considered far more thoroughly developed and field- tested than any other technology. One might expect that any consultant working in this field should be able to design, build and operate a P&T system. However, evidence of poor or failing designs is not uncommon, suggesting that the purveyors of this technology are not all of equal expertise, particularly when the conditions are far from ideal, as in the scenario of interest to these technology reviews.

A number of suggestions have been made to enhance the performance of P&T generally. For example, pulsed-pumping and chemical additions (surfactants, cosolvents, etc.) have been proposed as methods to increase the mass removal efficiency during P&T (average contaminant mass per unit volume of extracted water). Pulsed-pumping is asserted to achieve this by allowing more time for slow mass transfer processes to deliver contaminant mass from the immobile reservoirs to the mobile groundwater. Chemical additions are designed to increase the contaminant mass in the mobile groundwater by either increasing the effective solubility or creating pseudophases (micelles or microemulsions) in which the contaminant can be concentrated. Presumably either method might affect the rate of mass transfer from the immobile reservoirs to the mobile groundwater. However, neither are likely to offer much advantage when the major limitations to mass removal are relatively large-scale heterogeneities in hydraulic conductivity such as exist in the hypothetical scenario under consideration in these technology reviews (see, for example, Rabideau and Miller, 1994; Palmer and Fish, 1992).

There also have been enhancements specifically proposed for low permeability media. One example is hydro- or pneumatic-fracturing of the low permeability portions of the subsurface, creating relatively wide, permeable fractures; this technology is discussed in a separate focus area paper in this document. Another example is the imposition of relatively high vacuum in the extraction well, which is asserted to increase the radius of influence of the extraction well and lead to more rapid removal of water and contaminant mass (E. Nyer, Geraghty and Miller, Inc., personal communication, 1994). To the author's knowledge, however, the vacuum enhancements have not yet been described in detail or evaluated in peer-reviewed scientific publications. Thus, it is currently difficult to determine what promise it may hold for future applications of P&T in low permeability media.

7.0 CASE HISTORIES

The general issues discussed previously were conceived in part through discussions with practicing hydrogeological consultants, who, of course, drew their thoughts from their own case histories. Because time to prepare this review was limited and the case history information often privileged, no attempts were made to collect sufficient information to present capsule summaries of case histories here. Because of the limited effectiveness of P&T at complete restoration at low permeability sites, such case histories generally would illustrate the issues related to containment. That particular goal, however, does not appear to be the focus of this document.

It is worthwhile to note that while there have been a number of controlled field experiments conducted within existing plumes specifically to evaluate the processes controlling P&T of relatively permeable subsurface environments (Whiffen and Bahr, 1985; Mackay and Thorbjarnarson, 1990; Myller et al., 1992), there have been none of which the author is aware conducted in lower permeability environments (at least reported in peer-reviewed literature to date). Such experiments might be very useful in establishing the baseline against which the performance of supposedly more efficient technologies could be compared.

The effects of mass transfer limitations on the growth and subsequent remediation of plumes in fractured rock have been examined via simulations by Moncur (1992). As discussed by Mackay and Sudicky (1992), these simulations, which addressed only a nonsorbing contaminant, illustrate that 1) mass removal by P&T would be expected to be very slow once the contaminants have had an opportunity to invade the rock matrix by diffusion from the fractures, 2) the effect is greater for rock matrices with greater porosity (i.e. greater immobile reservoir volume), 3) the efficiency of mass removal is very sensitive to location of the extraction well(s), 4) optimal well location would be very difficult if not impossible since the 3D distribution and interconnectedness of fractures would never be completely known, and 5) nonoptimal well location can exacerbate the problem by pulling contaminants into relatively uncontaminated portions of the media, thereby allowing more mass transfer into the immobile reservoirs. These problems would presumably be increased for contaminants which sorbed to the relatively impermeable geologic media, in a manner similar to that explored by Haggerty and Gorelick (1994) for permeable media.

Clearly it would be advantageous to conduct additional simulations, preferably in 3D, to explore a range of questions regarding the limitations and sensitivity of P&T in low permeability and mixed permeability environments. Note, however, that there is very little information available on the 3D variations in the important characteristics of such media. Often the fracture networks are computer generated to fit generally accepted understanding of fracture spacing, aperture, interconnectedness, etc. However, relatively little is known about sorption and desorption of organic contaminants by low permeability geologic media, let alone the 3D variability of the characteristics. Recently, Allen-King et al. (1995a,b) proposed a method for relatively unambiguous analysis of the sorption isotherms for unconsolidated clays and reported isotherms for several clays from markedly different low permeability environments. Their findings indicate that a great deal remains to be done to understand the sorption and desorption of contaminants in such media, especially across the extremely wide concentration range of interest in source areas containing NAPLs and when multiple contaminants are present (with the attendant probabilities of competitive, cosolute or even cosolvent effects, depending on the species and concentrations present). Furthermore, given that sorption characteristics of permeable media are known to have significant spatial variability in some environments (e.g. Mackay et al., 1986; Mackay and Thorbjarnarson, 1990; Allen-King et al., 1995c), it should be expected that the same would be true of some low permeability media and efforts should be made to determine to what extent this variability is likely to affect the performance of P&T or other remediation technologies applied to such media.

8.0 SUMMARY

P&T is a commonly applied technology whose primary promise for the low permeability environments of interest to these technology reviews is almost certainly containment of the problem. Conventional P&T would be expected to offer little promise of complete restoration in such environments, unless very long time frames (decades or centuries) are considered, because of the very slow processes that control the transfer of contaminant mass from relatively immobile reservoirs (including NAPLs or dissolved contaminants in narrow or dead-end fractures, and dissolved and sorbed contaminants within the impermeable matrix). A variety of approaches have been proposed to enhance the efficiency of P&T; some appear to offer little promise in low or mixed permeability environments, while others may offer more promise (e.g. hydro- or pneumatic-fracturing, which are described elsewhere in this document, and application of vacuum to the extraction well(s). Understanding the potential advantages and means of optimizing these enhancement approaches requires more understanding of the basic processes limiting P&T performance in low or mixed permeability media. This understanding could be gained through a combination of carefully controlled field experiments in such environments (including at existing contaminated sites), laboratory evaluation of basic processes such as sorption and desorption, and numerical simulations. These efforts are probably also necessary to understand the advantages and means of optimizing many of the very different remedial technologies that may be applicable to low or mixed permeability environments. Finally, since a reasonably certain capability of P&T is containment (i.e. prevention of further migration of contaminants), P&T may generally be required as a sort of safety net around sites at which the alternative technologies are being tested or applied.

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AIR SPARGING IN LOW PERMEABILITY SOILS

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Sparging technology is rapidly growing as a preferred, low cost remediation technique of choice at sites across the United States. The technology is considered to be commercially available and relatively mature. However, the maturity is based on the number of applications of the technology as opposed to the degree of understanding of the mechanisms governing the sparging process. Few well documented case studies exist on the long term operation of the technology.

Sparging has generally been applied using modified monitoring well designs in uniform, coarse grained soils. The applicability of sparging for the remediation of DNAPLs in low permeability media has not been significantly explored. Models for projecting the performance of sparging systems in either soils condition are generally simplistic but can be used to provide general insight into the effects of significant changes in soil and fluid properties.

The most promising sparging approaches for the remediation of DNAPLs in low permeability media are variations or enhancements to the core technology. Recirculatory sparging systems, sparging/biosparging trenches or curtains and heating or induced fracturing techniques appear to be the most promising technology variants for this type of soil.

2.0 DESCRIPTION OF TECHNOLOGY

Accidental releases of organic compounds into the subsurface in the form of petroleum products or industrial solvents can result in costly remediation. Removal of the contaminant source is the primary consideration to ensure effective remediation. Soil contamination which lies under and in the vicinity of a leaking underground storage tank (LUST) or a surface spill is a potential long term source to the migration of hazardous vapors in vadose zone soil and to dissolved contaminants in ground water. Frequently, contaminated soils exist below the ground water table (GWT) when free phase product mounds on the GWT and is transported vertically in response to seasonal GWT fluctuations or drawdown from pumping in nearby ground water and product recovery wells. Dense, non-aqueous phase liquids (DNAPLs) are frequently found on soils below the GWT as globules, residuals, and possibly free product pools due to their density driven vertical transport.

Few commercially applicable in-situ remediation technologies exist that can be applied as remedial alternatives for contaminants below the GWT. Artificial water table drawdown is one approach that may be used to expose contaminated soils in the saturated zone to the soil vapor extraction process. However, in some cases, this is not a practical, nor cost effective approach. A potential innovative, alternative approach is the application of sparging technology, which entails injecting a hydrocarbon-free gaseous medium (such as air) into the saturated zone below and within the areas of contamination. With air sparging, volatile organic compounds (VOCs) dissolved in the ground water and sorbed on the soil physically partition into the advective gaseous phase effectively simulating an in-situ, saturated zone air stripping system. The stripped contaminants are subsequently transported in the air phase to the vadose zone, commonly within the radius of influence of an operating soil vapor extraction system.

Aeration of ground water can occur or can be the primary objective of a sparging system. Under this condition and assuming that additional relevant environmental parameters are or can be manipulated to be within an acceptable range, contaminant remediation via enhanced in-situ biodegradation can result (bio-sparging). A schematic depicting a typical sparging system configuration under idealized conditions is presented in Figure 1.

Limited references exist in the literature on the design and/or success of laboratory or field applications of the sparging process. Apparently the process was first utilized as a remediation technology in Germany in the mid-1980s, predominantly to enhance the clean-up of chlorinated solvent contaminated ground water (Gudemann and Hiller, 1988). More recently the technology has been utilized in the enhanced remediation of gasoline contaminated saturated zone soils and ground water (Ardito and Billings, 1990; Marley, 1991; Marley, Hazebrouck and Walsh, 1992; Brown, Herman and Henry 1991).

There are many important criteria which must be considered when designing, installing, operating and monitoring sparging systems. Evaluation of these criteria are not only necessary to ensure effective remediation of saturated zone soils and ground water, but also to preclude displacing and mobilizing potentially hazardous soil gas vapors, free phase product or dissolved phase contaminants.

In developing a design process, it is necessary to better understand the mechanisms that occur during sparging. Air is injected into sparging wells at pressures in excess of the soil matrix air entry pressures. For coarse grained soils, minimum pressures are generally 1 to 2 pounds per square inch (psi) in excess of the hydrostatic head at the top of the injection well screen. For finer grained soils with significant air entry pressures, the required minimum injection pressures can be significantly higher (factor of 2 or more) than the hydrostatic head at the top of the well screen. Sparging in highly stratified or low permeability soils can require pressures that approach or exceed soil fracturing injection pressures. Uncontrolled fracturing of the soil matrix may or may not enhance the contaminant removal process. In many cases, the efficiency of mass removal may be significantly reduced because of limitations in the number and distribution of the uncontrolled fractures.

Soils possess a relatively random distribution of pore sizes, pore scale heterogeneities and hydraulic conductivities. As air enters the saturated soil matrix, it will displace water from the highest conductivity pores, forming an air channel to the vadose zone, in most soils. Limited laboratory studies have indicated that air bubble streams may only be expected in gravels (Ji et al, 1993). The displacement process is sensitive to the pore scale conductivity differences and results in an unpredictable distribution of air channels. These processes are contrary to the idealized perception of a uniform distribution of discrete air bubbles.

Under the assumption of the formation of a limited number of steady state air channels, the sparging process would be governed by contaminants being stripped or degraded in the immediate vicinity of the formed channels. If this were the only mechanism of contaminant removal, the air sparging process would be significantly less efficient than it has been demonstrated to be in the field.

It is speculated that three major mechanisms may be contributing to the field observed enhanced removal efficiencies. First, the buoyant and often transient movement of the air through the saturated zone may tend to create convective movement of water in the vicinity of the channel, which would induce movement of additional contaminants to the air channel for removal.

Secondly, because the water displacement process is so sensitive to the pore scale hydraulic conductivities, a change in the hydraulic conductivity of a pore could effect the spatial location of the channel. Noting this, it is preferred to pulse air sparging systems during operation. The pulsing has a number of potential benefits. Pulsing may cause a mixing of the water in the treatment zone effectively increasing the channel and contaminant contact. Pulsing may also cause a change in the air channel spatial distribution because the pore hydraulic conductivity can be effectively reduced because of the presence of residual air in the formerly preferred channels following a pulse event. Pulsing can also reduce capital and energy costs in the operation of this kinetically limited mass removal process.

Thirdly, the oxygen transfer into ground water and subsequent mixing associated with both the convective ground water movement and as a result of the pulsed mode of system operation can produce contaminant removal through enhanced biodegradation (biosparging).

Soil stratification is a critical geological feature to identify in terms of the expected performance of a sparging system. Air flow in the subsurface will generally follow the path of least resistance. The presence of less permeable soil strata above the air injection point can create significant lateral air movement and channeling. Determination of the potential for preferred lateral air movement is critical to predict lateral displacement of ground water and capture of VOCs in the vadose zone due to sparging activities. Figures 2 and 3 demonstrate the effects of macro-scale soil heterogeneities on air movement (Ji et al 1993).

In highly stratified or naturally fractured soils, restrictions in air movement would be expected to significantly reduce the effectiveness of ground water mixing. However, with appropriate introduction of the air more intimate contact with the contaminant within the preferred pathways is possible.

It is obvious that the sparging process still requires significant research to verify or to better describe the mechanisms occurring during system operation and to design and monitor sparging systems. As with most remediation technologies, it is not appropriate for all sites and is generally one of an integrated train of technologies required for a site clean up.

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

A) *Is the technology primarily geared to soil or ground water contamination?*

Sparging technology has been used with the primary focus to remediate soils or to remediate ground water or in many cases both (Ardito and Billings 1990; Gudemann and Hiller 1988; Loden and Fan 1992; Marley, Hazebrouck and Walsh 1992, Fairbanks, Pennington and Rabideau 1993). On a cost evaluation basis, it is generally most applicable to utilize sparging as a soils (contaminant source) remediation strategy. In cases where the contaminant plume is large and at depth (with respect to the ground surface), the cost of implementation of the technology may be in excess of that for less innovative techniques (pump and treat).

B) *To what extent is the technology suited to remediating petroleum as well as chlorinated hydrocarbons?*

In the United States, the principal application for sparging technology is for the remediation of petroleum hydrocarbons. The technology is generally considered to be more applicable to petroleum hydrocarbons because:

1. Petroleum hydrocarbons generally remain within the upper few feet of the saturated zone and are generally fairly uniformly distributed. Chlorinated hydrocarbons on the other hand, can penetrate deep into an aquifer system and due to their density and viscosity are normally distributed in a very non-uniform pattern within the subsurface (ganglia and trapped product pools). Therefore, petroleum hydrocarbons are more readily available and more easily accessible to the sparging process.

2. In situations where the remediation of the contaminant is dependent on biological degradation, petroleum hydrocarbons are generally more readily degradable (under typical, natural conditions) than chlorinated hydrocarbons. Chlorinated hydrocarbons generally need the presence of an inducing substrate (co-metabolism) or the addition or existence of constitutive (self-inducing) micro-organisms.

C) *How well is the technology able to access under buildings or pavement?*

Sparging wells resemble common monitoring wells and may be installed vertically, angled, or horizontally. The radius of influence of a typical sparging point is between 15 and 30 feet. Under these conditions, the technology is well suited for application under buildings and/or pavement. An area of concern with respect to sparging beneath a building is the capture of potentially hazardous vapors that can emanate from the ground water during sparging system operation. Appropriate means of vapor capture (commonly soil vapor extraction) must generally be implemented to ensure an acceptable level of health and safety for the area residents and workers.

D) *What is the maximum depth of remediation?*

There is no theoretical maximum depth of remediation for sparging, since a well can be installed to depths in excess of hundreds of feet. However, from a cost and practical evaluation, few sparging systems operate at depths in excess of one hundred feet. Many sparging applications are to depths of less than fifty feet. In many applications sparging at depths below the level of contamination did not significantly increase the radius of influence of the sparge point. In many cases, in addition to the extra costs, at the increased depth of application less desirable geological profiles were encountered. Due to the sensitivity of air movement to pore scale heterogeneities, site geology essentially dictates the applicability/success of sparging and the required sparging system design.

E) *What are the utility, operation and maintenance requirements?*

The equipment utilized to operate sparging systems are generally standard electric blowers and motors. Dependent on the air flow rate and pressure requirements at a particular site, the sparging system may vary from a 1 1/2 HP off the shelf compressor to an industrial grade 50 plus HP rotary screw compressor system. Operation and maintenance of the equipment is standard. Following an initial system debugging period (1 day to a few weeks) standard weekly to monthly maintenance is required.

F) *Are secondary waste streams produced?*

Under normal operating conditions, the secondary waste stream developed from the operation of a sparging system is a contaminated vapor. Under typical conditions, the vapor waste stream is captured through the application of a soil vapor extraction system. The vapor stream is commonly destructed through a thermal or biological system or captured on activated carbon for subsequent disposal or destruction. In a number of cases, on a site specific basis, the vapor stream can be treated in-situ through biological degradation mechanisms.

G) *Are there potential environmental impact or safety risks associated with the use of the technology?*

The major potential environmental impact or safety risks from the application of sparging technology are the possible uncontrolled migration of a product, dissolved or vapor phase contaminant plume. Liabilities associated from plume migration off-site or health risks could result. However, an appropriate system application, design and monitoring program should eliminate these potential hazards.

H) *Are models available to predict performance in porous media and to what extent are they developed?*

No commercially available models presently exist to appropriately describe the standard point sparging application. It is unlikely that any model will be available to deterministically project the random distribution of channels that form during the point sparging process. A number of simplified models relating the mass transfer characteristics of the physical sparging process to empirically factored bubble (film) theory have been presented (Sellers and Schreiber 1992, Wilson, Kayano, Mutch and Clarke 1992).

A number of deterministic models have been developed to help evaluate the potential effects of general soil and fluid properties on the sparging process (Marley and Li 1993, Lundegard and Anderson 1993). While these models can not accurately describe the random channel distribution in the subsurface, they do provide insight into the impacts of geology and system operating conditions on the sparging process.

In addition, models do exist for predicting the behavior of non-point sparging applications such as trenches (Marley, Droste, and Cody 1994) and recirculatory systems (Herrling, Stamm, Alesi, Brinnel, Hirschberger and Sick 1991).

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

A) *What is the effect of soil water content on contaminant removal?*

Since sparging is applied in the saturated soil zone this question is not considered applicable beyond the consideration of air channel formation and ground water mixing as previously described.

B) *Is hydraulic control of the water table critical to success?*

The concern with the need to control the water table during sparging activities is generally associated with the potential for the inappropriate application of the technology with the corresponding uncontrolled plume migration and potential associated liability and health and safety issues. The concern is legitimate where the geology of the chosen sparging site (or pilot test results) demonstrate the potential for significant lateral migration of the injected air and/or where the contaminated plume is in close proximity to the site property boundary.

In many cases with the use of sparging trenches (Figure 4) or recirculatory systems (Figure 5) in-situ ground water control is an integral part of the system design. In addition, sparging points can also be designed (sparging curtain) to control the movement of the contaminated plume.

Additionally, in many cases where the geology is appropriate for the application of point sparging, no ground water control is needed as remediation is relatively rapid, and ground water movement is limited during the remediation time frame.

An important distinction to be made is the impact of mounding on the movement of ground water under conditions where point sparging is appropriate. Hydraulic head measurements recorded during sparging, in conjunction with the application of Darcy's Law, indicates that macro-scale ground water movement appears very limited in these cases. Therefore, mounding in these cases does not appear to provide a mechanism for significant plume migration.

C) *Can the porous media models (if available) be reliably adapted to predict performance in low permeability media, as in the given scenario?*

1) Free product pooled as clay.

As free product is pooled within and above the saturated zone on top of clay, the utility of sparging is limited. As it has been stated that the continuous fractures can be drained by dewatering the underlying sand, it is assumed that the product thickness on the clay is insufficient to displace the water in the continuous fractures and move down through the clay. In that case, the potential for enhancing vertical product movement by creating a partial saturation condition in the fracture must be evaluated. Sufficient air pressure must be applied to counteract the gravitational forces that would tend to cause DNAPL to migrate vertically.

Under the condition of sparging air passing through the fractures with sufficient resistance to product migration downward, the potential benefits of enhanced product volatilization could be realized. Additional limitations would be the ease of movement of the product within the sands atop the clay, toward the sparging air channels. Standard vapor equilibrium models could be utilized to provide an optimistic evaluation of the potential rates of product removal.

2) Separate phase product trapped in continuous clay fractures.

The potential benefits and constraints for product removal as described above also applies for product trapped in continuous clay fractures. However, it would be expected that under conditions where sparging is controlled to avoid vertical product migration, more efficient removal of the product in the fractures would be expected.

3) Separate phase product trapped in discontinuous or "dead end" fractures.

Removal of product from "dead end" fractures would be diffusion limited unless system adjustments were made. Figures 6 and 7 present the potential unassisted and assisted performance of sparging in a naturally fractured soil. Figure 6 displays the low probability of point sparging to be effective in providing efficient contact between the air flow and the trapped product. Figure 7 demonstrates the potential for induced horizontal fractures in combination with sparging to improve the effectiveness of the technology in this setting. Further, in soil conditions where the natural pattern of fractures is predominantly horizontal, the sparging trenches presented in Figure 8 could be used to improve the effectiveness of the process.

4) Dissolved phase product diffused into the matrix blocks.

Unassisted sparging would be expected to have a negligible effect on the removal of the dissolved phase product diffused into the matrix blocks. Preliminary evaluations of aqueous phase diffusion of TCE from the clay matrix are provided in Figure 9. It can be observed that significant time frames may be required to remove the TCE from the matrix by diffusion. Planar fracturing or matrix heating may be utilized to enhance the rate of removal of TCE by diffusion, if cost effective. Alternatively, a risk assessment may indicate that the probable TCE diffusion rate from the clay may pose an acceptable risk under the site specific conditions.

It is important to note that while a number of potential engineering solutions to the potential problems encountered in using traditional air sparging has been presented, it is likely that unassisted sparging technology may not be the most appropriate approach for this scenario.

5.0 COST AND RELIABILITY

Costs provided in the following sections are very preliminary and are based on the remediation of a 40 M by 40 M area at an initial contaminant concentration in the clay of 2,000 mg/kg.

A) Costs to remediate to a target of 200 mg/kg.

The costs have been broken up into sparging capital costs, complimentary SVE capital costs, the costs of an alternative sparging system utilizing induced planar fractures and O & M costs. The numbers provided are relatively conservative and are produced utilizing numerous logistical assumptions for which detail is not provided.

Sparging pilot test (range $3,000-$30,000)	$16,000
Sparging system capital costs	$43,000
SVE System capital costs	$ 36,000
Alternate Planar Sparging capital cost	$100,000
Annual O & M Costs	$ 42,000

For an assumed operational period of two to four years and based on the results of the diffusion modeling the expected cost range is: $179,000 - $336,000.

B) Time to clean up target

Again, using traditional sparging and assuming that cleanup will be limited by removal of the TCE from the clay matrix by diffusion, a remediation time frame on the order of two to four years may be expected. The rate of removal would be low due to the diffusional flux limitations and would decrease significantly over the clean-up period. An average removal rate on the order of 2 mg/kg day is expected.

C) Economics of Scale.

For the application as outlined above, it is expected that the capital costs for implementation of the technology will increase in a relatively linear manner. Alternatively, significant savings (deviation from linearity) would be realized in the O & M costs.

D) Confidence/Reliability of Achieving Goal

For the given conditions, it is unlikely that unassisted sparging would be the commercially selected technology of choice. A system could be engineered to provide a reasonable degree of confidence and reliability of achieving the clean up goal, but the solution would not likely be cost effective.

E) Cost and Time to Remediate to 1,000 mg/kg.

Based on the data provided above, the costs for achieval of the 1,000 mg/kg goal are:

Sparging pilot test (range $3,000-$30,000)	$16,000
Sparging System Capital Costs	$ 43,000
SVE System Capital Cost	$ 36,000
Alternate Planar Sparging Capital Cost	$100,000
Annual O & M Costs	$ 42,000

At an estimated remediation timeframe of one to two years, the remediation cost is estimated between $136,000 - $256,000.

6.0 COMMERCIAL AVAILABILITY

A) Stage of Development of the Technology

Unassisted sparging is considered to be a relatively mature and commercially available technology today. However, the status of the technology is based more on the number of pilot or full scale applications of the technique as opposed to the degree of understanding of the technology or on the number of applications of technology variations or enhancements.

As previously noted, there are a number of theories on the mechanisms ongoing during a sparging system operation. Few controlled and detailed laboratory or field experiments have been performed on the technology to date. Additionally, few commercial applications on variations of the technology (e.g. recirculatory systems, planar fracturing and steam sparging) have been reported. Further, even though there are a large number of sparging technology applications across the country, there are very few well documented studies on the long term operation of the technology. This is particularly true for the application of sparging technology for DNAPLs in low permeability media.

B) Commercial Availability of the Technology

As stated above, standard sparging technology is considered to be readily available within the industry today. This is due to the relative simplicity of the concepts upon which the technology is derived. However, it must be re-emphasized that in reality, the basics of the technology are not yet well understood. Numerous variations to the base technology are continually being tested and evaluated; however, the technology variations are not generally considered to be commercially available as yet.

C) Likely Future Enhancements

A number of the likely future enhancements have been mentioned in the previous text. The projected major commercial enhancements are most likely to be related to recirculatory based systems, and to heat and/or biologically and/or induced fracturing assisted systems.

D) Complimentary Technologies that would Enhance Cleanup if Incorporated in a Treatment Train.

Again, many of the potential complimentary technologies have been previously mentioned. The major complimentary technologies are:

- soil vapor extraction
- heating techniques (DNAPLs boil-off, enhanced diffusion rates),
  - radio frequency
  - steam injection
- biological (bio-sparging, bio-curtains/trenches)
- pneumatic and hydraulic fracturing
- the application of sparging for plume containment.

7.0 CASE HISTORIES

As previously mentioned, there are few well-documented case studies that include long term operational data for sparging systems, including sparging systems for DNAPLs in low permeability media. Two case histories are presented below that may not specifically address long term operation at DNAPL sites but do consider the technology in stratified or low permeability soils. The first is a trench sparging approach and the second a point sparging approach.

Sparging Trench Design

A sparging trench was designed as part of a corrective action plan (CAP) at a bulk fuel storage terminal in Virginia which had a release of fuel to the subsurface. A sparging trench was proposed to remove dissolved VOCs from ground water to acceptable levels as it migrated through the sparging trench. Site geology consists of unconsolidated silts and clays overlying ledge. Based on slug test data, hydraulic conductivity for the unconsolidated materials is 0.0002 cm/sec and depth to ground water at the site is approximately two feet below surface grade level.

The proposed design uses a 400-foot segmented trench installed perpendicular to the ground water flow direction and across the delineated contaminant plume to intercept and treat dissolved-phase VOCs. Dissolved VOCs entering the trench will be removed to regulatory standards from the ground water utilizing a trench-based sparging well design. The relatively low hydraulic conductivity of the native materials surrounding the trench essentially allows the trench to perform as an *in-situ*, batch reactor air stripper.

The primary considerations associated with the design of the air sparging trench were:

a) ensuring that the existing ground water flow patterns at the site will not be negatively impacted by the presence of an air-water mixture in the trench (i.e., the contaminated ground water plume will flow through, not around the sparging trench);

b) reducing the target contaminant concentrations to acceptable levels in the ground water as it flows through the trench;

c) ensure uniform distribution of air flow over the entire length of the distribution pipe system.

Ground water flow through the trench is attained by ensuring that the relative hydraulic conductivity of the trench backfill material is greater than the saturated conductivity of the native material under active sparging conditions. The relative conductivity of the backfill material is related to its saturated conductivity and the volumetric percentages of air and water in the material pore spaces during sparging operation. A quantitative evaluation of the relative backfill material conductivity is obtained through the application of the Van Genuchten (1980) equations. These equations allow the determination of hydraulic conductivity of porous materials for varying water content values.

Contaminant removal in the trench during sparging can be described by an exponential decay curve as presented by Sellers (1992). The contaminant removal rate is a function of the residence time in the trench and the mass transfer kinetics of volatilization from the aqueous phase into the advective air phase (sparging air). For specific trench dimensions, the residence time is fixed due to the relatively constant flow of ground water in the native material surrounding the trench. The mass transfer kinetics are related to a number of relatively fixed parameters (e.g., trench dimensions, backfill material properties, contaminant properties) and to the air flow rate and distribution in the backfill materials. The governing mass transfer equation is solved to calculate the required air flow to achieve the target contaminated ground water cleanup levels with a fixed residence time in the sparging trench.

An additional check on the mass transfer design approach (which is considered to be conservative), was performed by modeling the system based upon equilibrium partitioning principles (e.g., Henry's Law). The trench was modeled as a continuous stirred tank reactor. The results of the equilibrium partitioning-based calculations confirmed the results of the previous analysis.

To intercept the entire plume, the trench system is approximately 400 feet in length and aligned perpendicular to the ground water flow direction. To minimize the dependence of system performance on one trench, the trench design will consist of ten individual trenches, each approximately 40 feet in length. The individual trenches will be overlapped to prevent the possibility of ground water flow bypassing the individual trench segments.

The individual trench manifold lines will traverse to a centrally located pump and blower area and be connected to a regenerative blower. After the required sparging air flow rate was determined to achieve the desirable relative hydraulic conductivity of the trench and adequate VOC removal efficiencies, it was necessary to design the air distribution manifold within the sparging trenches. Mathematical equations describing fluid flow in pipes were uses to design the air distribution system (Gill 1987, Chaudhry and Reis 1992, Hudson, Uhler and Bailey 1979). The total energy head in the line is equated with the pressure differential (pressure drop) at a pipe orifice or slot. The use of these equations allowed for the design of a uniform distribution of fluid flow from a multi orifice/slot system.

During the modeling process, various methodologies for ensuring a uniform air flow distribution, such as diffusers, slots and nozzles were evaluated in consideration of practical operational criteria (flow rates and operating pressures). The analysis indicated that the use of diffusers and/or nozzles in this specific trench system may be logistically complex and costly.

The modeling analysis results also indicated that conventionally slotted (10 or 20 slot size), 1" diameter PVC pipe would have required excessive air flows in order to achieve a relatively uniform air distribution in the trench. However, the analysis indicated that modification to the conventional slot pattern would deliver the required air flow yet maintain a stable and uniform air pressure and velocity throughout the entire pipe, thus ensuring a relatively uniform air distribution.

Calculations were performed in order to estimate the maximum air emission rate of VOCs from the sparging trench system. The results of the calculations indicate that the worst-case emissions from the air sparging trench would be below the levels requiring an air discharge permit. Therefore, the sparging air will discharge directly to the atmosphere without the need for prior collection or treatment. The overall system design was reviewed and approved by the relevant state agencies. The cost of design and installation is approximately $50,000.

Point Sparging System Design

Air sparging was utilized to expedite ground water remediation at a gasoline spill site in Rhode Island. Ground water and product recovery and soil vapor extraction had been used at the site from 1985 to 1989 and were successful in removing free product and remediating vadose zone soils to non detectable (less than 5 parts per billion (ppb)) total BTEX levels. However, ground water total BTEX concentrations remained at approximately 20,000 to 30,000 ppb within the vicinity of the former tank pit. The Rhode Island Department of Environmental Management had set a varying closure limit of up to 10,000 ppb total BTEX for the site. In August 1989, the site was evaluated for the application of air sparging in conjunction with the existing soil vapor extraction system to expedite site remediation. Based on the parameters evaluated during pilot scale testing, a full scale sparging system was designed and installed at the site consisting of seven shallow sparging wells and six deep sparging wells. Shallow sparging wells were installed in coarse sand and gravel which extended from the water table to approximately six feet below the water table. The deep sparging wells were installed within a fine to very fine sand that lay beneath the coarse sand and gravel. The sparging system was operated intermittently over a 60 day period at injection flow rates of 2 to 6 scfm and pressures of 6 to 8 psi. Within the first two to three weeks of operation, the designated closure criteria had been achieved. Except for an anomalous rise in total BTEX levels in October 1990, the closure criteria set for the site have been maintained. The levels achieved and maintained at the site are below the MCLs for the BTEX compounds. The total cost of system pilot testing, design, installation and operations was approximately $57,000.

8.0 SUMMARY

Air sparging, due to its conceptual simplicity, is generally considered to be a commercially available treatment technology for chlorinated and non-chlorinated hydrocarbon contaminated saturated zone soils and ground water. However, in reality details on the mechanisms that govern the application of the technology are not yet well understood, even in uniform permeability media. Few, if any, well documented case studies exist on the application of air sparging for DNAPL remediation in low permeability media.

It is likely that standard point sparging techniques will have limited applicability for DNAPL in low permeability media remediation. However, engineered variations of the technology in the form of recirculatory systems, bio-sparging, sparging or biosparging curtains/trenches and induced fracturing techniques will likely increase the applicability of the base technology in this type of soil.

In many cases, sparging technology is used as one component of an overall treatment train for a contaminated site. Past experiences indicate that the most cost effective application of the technology has been for the removal of applicable contaminants from source areas.

When utilized appropriately, the technology can achieve low clean up levels in relatively fast timeframes.

It is likely that in the immediate future, significant experience and understanding of the base technology and its variants will be gained from both field applications and research efforts. It is expected that the understanding developed from the collected data will create a broadened scope of application of the technology and its variants while simultaneously better defining the technology limitations.

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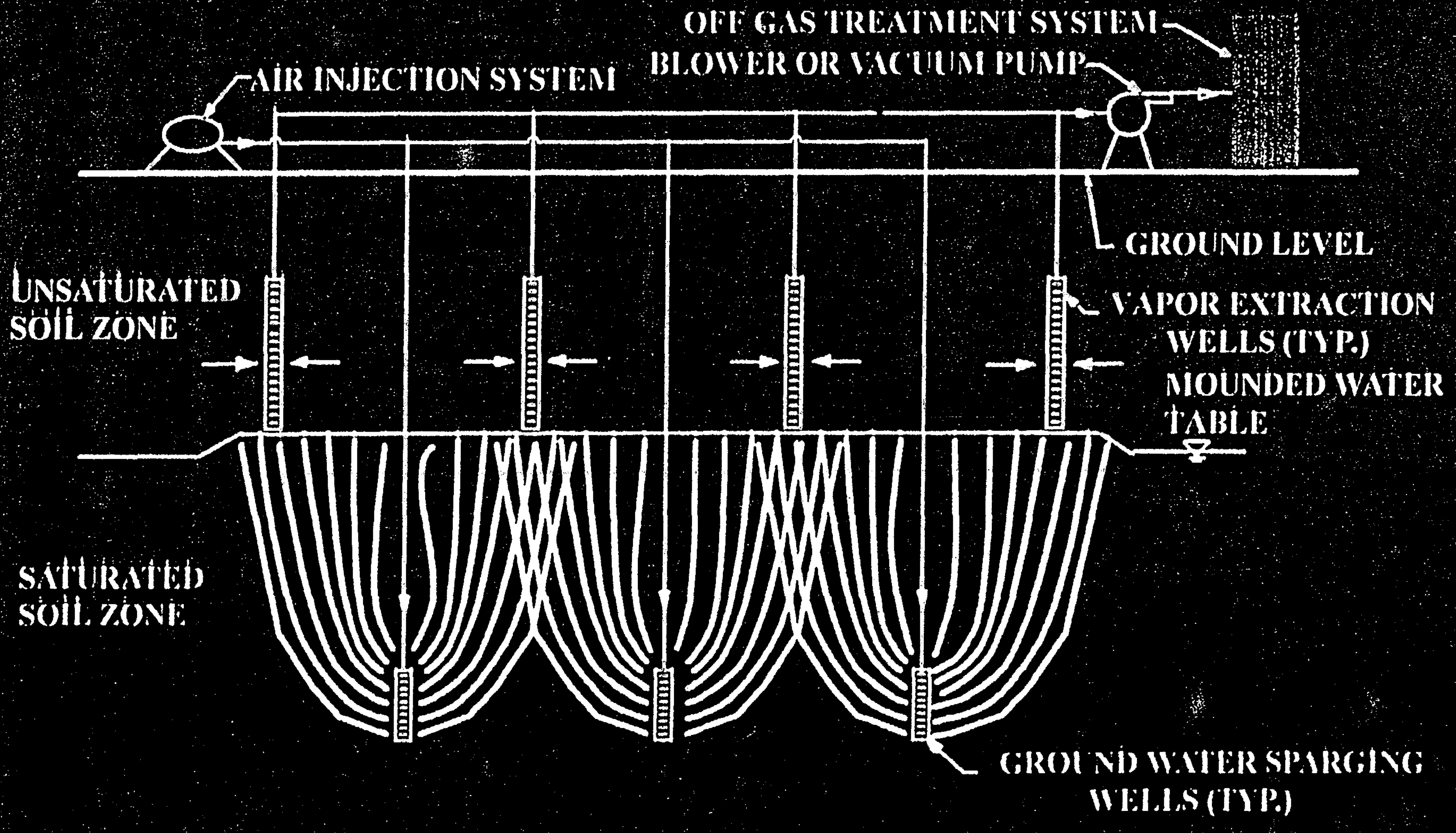
TYPICAL SOIL VAPOR EXTRACTION AND AIR SPARGING SYSTEM CONFIGURATION



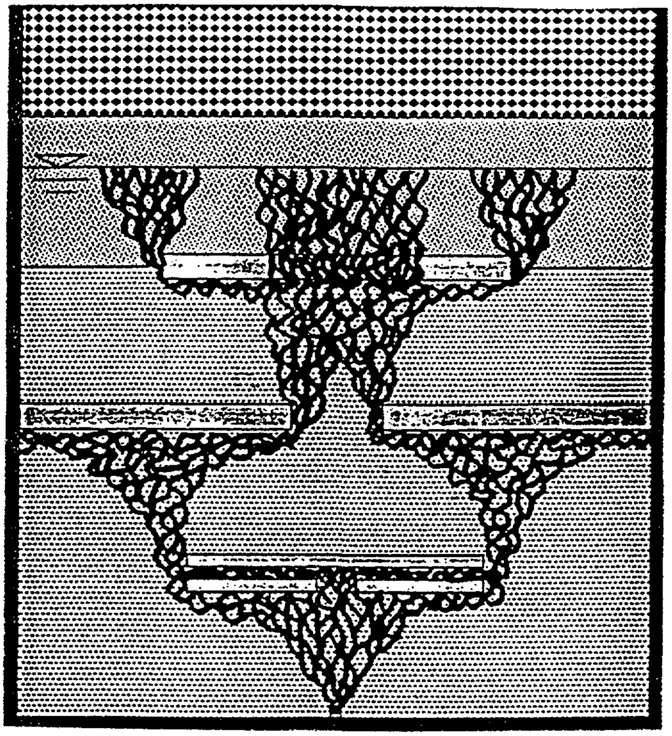


Figure 2. Air channel pattern in a stratified medium at lower air injection rates.

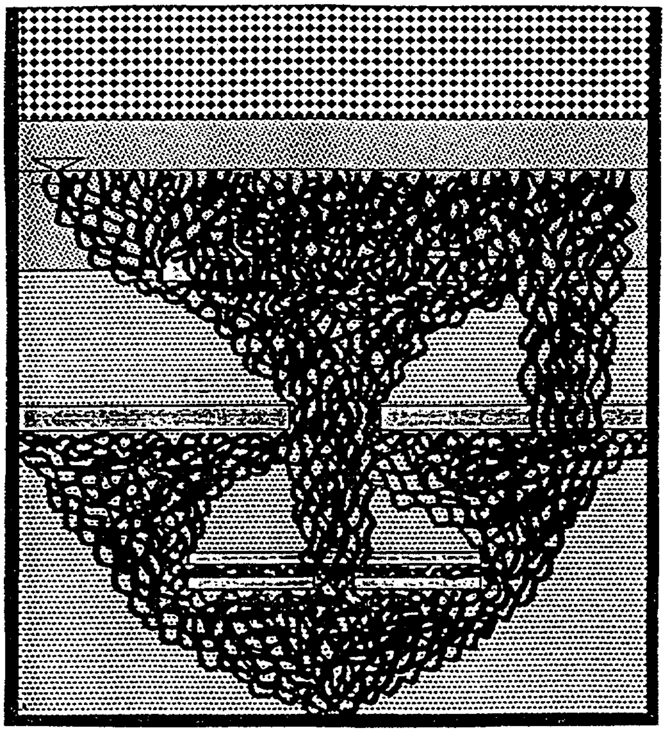


Figure 3. Air channel pattern in a stratified medium at higher air injection rates.

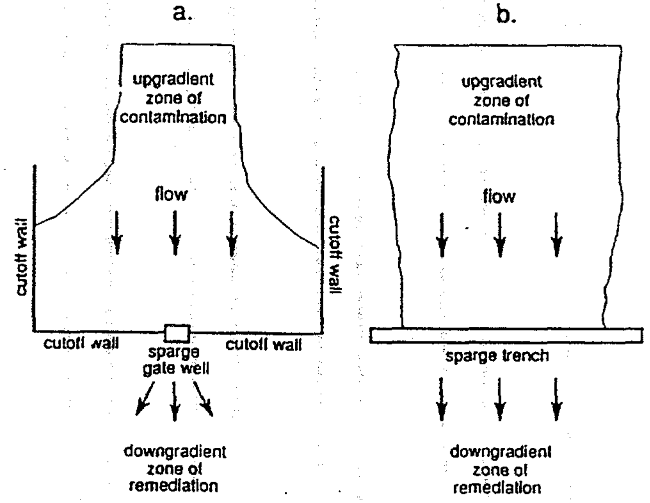


Figure 4. a. Sparging in a gate well in a cutoff wall for interception and treatment of a flow of contaminated ground water (plan view). Note the tendency of the plume to widen behind the cutoff wall. b. Sparging in a rectangular trench for interception and treatment of a flow of contaminated ground water (plan view).

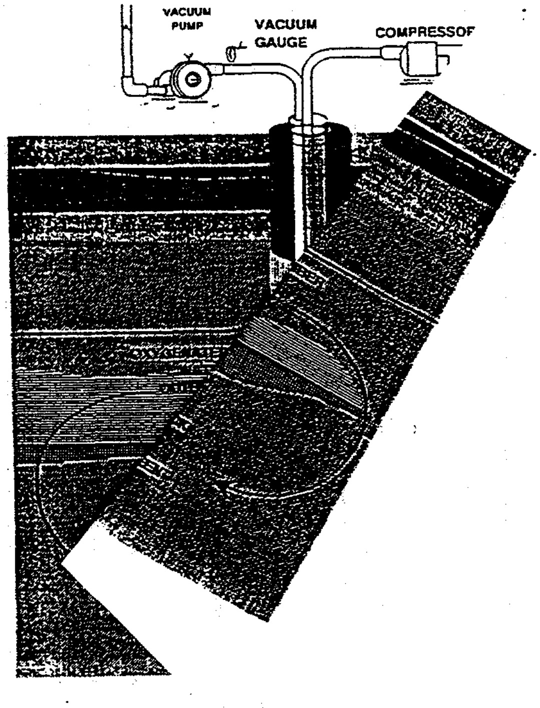


Figure 5. Example of Recirculatory Sparging System.

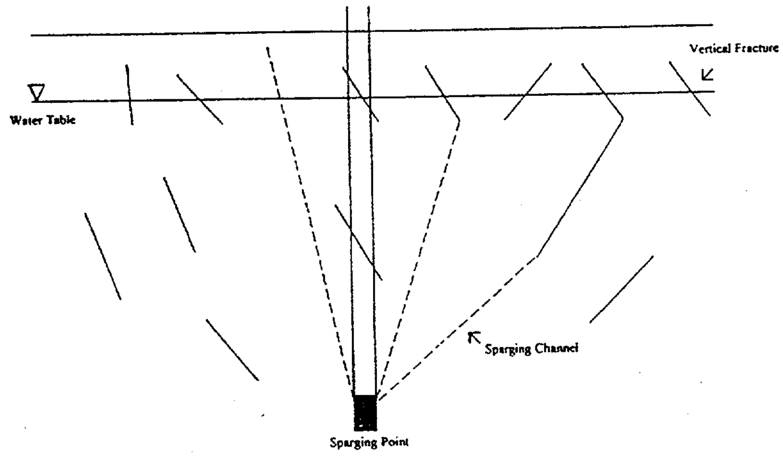


Figure 6. Vertical Fracture (secondary porosity) Pattern: Point Sparging.

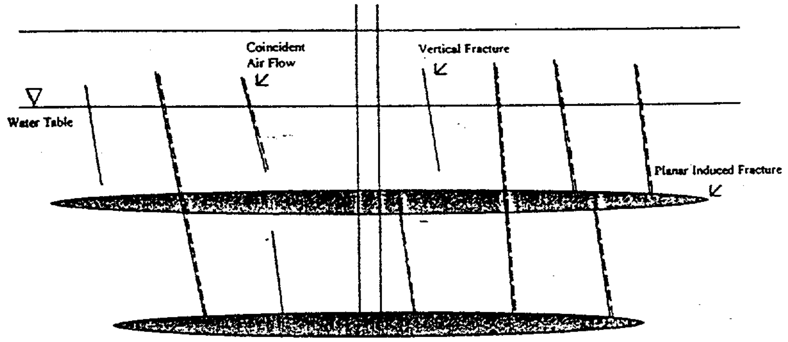


Figure 7. Vertical Fracture (secondary porosity) Pattern: Planar Sparging.

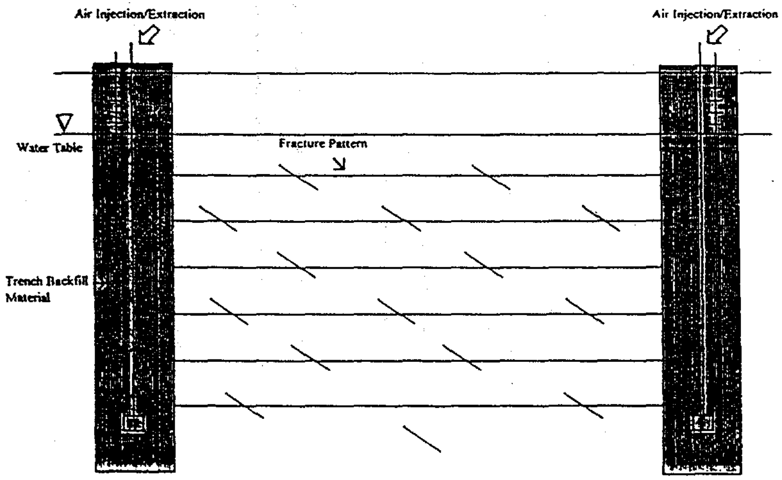


Figure 8. Preferential Horizontal Fracture (secondary porosity) Pattern: Trench Sparging.

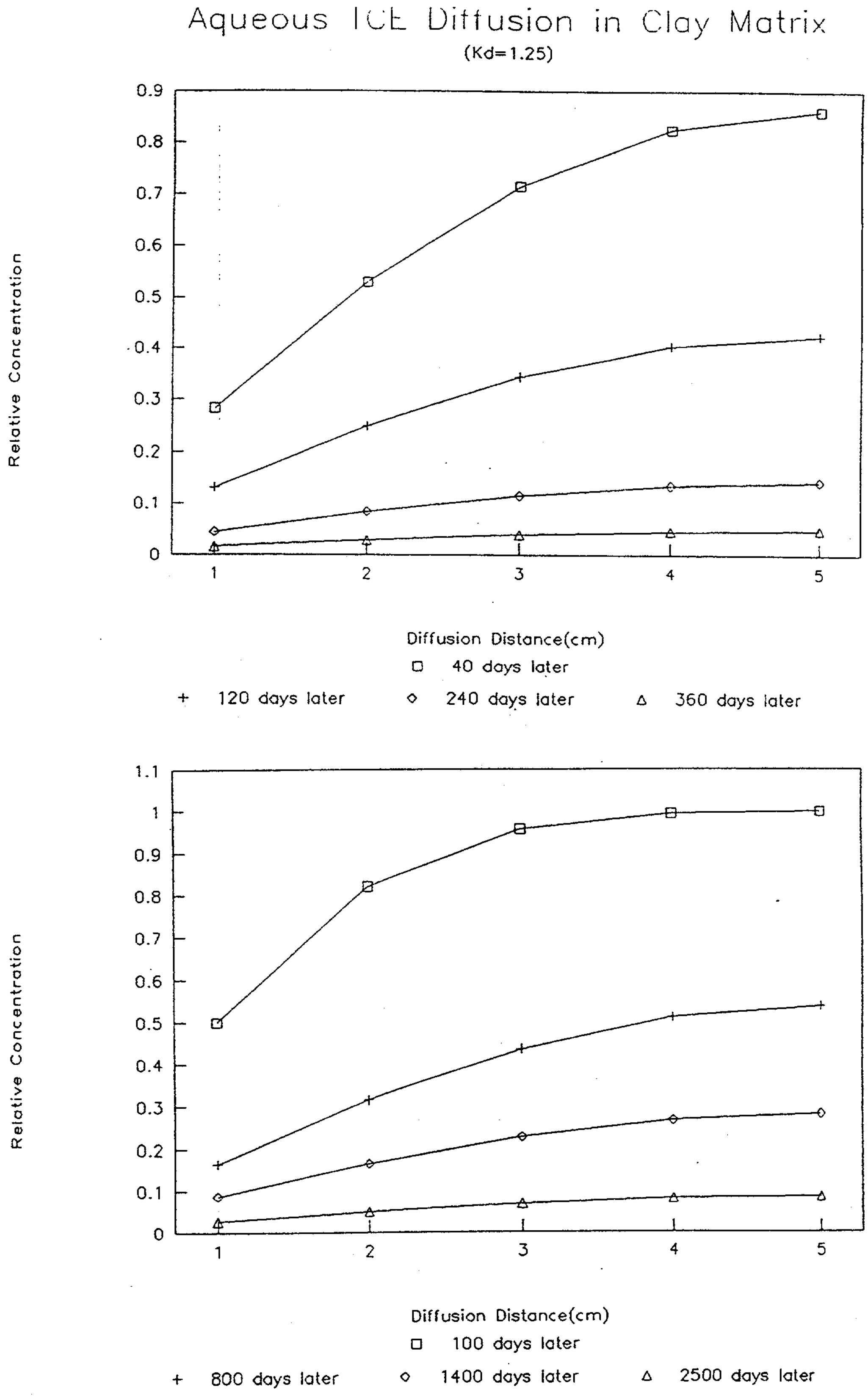


Figure 9. Aqueous TCE Diffusion in Clay Matrix.

HYDRAULIC FRACTURING TO ENHANCE THE REMEDIATION OF DNAPL IN LOW PERMEABILITY SOILS

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Meager rates of fluid flow are a major obstacle to in situ remediation of low permeability soils. This paper describes methods designed to avoid that obstacle by creating fractures and filling them with sand to increase well discharge and change paths of fluid flow in soil. Gently dipping fractures 10 m in maximum dimension and 1 to 2 cm thick can be created in some contaminated soils at depths of a few m or greater. Hydraulic fractures can also be used to create electrically conductive layers or to deliver granules of chemically or biologically active compounds that will degrade contaminants in place. Benefits of applying hydraulic fractures to DNAPL recovery include increasing rates of fluid recovery, enhancing upward gradients to improve hydrodynamic stabilization, forming flat-lying reactive curtains to intersect compounds moving downward, or improving the performance of electrokinetics intended to recover compounds dissolved in water.

2.0 DESCRIPTION OF THE TECHNOLOGY

Hydraulic fracturing has been used for more than 50 years to stimulate the yield of wells recovering oil from rock at great depth, and it has recently been shown that hydraulic fracturing will stimulate the yield of wells recovering liquids and vapors from soil at shallow depths (Murdoch and others, 1991; 1992). Thus, hydraulic fracturing should augment in situ remedial techniques that require fluid flow in the subsurface (e.g. vapor extraction, pump and treat, bioventing, steam stripping, or soil flushing).

The utility of hydraulic fractures is by no means limited to well stimulation. Relatively large volumes of solid compounds can be delivered to the subsurface as granular materials filling hydraulic fractures. The capability to deliver solid compounds, which previously required excavation techniques, presents a variety of possible new applications. Our colleagues have developed a solid compound (Davis-Hoover and others, 1991), which slowly releases oxygen, that we inject into hydraulic fractures along with slowly dissolving nutrients to stimulate in situ aerobic degradation of organic compounds in soils. We have recently initiated a project to investigate the feasibility of filling hydraulic fractures with electrically conductive material, particularly graphite, to enhance electroosmosis and perhaps the electrical heating techniques. In addition, it is feasible to fill hydraulic fractures with metal catalysts, such as iron particles, which Gillham and Burris (1992) have proposed as a method of degrading a wide range of halogenated organic compounds.

During the past several years we have created several hundred hydraulic fractures in silty clay at more than 20 locations in the midwestern United States, and most of the fractures have been explored to estimate their form. In several dozen cases the ground containing the fractures was excavated to provide detailed cross-sections of the fractures (Murdoch and others, 1991), whereas in other cases the exploration consisted of intersecting the fracture with a split-spoon or hand auger.

Method

Hydraulic fracturing begins by injecting fluid into a borehole at a constant rate until the pressure exceeds a critical value and a fracture is nucleated. Coarse-grained sand, or some other granular material, is injected as a slurry while the fracture grows away from the borehole. Guar gum gel, a viscous fluid, is commonly used to facilitate transport of the sand grains into the fracture. After pumping, the fracture is propped open by the sand and the guar gum gel is decomposed by an enzyme added during injection.

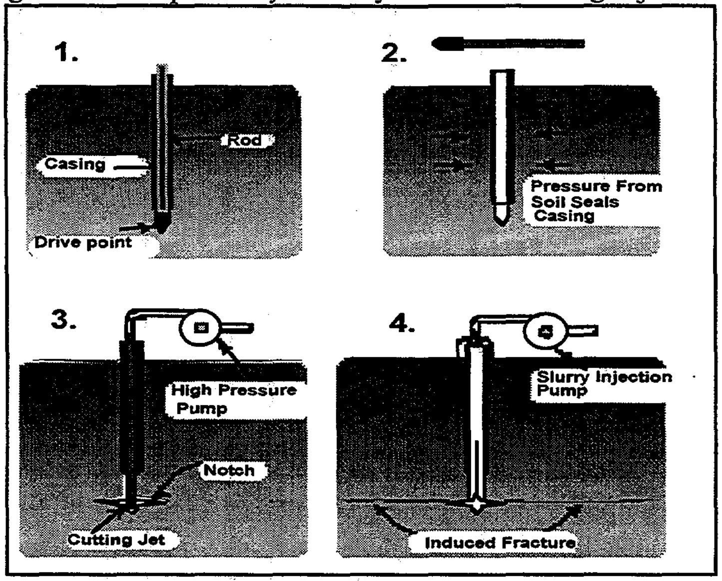

Figure 1. Fracture at the bottom of driven casing.

In fine-grained soil, we generally create hydraulic fractures beneath casing that is driven to depth with a hammer. Lateral pressure of the soil seals the casing during injection and the casing can be driven to greater depth to create another fracture (Fig. 1). Stacks of gently dipping hydraulic fractures have been created with vertical spacing of 0.15 to 0.3 m using the driven casing method. Vertical spacings of less than 0.15 m tend to result in fractures that merge at short distances from the borehole, according to exposures of hydraulic fractures in shallow excavations (Murdoch and others, 1991).

The injection pressure required to create hydraulic fractures is remarkably modest. For example, at the beginning of injection during a test at 2 m depth (Fig. 2), the pressure increased abruptly to 490 kPa (70 psi), but then decreased sharply when the fracture began to propagate. Injection pressure decreased from 200 to 100 kPa (30 to 15 psi) throughout propagation.

Fluid injected during fracturing must lift and deform the overburden, provide enough energy to break the formation at the fracture tip, and overcome viscous losses. Pressure due to the weight of the overburden at 6 m is 35 to 40 kPa, so the remaining 60 to 160 kPa is either lost during viscous flow through the fracture or required to deform the formation.

Fracture Form

Details vary considerably, but hydraulic fracturing generally produces a single parting (multiple fractures require repeated operations), that assumes one of two typical forms. One form consists of a steeply dipping fracture that has a greater vertical than lateral dimension. This type of fracture climbs rapidly and reaches the ground surface in the vicinity of the borehole after modest volumes have been injected. Significant propagation ceases after this has occurred. Thus, it has been our experience that, using techniques described above, vertical fractures in soil are of limited size and probably of limited value to remediation when used with vertical wells.

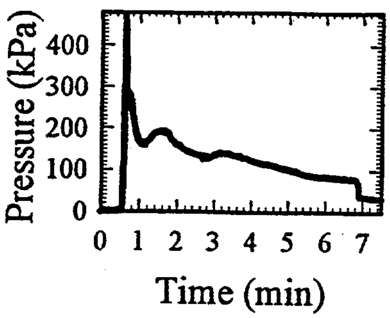

Figure 2. Injection pressure during hydraulic fracturing

The other type of fracture can get large enough to be of value, and it is the feature that is important for environmental applications. This fracture form is equant to slightly elongate in plan and dips gently toward the parent borehole. In some cases, the fracture is essentially flat-lying, whereas in others it is nearly flat-lying in the vicinity of the borehole and the dip increases to approximately 20° at some distance away (Fig. 3). In other cases, hydraulic fractures maintain a roughly uniform dip from the borehole to the termination.

Fractures commonly have a preferred direction of propagation so that the borehole is off the center of the fracture. The area of the fracture containing the thickest sand, however, nearly always occurs in the vicinity of the center, so that the thickest point rarely coincides with the borehole (Murdoch and others, 1991). The preferred direction of propagation is commonly related to distribution of vertical load at the ground surface, with the fractures propagating toward regions of diminished vertical load. Beneath sloping ground, therefore, it is possible to anticipate the preferred direction; it is downslope. We have used vehicles to load the ground surface and influence the propagation direction away from the vehicles.

Hydraulic fractures have been created between 1.2 and 12 m below the ground surface during our work. All of them have been in silty clay, and most have been in glacial drift that probably was overconsolidated. Maximum dimensions increase with depth, but are in the range of 7 to 10 m. Between 200 and 600 kg of sand are injected into a fracture. The average thickness of sand in a fracture ranges from 5 to 10 mm. The largest fracture that has been characterized was 17 m in maximum dimension, the most voluminous contained 2000 kg of sand, and the thickest was approximately 25 mm.

In general, fracture radius and aperture increase as the volume of injected slurry increases at a given depth and formation. Radius and aperture are functions of depth, however, with fractures of a given volume becoming broader and thinner as depth increases. The magnitude of those relations can be estimated by theoretical analysis using linear elastic fracture mechanics, which shows that

$$\delta_{max} \propto a^4 d^{-3}$$

or

$$\delta_{max} \propto V^{2/3} d^{-1}$$

where δ_{max} is the maximum aperture immediately after injection, *a* is the radius, *d* is the depth, and *V* is the total volume of fluid injected into the fracture. The fracture will close as the liquid portion of the injected fluid leaks off, so that the final aperture is some fraction of δ_{max}. It is our experience that the ratio δ_{max}:final sand thickness is roughly equivalent to the ratio total slurry volume:bulk volume of sand in the slurry. Accordingly, the final thickness of the propped fracture increases with the concentration of sand in the injected slurry.

Although the maximum dimension of a hydraulic fracture increases with injected volume, this dimension is not without bounds because prolonged injection can cause a fracture to climb and vent at the ground surface. Some applications are insensitive to whether the fracture vents, but others, such a vapor extraction, may benefit if the fracture is confined to the subsurface.

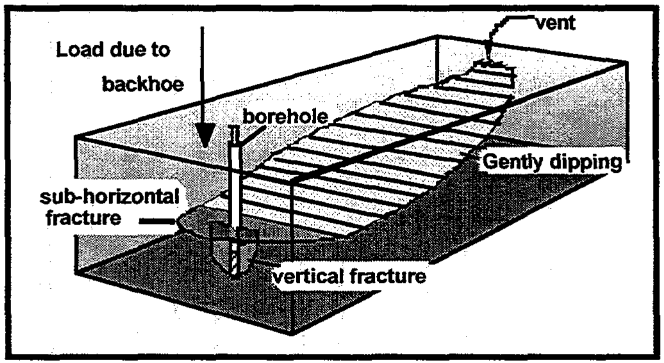

Figure 3. Idealized hydraulic fracture in shallow overconsolidated soil (based on Murdoch, 1994).

The volume of injected slurry then becomes critical; a small volume will reduce the chance of reaching the ground surface but limit the size and effectiveness of the fracture, whereas a larger volume will produce a more effective fracture but increase the chance of reaching the ground surface. We have developed a simple theoretical analysis based on principals described by Murdoch (1993) to analyze basic features, and we are currently pursuing numerical analyses of fracture propagation to develop methods of analyzing the details of hydraulic fractures in soil. Currently, however, empirical methods that make use of observations and field measurements serve to develop an initial design. That design is tested by creating a fracture in an uncontaminated area, and then adjusting the design based on monitoring data before creating a fracture in contaminated ground.

Monitoring

The fracturing procedure is monitored by recording both pressure and deformation of the ground surface as functions of time. Records of injection pressure show a rapid increase followed by a rapid decrease in pressure that marks the onset of fracturing (Fig. 2). The shape of the pressure record is used to diagnose various processes related to fracture propagation and problems related to pump performance.

The ground surface over a shallow hydraulic fracture will lift by an amount that is similar to the fracture aperture, so the pattern of uplift can be used to infer the location of the fracture at depth. According to our experience, the preferred direction of propagation can be readily determined from the pattern of uplift. Moreover, the extent of sand in the fracture is slightly less than the area of uplift, and the thickness of sand in a fracture is roughly half the observed uplift. These observations can be explained by accounting for the size of sand grains and volume fracture of sand in the injected slurry. Those generalizations are based on our experience with shallow, gently dipping hydraulic fractures in silty clay till. The generalizations must be applied to other situations with caution because the relationship between aperture and ground surface deformation becomes complicated with increasing depth and different fracture geometries (Holzhausen and others, 1985; Davis, 1983).

Deformation of the ground surface is determined by measuring the elevations of an array of stations overlying the fracture. Surveying stations with a leveling telescope is a straightforward method of measuring the net uplift resulting from a fracture. Tiltmeters are used when deformation is required as a function of time.

<u>Limitations</u>

The primary limitations to this technique are that the orientation of hydraulic fractures is affected by geologic conditions and that the ground surface will be displaced over the fractures.

Geologic conditions

The primary geologic factors affecting the orientation of a hydraulic fracture appear to be the state of stress and anisotropy resulting from stratigraphic bedding or fabric in the formation. Once a hydraulic fracture grows beyond the vicinity of the borehole it will curve to an orientation where propagation occurs with the least expenditure of energy. In most cases this orientation places the plane of the fracture normal to the direction of least compressive stress in the soil. Geotechnical engineers recognize that the ratio of lateral to vertical compressive stress is less than unity in some soils, such as fill and much alluvium. The stress ratio can be greater than unity in soils that have been consolidated under a great load, such as a glacier, or that contain swelling clays (Brooker and Ireland, 1965). Many soils where the stress ratio is greater than unity are also highly consolidated, with the degree of consolidation exceeding that which results from the existing overburden load; so-called overconsolidated soils. The degree of consolidation is easier to measure than the state of stress, so measurements of consolidation are commonly used to infer state of stress. The relationship between the degree of consolidation and the state of stress depends on a variety of site specific factors, however, so quantitative estimates of stress state from consolidation measurements are tenuous. Accordingly, overconsolidated soils at many sites where hydraulic fractures have been created indicate that the lateral stress probably exceeds the vertical stress, although consolidation data alone are insufficient to quantify the state of stress.

We expect that hydraulic fractures in massive, normally consolidated soils will be steeply dipping, whereas those in overconsolidated deposits will be gently dipping. Other processes affecting details of the state of stress in the vicinity of a shallow fracture may explain the tendency for fractures to climb toward the ground surface (Murdoch, 1994).

There are several mechanisms that will produce overconsolidation. Most of our work has focused on creating fractures in silty clay glacial drift, which was consolidated by the weight of an overlying glacier. When the glacier melts and the weight is removed, the vertical stress is the present overburden load, whereas the lateral stress retains a residual component of the glacial loading. Similarly, any soil that has experienced removal of overburden, by erosion or excavation, could be overconsolidated. In other cases, overconsolidation can be produced without a large vertical load. Soils containing swelling clays will shrink and crack when they are dry. Some of the cracks become filled with slough, preventing the soils from expanding laterally to their original dimension when they swell during hydration. Cycles of shrinking and swelling can therefore produce a lateral stress that is greater than the vertical stress (e.g. Mahar and O'Neill, 1983), provided the soil is hydrated at the time of testing. This process is particularly acute in vertisols, which are soils composed of more then 35 percent swelling clay, but it may occur in other soils as well. Recent field tests in the vicinity of Beaumont, Texas, have confirmed the feasibility of creating useful fractures in swelling clay. The distributions of major glaciated areas and major areas containing vertisols in the U.S. are given in Murdoch (1993).

The degree of consolidation is by no means the only factor affecting fracture orientation; stratigraphic layering may cause fractures in some normally consolidated soils to be flat-lying. Presumably this occurs because the fracture toughness (Murdoch, 1993) parallel to layering is less than it is normal to layering. We created nearly horizontal fractures in soft, interbedded sand, silt, and clay sediments in southeastern Texas and in soft, normally consolidated clay in Nebraska. Consolidation data for those sites are unavailable, although we presume that the sediments were normally consolidated based on their geologic setting. Horizontal fractures have also been created in normally consolidated glacial sediments containing fine laminations (varves), according to Brian Leach who conducted tests in Alberta, Canada. Clearly, useful fractures can be created in a wide range of geologic settings.

We should point out that measurements of in situ stress and fracture toughness of layered soils are unavailable for most sites where hydraulic fractures have been created for environmental applications. Additional research is required to obtain the data that will quantify the effects of those, and perhaps other, parameters on fracture form.

Ground displacement

Displacement of soil will accompany hydraulic fracturing and the effects of this displacement must be evaluated at each site; many structures can accommodate the displacement whereas others probably cannot. Creating a shallow fracture (2 to 3 m depth, for example) in soil typically forms a broad dome roughly 2 cm amplitude and 8 to 10 m across, and structures overlying the hydraulic fracture should be capable of accommodating these displacements. At the ground surface, vertical fractures in soil or pavement are commonly dilated during the doming that accompanies fracturing.

Potential Applications

Hydraulic fracturing is a method of improving the performance of remedial methods; it has no remedial effect on its own. To that end, most of the remedial methods that require fluid flow can benefit by hydraulic fracturing. In some cases, the fractures can improve the performance of a remedial method, whereas in others they allow a remedial method to be considered where the method would otherwise be infeasible. Remedial methods that involve fluid flow and could be improved by hydraulic fracturing include: vapor extraction, pump and treat, free-product recovery, soil flushing, steam stripping, bioremediation, bioventing, and air sparging.

Some innovative remedial techniques make use of the ability to deliver solid compounds to the subsurface using hydraulic fractures. Electrokinetics, for example, potentially can be enhanced by filling hydraulic fractures with granular graphite to create flat-lying electrodes (Murdoch and others, 1995). Moreover, reactive compounds can be injected into hydraulic fractures to create in situ treatment zones capable of intercepting downward moving contaminants. This application is the horizontal analog to treatment zones described by Starr and Cherry (1993) and could be used to treat downward moving liquids in the vadose zone or downward flowing DNAPLs in the saturated zone.

3.0 GENERAL CONSIDERATIONS

The following section addresses general considerations related to the application of hydraulic fracturing.

Applicable Media

The applicability of hydraulic fracturing spans a wide range of geologic formations and contaminant types. The technique can be used with in situ technologies that address contamination in either soil or ground water, and it has been used with technologies that address chlorinated solvents and hydrocarbons. Thus, the wide applicability is derived from a wide range of technologies that can benefit from hydraulic fracturing.

Access

It is technically feasible to create hydraulic fractures beneath buildings or pavement. In some cases, access beneath buildings may be facilitated by using directional drilling. Deformation of the ground surface is a major consideration when creating fractures beneath structures. Hydraulic fractures will deform overlying materials, lifting a dome in uniform soils that is 1 to 2 cm high and 8 to 10 m across. Many buildings, slabs, or other structures can accommodate some displacement, although the consequences of the displacement must be evaluated before proceeding with the project. Methods are available to monitor displacement of structures in real time, so that hydraulic fracturing can be conducted and discontinued if displacements exceed some predetermined value. One approach is to create small fractures so that displacement is limited if sensitive structures are nearby.

Depth

Hydraulic fractures can be created at depths far below the possible requirements of environmental applications. Shallow depths will limit shallow applications, particularly in weathered soils, because fractures will tend to climb and intersect the ground surface. We created a substantial fracture at a depth of 1 meter in fresh till, but depths of 1.5 to 2 m were required to contain fractures in weathered till (Murdoch and others, 1991).

Operation and Maintenance

The operation and maintenance required will be related to the technology that is used with the hydraulic fractures. Hydraulic fractures propped with coarse-grained sand maintain their permeability for longer than a year, so they appear to be essentially maintenance free. We expect that the pores of sand-filled fractures may eventually become clogged from entrained silt, biological growth, mineral precipitates or other factors, but this effect appears to be minor based on available data. Some well designs allow additional sand to be injected into a fracture should it become clogged during operation.

Secondary Waste

The primary secondary waste is drill cuttings produced during installation of wells following hydraulic fracturing. Driven casing techniques are available to eliminate this waste when it is a concern. In addition, fracturing techniques that are commonly used involve cutting a notch with a water jet to nucleate the fracture. Approximately 20 L of water and cuttings from the vicinity of the well bore are generated for each fracture.

Safety

The creation of hydraulic fractures makes use of mechanical and hydraulic equipment, and there are the usual safety issues related to the operation of such equipment.

Models

Theoretical models are available to predict both fracture propagation and performance. Investigators in the oil industry have developed a wide range of powerful models to simulate the details of fractures created in oil wells. Many of those models consider fractures that are deep and vertical, the primary conditions of most oil wells, and relatively little work has been done to analyze fractures that are shallow and flat-lying. One notable exception is Perkins and Kern (1961), who analyze a flat-lying circular fracture that lifts the overburden. A similar geometry was used to develop an analysis of fractures in soil based on methods described in Murdoch (1993). That analysis is able to predict essential details, such as pressure, uplift and growth rate as functions of time, from records of fractures created at contaminated sites. As such, it is a useful design tool, although it cannot replace feasibility testing to estimate fracture form. This is because the analysis assumes the fracture has a certain shape, circular and flat-lying, and this assumption is necessary to develop the rather simple results used for design. More sophisticated analyses have been developed to predict the path of fracture growth. Narendran and Cleary (1984), for example, present an analysis that shows how an initially flat-lying fracture will curve upward to produce a gently dipping feature that resembles the fractures commonly created in overconsolidated silts and clays.

Availability of appropriate models describing fracture propagation is limited. The analysis presented by Perkins and Kern (1961) is expressed in analytic form and can be readily solved with a calculator or computer. The analysis developed to design shallow hydraulic fractures in soil will be submitted for publication in the near future. It is an analytical solution that is easily solved. Codes developed for oil industry applications are widely available through the Society of Petroleum Engineers or private vendors. However, those codes should be applied to environmental applications only when they address the conditions encountered in the proposed setting.

4. 0 LOW PERMEABILITY CONSIDERATIONS

Soil water content

The creation of hydraulic fractures in soil is nearly independent of water content. Fractures have been created in both saturated and unsaturated conditions and essentially no difference could be detected. This is because hydraulic fractures are typically created by injecting a slurry formed from stiff gel, which will remain nearly completely contained within the fracture when it is relatively small and cuts through silt and clay. In this case, the interaction between injected fluid and pore fluid will be minor and the degree of saturation of the wall formation is irrelevant. The interaction with pore fluid will increase as fractures get larger, the formation becomes more permeable, or the viscosity (or shear strength) of the injected fluid decreases.

The effects of water content will strongly influence remedial methods that can be used in with hydraulic fractures. Those effects are discussed elsewhere in this volume. Hydraulic fractures can contribute to the control of the water table, principally by increasing the rate at which water can be recovered.

Modeling

The effect of hydraulic fractures on flow and transport in porous media can be simulated using most numerical models that include heterogeneities; We are unaware of models developed specifically to analyze for hydraulic fractures. The fractures can be treated as open slots with an effective aperture, or they can be treated as discrete layers with a permeability and thickness that corresponds to the distribution of sand injected during their formation. Determining the effective aperture or the effective permeability and thickness of the fracture is done using hydraulic and tracer tests developed for natural fractures (Novakowski, 1992) and the results of monitoring during fracture creation.

It is important to recognize that hydraulic fractures are generally discrete features with a specific geometry, and flow modeling should take this geometry into account. In contrast, ignoring fracture geometry and simulating the effects of hydraulic fractures by increasing the effective permeability of a homogeneous medium will overlook details of the geometry of flow in the vicinity of the fractures. This can obscure important effects and limit design potential (Murdoch and others, 1994).

Applications

Free product pooled in sand on top of clay

Recovery of free-phase DNAPL in sand on top of the clay probably will not be limited by low permeabilities. Accordingly, permeability enhancement by hydraulic fracturing may be unnecessary for recovery.

Separate phase in continuous fractures in clay

Hydraulic fractures should provide an excellent method of accessing continuous fractures in clay. This is particularly true where naturally occurring fractures are vertical, because a conventional vertical bore may miss any continuous fractures and therefore be isolated from the primary porosity that provides flow (Fig. 4). In overconsolidated formations, such as glacial drift or vertisols, hydraulic fractures will be gently dipping and cut across steeply dipping fractures, which occur naturally and provide the primary pathways for downward migration of DNAPL.

Pumping from a well that accesses a hydraulic fracture should increase the rate of recovery of DNAPL that can be transported by advection. Moreover, draining major fractures will induce chemical potential gradients that will promote diffusion out of the matrix. Upward flow from beneath the fracture will tend to arrest the downward movement of DNAPL, potentially stabilizing regions where flow rates are insufficient to effectively recover. Although responses at individual sites vary considerably, improvements in recovery rates by at least an order of magnitude are typical following hydraulic fracturing.

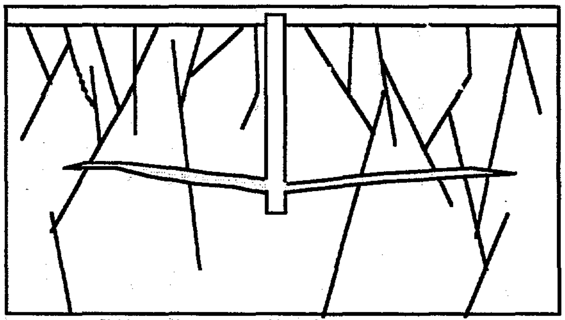

Figure 4. Schematic of a sand-filled hydraulic fracture cutting naturally occurring vertical fractures. Without the hydraulic fracture, the well would have missed all of the major vertical fractures.

Separate phase in discontinuous fractures

Even one to two orders of magnitude improvement in recovery may be insufficient to effectively remediate a site if only the continuous fractures are accessed. Hydraulic fractures can provide access to continuous fractures in the vicinity of discontinuous fractures, but they are unable to access the discontinuous fractures themselves. The same hydraulic fractures that were used to recover contaminants can also be used to deliver steam or hot air to heat the formation. This approach has been demonstrated in uncontaminated ground, where the fractures increased the rate of steam injection by more than an order of magnitude (Murdoch and others, 1994). A fracture placed below the steam injection zone can be used to recover DNAPL that is mobilized in the condensate front (Fig. 5).

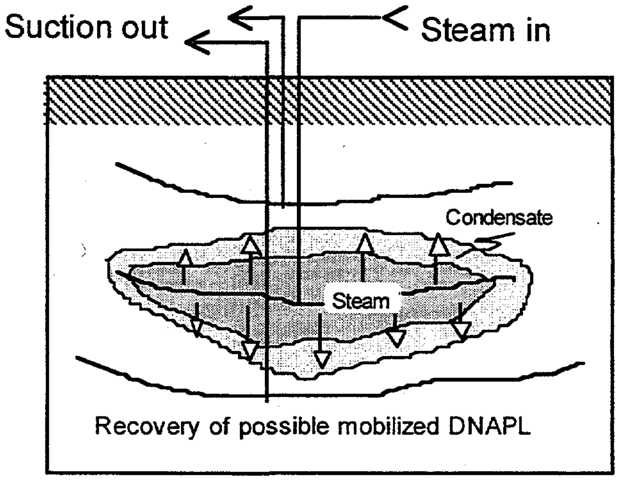

Figure 5. Schematic of steam stripping using gently dipping hydraulic fractures.

Dissolved phase diffused into matrix

Hydraulic fractures can improve the ability to recover dissolved phase contamination that has diffused into matrix by enhancing the ability to recover from continuous fractures. This will reduce the chemical potential in continuous fractures and shorten the diffusive path to zones where advective transport is feasible. Shortening the diffusive path will markedly increase the rate of diffusion out of matrix blocks, as described in detail in another chapter of this volume.

As with conditions discussed above, the improvements provided by hydraulic fractures under advective and diffusive conditions alone may be insufficient to effectively remediate some sites. An alternative is to make use of electrokinetics to induce migration of the dissolved phase. In this process, a DC current is applied to a porous media, inducing osmotic movement of water away from a positively charged anode and toward a negatively charged cathode (Casagrande, 1949). Ions and colloids migrate toward the electrode with a charge opposite from the one that they carry (Hamed and others, 1989; Shapiro and Probstein, 1993). Based on the results of laboratory tests and limited field applications (e.g. Langeman and others, 1989), electrokinetics has been shown to be a promising method of recovering ionic and water-soluble contaminants.

Hydraulic fractures filled with electrically conductive graphite can be used to improve the performance of electrokinetics, much as hydraulically conductive fractures improve fluid flow (Fig. 6). This process is currently being evaluated at the University of Cincinnati (Murdoch and others, 1995).

Hydraulic fractures can potentially be used to create treatment zones, formed from chemically or biologically active compounds, that immobilize or degrade contaminants in situ (as mentioned earlier). It may be feasible to create flat-lying treatment zones by injecting suitable compounds into flat-lying hydraulic fractures. Such treatment zones could be positioned to intercept downward moving DNAPL, potentially degrading the compounds under a natural vertical gradient in much the same manner that vertical reactive walls are designed to remediate horizontally moving ground water (Starr and Cherry, 1993). This application is contingent on development of compounds with appropriate properties.

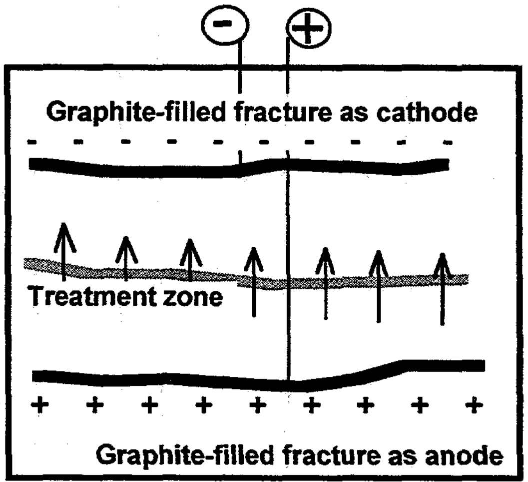

Figure 6. Possible configuration of hydraulic fractures as electrodes and treatment zone.

A particularly noteworthy potential method of remediating dissolved phases is to combine treatment zones and electrokinetics (Fig. 6). In this approach, the polarity of the electrodes is periodically reversed to repeatedly drive contaminants through treatment zones (Ho and others, 1993, Brodsky and Ho 1995). This process holds the potential of degrading contaminants in place. A consortium among private industry, the USEPA, and the University of Cincinnati is actively investigating this approach (Murdoch and others, 1995).

5.0 COST AND RELIABILITY

The typical costs of creating hydraulic fractures involve labor, materials, equipment usage, and mobilization expenses. The costs generally range from $850 to $1300 per fracture using current methods. The higher end of the range of cost per fracture are for jobs that involve large mobilization expenses and only a few fractures. Alternatively, large per fracture costs can be realized if the fractures are larger or deeper than typical environmental applications. Specialized requirements at individual sites, well completion costs, monitoring requirements, mobilization, or other factors could also cause the cost estimate to increase. Eliminating the costs of drilling support or reducing the amount of monitoring will cause this estimate to decrease. Several innovative methods of fracturing and well completion that are currently being developed promise to increase efficiency and reduce costs.

The number and placement of fractures will vary according to application and specific situation. Assuming the contaminants have relatively high vapor pressures, vacuum extraction would be a favored remedial technology. In such a case, fractures would be created so that sufficient suction could be effected across the site. Using conventional blowers, we have seen fractures effect 2.5 cm of water suction head approximately 8 m from recovery wells at our test site in silty clay. If this vacuum is sufficient, then a

0.25 hectare square could be adequately treated by a 3 by 3 grid of wells, with 3 fractures at each well. Each fracture should be screened individually so that it can be used either for recovery or air inlet.

The cost to create 27 fractures and complete 9 wells should be on the order of $25,000 to $35,000. Since hydraulic fracturing is a method to improve performance of remedial methods, the cost of the specific technique employed at each application needs to be considered, e. g. the cost of vacuum systems, vapor treatment equipment, and residual disposal will be in addition to the cost for fracturing.

The time and costs to reach clean up goals cannot be anticipated because the field data are typically for relatively short-term, pilot-scale tests. Those data show that hydraulic fractures increase the effectiveness of vapor extraction, for example, but cannot support extrapolation required to project short-term results to a full-scale remedial effort that results in closure. Moreover, the use of steam, electrokinetics, or other processes promise to further improve remedial efficiency and reduce costs, although performance data on those processes used with hydraulic fractures are unavailable.

There will definitely be an economy of scale. The cost per fracture will decrease as the size of the job increases, largely because mobilization costs are distributed over many fractures and monitoring efforts can be reduced once the effects of fracturing at a particular site have been characterized.

6.0 COMMERCIAL AVAILABILITY

Environmental applications of hydraulic fracturing are offered commercially by FRX Inc., who currently has the capability to design fracturing jobs, perform the service, monitor the fracturing process, and evaluate effects during remediation. More information can be obtained by contacting Bill Slack at the address given below.

FRx
Specialists in Fracturing
for Environmental Remediation

William Slack, Ph.D.
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45222
513-556-2526

State of Development

Hydraulic fracturing is a proven technique in soil and rock. It has been widely used in the petroleum and water well industries, and some deeper environmental applications may make use of experience in those industries. Methods and applications tailored to remediation of soils have been developed over the past 7 years by personnel at the University of Cincinnati and FRX, Inc.

Future enhancements

Current investigations include methods of improving the fracturing process and additional applications. Methods of increasing fracture thickness and size, controlling orientation, and facilitating the well completion process are currently under development. Methods of creating fractures from horizontal wells have been demonstrated and are currently being refined. Special methods of creating fractures with multiple properties, such as both large hydraulic and electrical conductivities, are currently under development.

Applications of hydraulic fractures that are currently under investigation include the creation of treatment zones, or reactive barriers, and the installation of planar electrodes. Methods of using fractures to facilitate heating by injection of steam or hot air are also being developed, as are applications of fractures to improve the performance of monitoring wells in tight formations.

Complementary technologies

Hydraulic fracturing itself is a complementary technology that is intended to augment the performance of any in situ remedial technique that requires fluid flow. To this end, there are several techniques that can be used with hydraulic fracturing, and then in turn combined with remedial methods. Impulse fracturing, which involves creating fractures with high velocity pulses of water, is capable of creating features that resemble hydraulic fractures. Impulse fracturing is less sensitive to in situ conditions, however, so it would be most appropriate in fill or normally consolidated formations (Murdoch, 1993).

Horizontal wells improve the ability to control subsurface fluids, and so their effects are related to hydraulic fractures (e.g. review in Murdoch and others, 1994). A horizontal well created using directional drilling will intersect a large number of vertical fractures and presumably increase recovery compared to a vertical well (Murdoch, 1992). Directional boring can have advantages over trenching because it avoids disposal of excavated soil, eliminates the need to seal the ground surface, is unlimited by depth, and does away with the access requirements during excavation. Compact, relatively inexpensive, directional boring machines that are remarkably accurate are currently being demonstrated during remediation of contaminated sites. Hydraulic fractures have been created from directional bores, so the techniques described here can be used with horizontal wells.

7.0 CASE HISTORIES

The following contains summaries of two case histories where hydraulic fractures were used to recover NAPL. The case histories describe pilot tests; performance data for full scale remediations are unavailable. Details of other case histories are described in Murdoch and others, 1994; Murdoch, 1993, Wolf and Murdoch, 1993; EPA EPA/540/SR-93/505, and references therein.

DNAPL recovery from bedrock

Naturally propped fractures were created a depths of 100 to 200 ft in limestone and shale to enhance the recovery of free-phase TCE and other DNAPLs from a site near Bristol, TN. The fractures were created in July, 1991, by injecting water into intervals of the well isolated by straddle packers. Pumping tests and vapor extraction tests were conducted to evaluate the effects of the fractures. The description of this case history is based on Lundy and others (1994).

Setting

The vicinity of the site is underlain by sandstone, shale and limestone, which form a broad fold and dip approximately 45° beneath the site itself. The site is in a local recharge area of a bedrock aquifer characterized by downward vertical hydraulic gradients of approximately 0.5 (Lundy and others, 1994). The hydraulic conductivity of the water-bearing formation was approximately 10^{-6} cm/sec, based on constant rate tests.

Contaminants

The site contains a free-phase plume of TCE, other solvents, and cutting oil that extends to a depth of 100 m. A dissolved-phase plume of primarily TCE occurs to greater depths, at least 130 m, and has migrated at least 300 m from the suspected source. The specific gravity of the free-phase liquid is 1.3 (Lundy and others, 1994).

Design

Recovery using a pump and treat system yielded approximately 3.7 L/min of water per well and fewer than 1.4 kg/day of DNAPL. Three new wells were drilled with open hole completion to 60 m. Each well was fractured by setting open hole packers spaced 15 m apart and injecting 4500 to 9000 L of clean water; no proppants were injected. Injection pressures ranged between 0.5 and 5 mPa and the injection rate was approximately 280 L/min. This approach is typical of methods used to increase the discharges of water wells (Smith, 1989). Injection was terminated when water flowed around the upper packer and began to spill to the surface (Lundy, 1994).

Results

The specific discharge of the three wells increased by factors ranging from 2.8 to 6.2, which is typical of the effects of naturally propped fractures created by hydraulic fracturing of water wells. Pumping tests were conducted to determine the effective hydraulic conductivity after fracturing. In general, the results indicate that the effective hydraulic conductivity increased by factors of 20 or more, but the actual values depend on the method of solution used to analyze the test data.

Vapor extraction appeared to be a feasible remedial technique after fractures were induced. Vapor discharges were on the order of 285 to 700 L/min and suction could be detected 10 m from the recovery well after fracturing. In contrast, both discharge and suction in the formation were negligible prior to fracturing.

Costs

A cost of $1500/well was reported to create the fractures used during this project (Lundy, personal communication, 1994).

LNAPL recovery from swelling clay, southeastern Texas.

Sand-filled hydraulic fractures were created in swelling clay to enhance the recovery of free-phase LNAPL at a site in Beaumont, Texas. Fractures were created in July 1993, and a pilot test was conducted in late February 1994.

Geology

Silty clay of the Beaumont formation underlies the site to a depth of 6 to 8 m, and fine-grained sand occurs below it. The Beaumont formation consists of kaolinite, illite, calcium smectite and fine-grained quartz (Mahar and O'Neill, 1983). Dessication cracks are common due to a large decrease in volume of the clays accompanying drying near the ground surface. Lateral stress is two to three times greater than vertical stress in the upper few meters (Mahar and O'Neill, 1983), in the interval where hydraulic fractures where created.

Contaminants

The area of the test contained gasoline and cyclohexane, which infiltrated from surface spillage. The contaminant occurred as free-phase NAPL from approximately 1.5 to 3 m depth.

Design

The pilot test was designed to compare the performance of two designs of fractured wells to a control well. One of the fractured wells consisted of two casings that access fractures at different depths, one in the LNAPL and the other in the water bearing zone below. The other well only contained one fracture near the bottom of the NAPL zone (Fig. 7; Murdoch and others, 1994). The approach of the two-fracture design is to recover NAPL from one fracture and water from another.

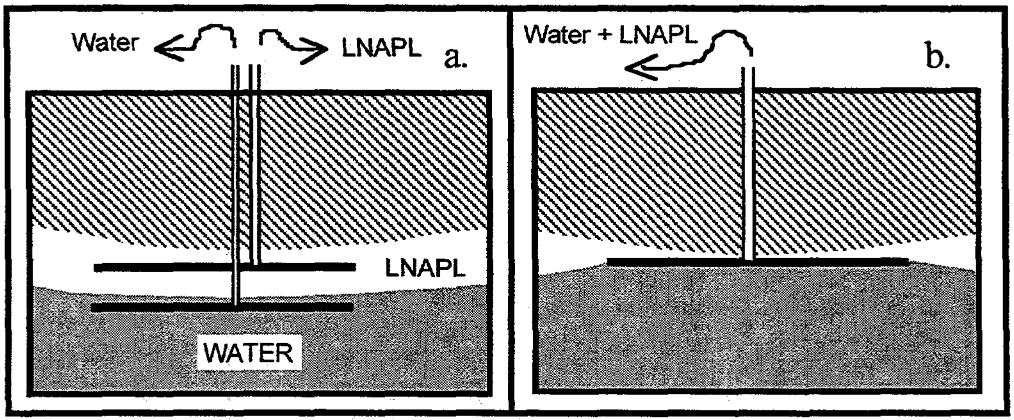

Figure 7. Methods of completing a well containing hydraulic fractures to recover LNAPL.

Sand-filled fractures were created at six locations at the site, but only two of them were used during the pilot test. A constant head was maintained approximately 10 cm above each fracture, so that the drawdown was 1.5 to 2 m. Fluid was pumped from the wells to storage drums and it was periodically diverted to a graduated cylinder to determine total discharge rate.

Results

Both wells containing fractures produced LNAPL at rates roughly an order of magnitude or greater than the conventional well. The C locations were particularly noteworthy, producing both the greatest NAPL rate and the greatest NAPL:water ratio. C-10 produced a high concentration of LNAPL at a rate that was 19 times greater than the control, whereas C-12 produced liquid that was almost completely water. The combined rate of liquid recovery from the C location was 50 times greater than from the control (Table 1).

Table 1. Average discharges and ratios of discharge.

	NAPL L/hr	Water L/hr	Total L/hr	NAPL/Water	NAPL/PW-1	Total/PW-1
C-10	4.33	0.34	4.7	13	19	18
C-12	0.07	8.24	8.3	0.008	0.3	32
C (combined)	4.40	8.58	13.0	0.5	19	50
I-12	1.85	5.61	7.5	0.3	8	29
PW-1	0.23	0.03	0.26	7		

The distribution of head is consistent with the relatively large NAPL recovery by wells intersecting sand-filled fractures. Zones of significant drawdown were documented within 8 to 10 m using multi-level piezometers. Drawdown in the vicinity of the control was unavailable, but similar tests in the area have shown that drawdowns are negligible within 1 to 2 m from conventional wells.

Cost

The fractures cost approximately $800 to $1000 each to create and complete as wells. This cost includes mobilization, materials, labor and equipment. The pilot test itself cost approximately $40,000.

8.0 SUMMARY

Hydraulic fracturing is a method of increasing the discharge and affecting the pattern of flow in the vicinity of wells. The method is particularly suited to low permeability materials, such as bedrock and fine-grained soils. In fine-grained soils, sand-filled hydraulic fractures typically increase the discharge of wells by factors between 10 and 50, and they increase the radius where pressure is influenced by a factor of 10. In addition to affecting the flow pattern by creating a permeable layer, hydraulic fractures can also be used to affect the electrical, chemical, or biological properties in the subsurface. Fractures filled with graphite are being evaluated as a means of improving the performance of electrokinetics, and fractures filled with chemically (such as zero-valence metals) or biologically (such as slowly releasing peroxides) reactive compounds are being evaluated as in situ reactive layers. Most of the applications can be used in some form to address either free-phase or dissolved DNAPL contamination.

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HOT AIR INJECTION FOR REMOVAL OF DENSE, NON-AQUEOUS-PHASE LIQUID CONTAMINANTS FROM LOW-PERMEABILITY SOILS

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

The performance of soil vapor extraction systems for the recovery of volatile and semi-volatile organic compounds is potentially enhanced by the injection of heated air to increase soil temperatures. The soil temperature increase is expected to improve soil vapor extraction (SVE) performance by increasing target compound vapor pressures and by increasing soil permeability through drying. The vapor pressure increase due to temperature rise relieves the vapor pressure limit on the feasibility of soil vapor extraction. However, the system still requires an air flow through the soil system to deliver heat and to recover mobilized contaminants. Although the soil permeability can be increased through drying, very low permeability soils and low permeability soils adjacent to high permeability air flow pathways will be treated slowly, if at all. All thermal enhancement methods face this limitation.

Heated air injection offers advantages relative to other thermal techniques, including low capital and operation costs. Heated air injection is at a disadvantage relative to other thermal techniques due to the low heat capacity of air. To be effective, heated air injection requires that higher air flows be established than for steam injection or radio frequency heating.

Heated air injection is not economically feasible for the stratified soil system developed as a standard test for this document. This is due to the inability to restrict heated air flow to the clay stratum when a low-resistance air flow pathway is available in the adjoining sand. However, the technology should be especially attractive, both technically and economically, for low-volatile contaminant recovery from relatively homogeneous soil formations.

2.0 DESCRIPTION OF THE TECHNOLOGY

SVE has become a common method for recovery of volatile organic compounds from porous vadose zone soils. Conventional SVE is most often limited to recovery of compounds that exhibit vapor pressures in excess of 0.5 mm Hg and from soils that have fluid permeabilities in excess of $1 \bullet 10^{-10}\,cm^2$. It is possible that a heat source can be applied to the target soils to improve the efficiency of SVE or to make SVE feasible at sites where it would otherwise be ruled out. Heated air injection is one of the potential means for thermal enhancement of the SVE process.

There are three basic goals for the heated air SVE technology:

1. Expand the universe of treatable compounds - Conventional SVE is limited to compounds that have more than 0.5 mm Hg vapor pressure at ambient soil temperature (Anon., 1991; Bennedsen, et al, 1985) and that exhibit a dimensionless Henry's Law constant greater than 0.01 (Hutzler, et al, 1988). Heated air injection can induce a temperature rise in the soil system sufficient to raise the vapor pressure of semi-volatile soil contaminants to more than 0.5 mm Hg. The induced temperature rise can also decrease the aqueous-phase solubility of some soil contaminants, which combined with vapor pressure increases may increase the Henry's Law constant to more than 0.01.

2. Increase contaminant yield rate - SVE yields are determined in part by the rate of contaminant release from various soil system components. System temperature increases that are induced by heated air injection will increase contaminant evaporation

and gaseous and aqueous-phase diffusion rates. Desorbtion and aqueous-phase degassing may also increase. Any of these temperature-dependent effects can increase system yield rate.

3. Decrease achievable endpoint concentrations - The concentration of contaminants remaining in a soil system following a unit effort of SVE reflects the equilibrium between gaseous, aqueous and adsorbed-phase materials. As system temperatures increase, the equilibration increasingly favors the gaseous phase for many compounds. This, in turn, lowers the endpoint soil concentrations that can be achieved by a unit effort of SVE.

The process flow for heated air injection SVE is initiated by an injection air pump drawing air from above the ground surface. The air stream is pressurized and heated indirectly, or as an alternative, serves as the combustion air source for a flame. The heated air is directed through injection wells into contaminated vadose zone soils. Vacuum wells create air pressure sinks that draw heated air from the injection points. The contaminated air stream passes through a vacuum pump, is treated and then discharged back to the atmosphere.

Heated air soil vapor extraction (HASVE) improves the performance of SVE in four ways:

A. Soil temperature increases induced by HASVE increase the vapor pressure of liquid-phase organic compounds. For compounds that exhibit a suitable vapor pressure at ambient soil temperature, the effect will be to increase contaminant yield due to evaporation. Semi-volatile compounds that have vapor pressures less than 0.5 mm Hg at ambient soil temperatures may be treatable at higher temperatures, as their vapor pressures increase. Phenol, for example, is a solid at 10°C, with a sublimation vapor pressure of less than 0.2 mm Hg (Montgomery and Welkom, 1990). If the system temperature is raised to 74°C, the phenol vapor pressure will increase to 10 mm Hg, well within the treatable vapor pressure range. For a volatile such as trichloroethene, the vapor pressure increases from 35 to more than 400 mm Hg under a comparable temperature rise.

B. Soil temperature modifies the aqueous-phase solubility of target contaminants. For compounds that increase in solubility with temperature, the vapor pressure increase may offset the solubility increase. If not, the system may have to be operated to soil dryness to eliminate the dissolved contaminant pool.

C. The reduction of soil moisture through dry air injection increases soil permeability. The maximum effective permeability for air is achieved when soil water content is eliminated. Benson, et al. (1993) present a modified Brooks-Corey method to quantify the permeability-saturation relationship for the two-fluid system in soils.

D. The soil moisture reduction of heated air injection also decreases the dissolved-phase contaminant pool. Compounds with high aqueous-phase solubility (eg. phenol) may not be recoverable to closure target concentrations in the presence of soil moisture.

The HASVE strategy can decrease contaminant removal efficiency in at least two ways:

E. Increasing the temperature of the SVE process air flow decreases pneumatic conductivity for any soil permeability. The behavior of pneumatic conductivity as a function of air temperature for any permeability can be determined from the following equation, given by by Freeze and Cherry (1979):

$$K = \frac{k \cdot \rho \cdot g}{\mu} \qquad \textbf{Eqn. 1}$$

where:
K = pneumatic conductivity (cm/sec)
k = soil permeability (cm^2)
ρ = air density (g/cm^3)
g = acceleration due to gravity (980 cm/sec^2)
μ = air viscosity (g/cm sec)

As air temperature rises, the viscosity increases does not offset density decreases. As shown in Table 1, pneumatic conductivity decreases nine-fold as the air temperature increases from 0 to 540°C. The decrease in pneumatic conductivity is offset by much greater increases in soil permeability due to the drying action of the hot air injection.

F. Elimination of soil moisture has also been suggested to increase the binding of certain contaminants to soil particles. Oja and Kreamer (1992) indicated that TCE binding to soils increases when soil moisture levels fall below 5% (w/w). Data given by Rogers, et al. (1990) indicate that soil moisture and organic carbon content decreases will increase TCE sorption in low temperature thermal desorption processes. This author has observed a temperature effect on residual phenol concentrations for soils that have been dried to less than 0.2 % moisture content in bench scale heated column experiments. The residual phenol concentrations decreased stepwise with temperature increases, suggesting a possible binding effect.

The technology is relatively new, and published results of field trials are quite limited. DePaoli and Hutzler (1992) studied the enhancement of JP-4 recovery by SVE with the addition of heat captured from a catalytic incinerator unit. Sittler, et al. (1992) reported on a diesel fuel recovery which also utilized heat captured from a catalytic incinerator. In both of these studies, the soil temperature increases were limited, with soil ΔT values on the order of 20-40°C. No tests are reported that operate at heat input levels required for soil drying or for removal of very low vapor pressure compounds.

Table 1. Values for viscosity (μ), density (ρ), and pneumatic conductivity (K) for dry air, as a function of temperature from 0 to 535°C. A soil permeability value of $1.0 \bullet 10^{-10}$ cm^2 was used for the calculations. Values for μ and ρ were taken from Weast (1969).

TEMP (°C)	μ (g/cm•sec)	ρ (g/cm^3)	K (cm/sec)
0	$1.71 \bullet 10^{-4}$	$1.29 \bullet 10^{-3}$	$7.4 \bullet 10^{-7}$
18	$1.83 \bullet 10^{-4}$	$1.21 \bullet 10^{-3}$	$6.5 \bullet 10^{-7}$
40	$1.90 \bullet 10^{-4}$	$1.13 \bullet 10^{-3}$	$5.8 \bullet 10^{-7}$
54	$1.96 \bullet 10^{-4}$	$1.08 \bullet 10^{-3}$	$5.4 \bullet 10^{-7}$
74	$2.10 \bullet 10^{-4}$	$1.02 \bullet 10^{-3}$	$4.7 \bullet 10^{-7}$
229	$2.64 \bullet 10^{-4}$	$7.03 \bullet 10^{-4}$	$2.6 \bullet 10^{-7}$
334	$3.12 \bullet 10^{-4}$	$5.81 \bullet 10^{-4}$	$1.8 \bullet 10^{-7}$
357	$3.18 \bullet 10^{-4}$	$5.60 \bullet 10^{-4}$	$1.7 \bullet 10^{-7}$
409	$3.41 \bullet 10^{-4}$	$5.17 \bullet 10^{-4}$	$1.5 \bullet 10^{-7}$
537	$4.35 \bullet 10^{-4}$	$3.69 \bullet 10^{-4}$	$8.3 \bullet 10^{-8}$

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

A. Is the technology primarily geared to soil or groundwater contamination?

The technology is primarily geared toward soil contamination. There are two main reasons why heated air injection would provide limited heating for groundwater:

- The specific heat of air is low, especially relative to water. Heated air sparge injection volumes would be quite high per unit aquifer volume.
- Current sparge literature indicates that air injected below the aquifer surface forms channels enroute to the surface. Heat transfer to the aquifer would be limited by the thermal conductivity of the groundwater.

B. To what extent is the technology suited to remediating petroleum as well as chlorinated hydrocarbons?

Hot air injection is equally well-suited to petroleum and chlorinated hydrocarbon remediation. The yield rate enhancement in petroleum may be greater due to the generally lower vapor pressures of petroleum compounds.

C. How well is the technology able to access under buildings or pavement?

The technology must be severely restricted for application beneath buildings and pavement. The desiccation associated with hot air injection may shrink certain soils and cause subsidence and structural damage to buildings or pavement. Further, the high injection temperatures required to efficiently operate hot air injection systems may directly damage buildings or pavement.

D. What is the maximum depth of remediation?

Depth does not limit the technology *per se*. The technology can be applied effectively throughout the vadose zone, independent of vadose zone thickness. If depth to groundwater is great, there may be design advantages to stratified installation, which allows the system operator to focus heat and air inputs over selected depth intervals.

E. What are the utility, operation and maintenance requirements?

Fuel for the hot air source is the largest operational cost item. Using natural gas, in a homogeneous system that requires soil drying, the fuel cost is likely to fall between $10 and $20 per cubic yard. If there is significant soil stratification, substantial heat distribution inefficiencies arise, and heat input costs rise by orders of magnitude. The electrical usage for HASVE is the same as conventional SVE; for a 10,000-ton treatment volume, the total system commitment should be approximately 50 HP (37.5 kW).

F. Are secondary waste streams produced?

All SVE systems produce a primary waste stream of contaminant-laden air. The indirect-fired hot air systems produce a secondary waste stream of combustion gases from the heat source that must be discharged to the atmosphere. In direct-fired systems, the combustion gas stream is directed into the contaminated soils and reaches the atmospheric discharge as part of the primary waste stream.

G. Are there potential environmental or safety risks associated with use of the technology?

The most significant safety risk associated with the heated injection technology is physical contact with hot surfaces. The piping network includes metal pipes that may achieve surface temperatures in excess of 500 °C. These surfaces must be insulated and marked to avoid contact. As with any heat source, these systems are unsuitable for use in areas of explosion hazard. There is a remote possibility of rapid steam venting, particularly as high temperature air is first injected into the soils.

The combustion gases may cause soil or groundwater contamination in direct-fired systems. Depending upon the choice of fuels and combustion technologies, compounds may be introduced into the soils which cannot be recovered by the HASVE system.

The injection of pressurized high-temperature air may cause groundwater contamination due to mobilization of contaminants that are relatively immobile at ambient soil temperature.

H. Are models available to predict performance in porous media and to what extent are they developed?

Although commercial vendors claim to possess proprietary models that can predict HASVE performance, the author is unaware of any published examples of field verification in heated systems. Thermal enhancement is anticipated by Lingineni and Dhir (1990, 1992) in a non-isothermal evaporation-driven model. Model verification was through column experiments using glass beads as the porous medium and ethyl alcohol as the volatile contaminant. The authors concluded that evaporative cooling was significant and would limit the utility of thermal enhancement for high-volatile compounds. This conclusion was contradicted by Gannon, et al (1989), who claimed that evaporative cooling will be insignificant under typical field SVE conditions. Lingineni and Dhir (1992) did conclude that SVE rates can be enhanced for low-volatility compounds, in which the thermal front moves through the soil more quickly than the evaporation front.

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

A. What is the effect of soil water content on contaminant removal?

There are two primary effects of soil water content on contaminant removal:

i. The soil water content decreases the effective soil permeability in a non-linear relationship, described by Benson, et al. (1993). The greatest air permeability occurs when no water is present.

ii. The soil pore water serves as a reservoir for aqueous-phase contamination, which reduces the rate of contaminant removal and may prevent the target soils from reaching intended closure standards. The removal of the pore water due to the drying action of the heated air injection eliminates this contaminant source.

B. Is hydraulic control of the water table critical to success?

HASVE systems require that water sources to the vadose zone be eliminated. This requires capping to prevent precipitation influx as well as water table stabilization.

C. Can the porous media models (if available) be reliably adapted to predict performance in low-permeability media, as in the following scenario:

Consider a scenario where the soil is stratified with layers ranging from a medium sand (hydraulic conductivity of 10^{-3} cm/s) to a clay (hydraulic conductivity ranging from 10^{-6} to 10^{-8} cm/s). The clay layer contains natural desiccation fractures that are spaced a few cm apart and have aperture of 10 to 40 microns. The effective soil porosity of the clay is <1%. Assume an underground storage tank of TCE and PCE leaked slowly over many years, and the hydrocarbon entered a sand layer overlying this clay aquitard, into which it has diffused. The clay layer is 3 m thick, and it in turn overlies a sand aquifer. Assume the water table is at the top of the clay layer, and the natural fractures in the clay can be dewatered by pumping the aquifer (if needed to enhance contaminant removal). Describe the ability of the technology to remove:

1. Free product pooled on top of the clay - The air flow characteristics of the medium sand are suitable for recovery of the free product, with or without temperature

enhancement. If the system is heated, the saturated vapor concentration overlying the free product layer increases according to Raoult's Law, and the removal rate is enhanced. Johnson, et al. (1990) provide the basis for mass removal calculations using saturated vapor concentrations.

2. Separate phase product trapped in the continuous clay fractures - The ability to recover separate phase product from continuous clay fractures requires elimination of the free product pool and then depends on the fracture apertures and the specific contaminant chemistry. HASVE would be expected to increase fracture apertures due to soil desiccation, and the product is likely to be removed effectively. A more complete analysis of the retention of product in fractures has been developed by McWhorter, in a companion article.

3. Separate phase product trapped in discontinuous or "dead end" fractures - The discontinuous fractures will not be subjected to advective air flow, and product recovery will be limited. The recovery rate will be limited by surface tension effects and gaseous diffusion rates, but yield rates should be higher in the heated system.

4. Dissolved phase product diffused into the matrix blocks - Although the fractures can be dewatered in this scenario, the clay matrix blocks would remain fully saturated. Recovery will be enhanced only slightly by a modest (say 30 °C) temperature increase, since contaminant release is limited by aqueous-phase diffusion. Effective contaminant recovery in this scenario requires that the clay matrix blocks be fully dried to allow advective flows.

Air flow can be established for both the sand and the clay strata in this scenario, which indicates that SVE is technically feasible, and heated air injection can enhance both the rate and extent of contaminant recovery. But it is important to note that the technology is not economically feasible due to difficulties in the efficient distribution of air and heat flows in a stratified system. This problem is discussed in more detail below. This author believes that hydraulic fracturing is probably essential to the economic feasibility of either conventional or heat-enhanced SVE in stratified settings like the one described.

5.0 COST AND RELIABILITY

For the scenario described under Section 4, assume that the contamination covers a plan area of 40 x 40 m and the clay layer is 3 m thick. The TCE concentration in the clay is 2000 mg/kg and the target cleanup level is 200 mg/kg (90% removal). For the clay layer, estimate:

A. Cost to remediate to target (including capital and operating expenses)

The capital costs for HASVE include and injection and withdrawal blower system, a heat source, a metal-piping and wellhead system, trench or vertical well installation and a site surface seal. Operating expenses include preventive maintenance (monthly at minimum), systems monitoring, off-gas control and utilities. The utilities dominate the operating expenses. The costs to remediate are detailed in Table 2.

Several additional clarifying assumptions were necessary to calculate costs to remediate to the target:

- The surface seal prevents any air losses.

- The permeability of the sand stratum is $1.5 \bullet 10^{-8}$ cm^2 , and for the clay stratum it is $1.5 \bullet 10^{-11}$ cm^2. This is the most optimistic value that can be used for the clay.

- The basic vapor extraction system utilizes trench construction, spaced at 3-m intervals through the treatment volume. A constant pressure drop of 1 atm is exerted across the system, which induces an air flux rate of 17.9 ft$^3 \bullet$sec^{-1} per meter trench length in the sand, and 0.0179 ft$^3 \bullet$sec^{-1} per meter trench length in the clay stratum.

  The design target temperature rise is 100°F, with a starting temperature of 50°F, and without any drying assumed. The soil specific heats are assumed to be equal, at 0.2 BTU/lb•°F and the specific heat of air is 0.0195 BTU/ft^3•°F. The soil density is assumed to be 125 lb/ft^3 for the sand and 150 lb/ft^3 for the clay. The volume of each layer is 170,000 ft^3, so the sand weight is $2.1 \bullet 10^7$ lb, and the clay weight is 2.610^7 lb. The sand layer requires injection of $4.2 \bullet 10^8$ BTU, and the clay layer requires $5.1 \bullet 10^8$ BTU.

- At a pressure drop of 1 atm across the 3m path length between trenches, the system-wide air flow rate through the clay layer will be approximately 10 ft^3/min, while the air flow through the sand will be 10,000 ft^3/min at the same pressure drop.

- If the heated air is injected at 1,100°F, delivery of the design heat load to the clay soil requires $2.4 \bullet 10^7$ ft^3 . At 10 cfm, this requires 1,729 days.

Table 2. Approximate costs for HASVE system in stratified clay-sand example.

Site Surface Cover	\$ 60,000
Trench Installation	\$ 300,000
Piping System Installation	\$ 100,000
Pumps - 10,000 SCFM	\$ 200,000
Electrical Demand - 1,000 HP (750 kW for 1729 days)	\$2,334,150
Maintenance and monitoring	\$ 400,000
Heating Energy Costs ($5.1 \bullet 10^{11}$ BTU)	\$2,040,000

These results indicate that heated air enhancement is not economically feasible for the scenario and assumptions given. Specifically,

i. To establish a pressure drop in the clay which allows a 5-yr treatment program, 10,000 cfm of air flow will occur in the overlying sand, and;

ii. While $5.1 \bullet 10^{8}$ BTU is being delivered to the clay, $5.1 \bullet 10^{11}$ BTU is being wasted in the sand.

To be economically viable, the heated air injection system must be enhanced by fracturing or by development of a mechanism to isolate air flows in the sand and clay units. Further, recapture of the waste heat that breaks through to the extraction side of the system must be developed to reduce energy costs.

B. Time to reach cleanup target with expected cleanup rate (mg/kg-day)

The total time to cleanup is controlled by the time required to induce the design temperature rise in the clay, which is 1,729 days under the assumptions given above. The average cleanup rate is therefore 1.15 mg/kg-day.

C. Economies of scale, if applied at a much larger site

The economies of scale are insignificant in this scenario since the fuel cost dominates the overall project cost.

D. Confidence or expected reliability of the technology in meeting this goal

The confidence level for the stratified scenario is low to moderate due to the possibility of airflow channeling and accidental re-wetting of the soils (due to power failure, for example).

E. Cost and time to remediate to 1000 mg/kg, assuming it as an asymptote

There is no time or cost difference relative to reaching the 200 mg/kg level, since the thermal front must progress from the injection to the withdrawal trenches.

There is a substantial economic feasibility problem with HASVE in starkly stratified soil systems. Air pressure gradients cannot be established independently for the various permeability zones, unless there is an effective sealant between them. Thus, during the time in which sufficient air (and heat) flow is delivered to the clay layer, 3 to 5 orders of magnitude more heat will have been delivered to the sand layer, all of which is wasted. Simplified calculations show a nominal \$10/yd^3 energy cost to heat and dry typical soils, but if the delivery efficiency is less than 0.1%, the real costs rise to more than \$10,000/yd^3. Fracturing is likely required to bring the delivery efficiency into a sensible range.

6.0 COMMERCIAL AVAILABILITY

A. Stage of development of the technology

The technology is in the conceptual stage of development, with field testing documented to a proof-of-concept level. Treatability documentation from low and medium-temperature thermal treatment equipment should be directly transferable to the in-situ methods for a wide variety of soil and contaminant types. The heat delivery information can be superimposed on existing air flow models for porous media.

B. Commercial availability of the technology

The author is unaware of vendors presently claiming commercial processes for application of this technology.

C. Likely future enhancements

Linkage to fracturing technology is the primary enhancement.

D. Complementary technologies that would enhance cleanup if incorporated in a treatment train.

The technology will likely be linked to fracturing methods, as described above.

7.0 CASE HISTORIES

Case History 1 - JP-4

DePaoli and Hutzler (1992) reported the results of a HASVE trial for enhancement of JP-4 recovery. Removal rates were increased by 60% relative to ambient-temperature SVE in the same system. The following summarization is taken from their report:

Physical setting - Hill Air Force Base, Utah, at the site of a 27,000-gallon JP-4 spill.

Geology - The soils were comprised of sands with thin clay laminations. Permeability ranged from $3 \cdot 10^{-8}$ to $6 \cdot 10^{-7}$ cm^2. Moisture contents ranged from 3 to 7 % (w/w) for the sands, with 10 to 25% (w/w) for the clay lenses.

Contaminants (including depth of contamination, distribution in fractures and matrix, existence of pooled product, etc.). - The contaminants consisted of JP-4 compounds, although neither the age of the spill nor composition of residual contamination were identified. Contamination was observed to a depth of 50 feet, underlying a surface area of 1440 ft^2. The maximum total hydrocarbon was 6400 mg/kg.

Constraints - Air emissions control was required, which was a significant cost element.

System design and operating characteristics - The system was operated at ambient temperature for 8 months using two vacuum withdrawal wells with a passive air inlet approximately midway between the two vacuum wells. To begin the heated air portion of the test, the passive inlet air was routed through a heat exchanger linked to a catalytic incinerator unit that served as the air emission control device. Air arrived at the inlet well at a temperature of 99°C (210°F). The heat injection phase lasted 51 days.

Performance monitoring and methods used to evaluate results - Thermocouples placed in the target soils were used to measure the induced heating, while off-gas hydrocarbon concentrations were used to monitor system performance. The ambient air system was operated for 8 months, during which time a linear relationship developed between hydrocarbon concentration and cumulative extracted air. An increase in system production relative to the linear projection developed in the production curve, which was attributed to the effects of heating.

Degree of mass removal and concentration changes in soil and groundwater - The study limited its reporting to removal rates, not extent. No post-treatment soil concentrations were given.

Duration and cost of cleanup - The study did not run to a completion point.

Comments and recommendations on any technology enhancements that would be worthwhile (given additional resources) - The study did not seek to measure the relative contributions of biological and evaporative recovery enhancement due to increased temperature. Without this determination, the possiblity of additional enhancement with further temperature increases cannot be assessed.

Case History 2 - Diesel

Sittler, et al. (1992) reported on the use of thermally enhanced SVE for the remediation of diesel-contaminated soils. The project was undertaken to accelerate a remediation due to property transfer considerations.

Physical setting - The project was located at a retail fuel outlet, in soils underlying dispenser islands and tank locations.

Geology - The site soils graded from silts, silty clays and sandy clays in the upper 8 feet to sands and silty sands from 8 to 22 feet below grade. Groundwater was approximately 37 feet below grade.

Contaminants (incl. depth of contamination, distribution in fractures and matrix, existence of pooled product, etc.). - The contaminant was diesel fuel, which was found in the upper 15 feet, at concentrations ranging up to 26,000 mg/kg in the upper stratum (0-8 ft) and up to 2,060 mg/kg in the lower treatment stratum (8-22 ft). The surface area underlain by contaminated soils was 8,000 ft^2, which gives a total treatment volume of 4,444 yd^3.

Constraints - The site was fitted with a catalytic incinerator for air emission control. The state regulatory closure standard for diesel was 100 mg/kg.

System design and operating characteristics - SVE injection and withdrawal wells were spaced at 25 to 30-foot intervals over the treated area. Heated air was generated by a heat exchanger at the catalytic incinerator unit, which developed an injection air temperature of 316°F. Since the injector well temperatures ranged near 140°F, heat losses must have occurred in transit.

Performance monitoring and methods used to evaluate results - Injection and extraction well temperatures were monitored at the wellheads, but soil temperatures were not measured directly. Remedial performance was measured by pre-, interim- and post-treatment soil borings.

Degree of mass removal and concentration changes in soil and groundwater - Mass removal was not quantified. Soil concentrations in final soil borings fell below the state-mandated closure level of 100 mg/kg. Groundwater was not discussed.

Duration and cost of cleanup - The system operated for a total of 10 months, at a reported cost of $90,000.

Comments and recommendations on any technology enhancements that would be worthwhile (given additional resources) - The authors concluded that heat distribution was good because injection and extraction well temperatures tracked very closely. This author contends that such a relationship indicates system short-circuiting; the high specific heat of soils should yield a significant lag time between injection of heat and a temperature increase at the extraction point, unless the heat is not being effectively absorbed by the soils, as with short circuiting. Since the soil temperatures were not directly measured, the heat exchange efficiencies cannot be evaluated.

8.0 SUMMARY

The HASVE concept is not economically viable in the bulk-stratified scenario designed for this series of papers. The efficiency of HASVE exactly mimics the efficiency of conventional, ambient temperature SVE since the heat must be injected in advective air flow.

The bulk-stratified scenario brings out the worst in SVE. In finely stratified (ie lamellar) soils, thermal conductivity and gaseous diffusion over very short distances should allow efficient distribution of heat and recovery of mobilized contaminants.

HASVE has not been demonstrated in full-scale field applications. Limited field testing results can be found in the literature, which indicate that contaminant release rates can be enhanced and soil concentrations may be reduced to below regulatory action levels.

It is expected that SVE can be used to recover low-volatility compounds from vadose zone soils, but no studies were found in the literature that document this technology.

Soil permeability is expected to increase as heated air injection dries the pore spaces, which should accelerate soil remediation. Again, this theoretical benefit of HASVE has not been documented in the available literature.

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Chemically Enhanced In Situ Recovery

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Chemically enhanced recovery is a promising alternative to current technologies for management of subsurface releases of organic liquids. Through the inclusion of surfactants, solvents, polymers, and/or alkaline agents to a waterflood, the transport of targeted organic compounds can be increased and rates of recovery enhanced.

By far, the vast majority of work done in the field of chemically enhanced recovery has been at a laboratory scale. The following text focuses on chemically enhanced recovery from a field application perspective with emphasis given to chlorinated solvents in a low permeability setting. While chlorinated solvents are emphasized, issues discussed are also relevant to organic liquids less dense than water such as petroleum products. Topics reviewed include:

- Description of technology
- General technology considerations
- Low permeability media considerations
- Cost and reliability considerations
- Commercial availability
- Case histories

Through this paper an appreciation is developed of both the potential and limitations of chemically enhanced recovery. Excluded from the scope of this paper is the in situ destruction of organic compounds through processes such as chemical or biological oxidation, chemically enhanced recovery of inorganic compounds, and ex situ soil treatment processes.

2.0 DESCRIPTION OF TECHNOLOGY

The potential to enhance the recovery of organic compounds from porous media using chemical solutions is widely recognized and has been applied in petroleum reservoirs since the mid-1920s. Over the last 15 years, a growing interest has developed relative to the use of chemical solutions to mitigate risks posed by organic chemicals inadvertently released to the near surface vadose and groundwater zones.

The level of interest in this approach has heightened in the last few years with the growing recognition of the limitations of conventional subsurface remediation techniques. These limitations are illustrated in EPA's guidance regarding technical impracticability (EPA, 1993) that states "experience over the past decade has shown that restoration to drinking water quality may not be achievable due to the limitations of available remediation technologies."

Chemically enhanced recovery is increasingly being considered for its potential to fill the gaps between site restoration goals and the limitations of existing remedial technologies. For the purpose of this paper, chemically enhanced recovery is defined as addition of organic or inorganic compounds to an aqueous solution to enhance in situ recovery of organic compounds.

Process Considerations

From an engineering process perspective, chemically enhanced recovery involves:

- Preparation of the chemical flushing solution
- Delivery of the solution to the subsurface
- Recovery of the solution from the subsurface
- Treatment of the produced fluids, optimally with the goal of separating out the targeted compound and reusing the soil flushing solution

From an in situ treatment perspective, chemically enhanced recovery involves delivering a solution that enhances the transport of the targeted compound within a targeted zone and subsequently recovering both the delivered solution and targeted compound. Fundamental to this process are the concepts of sweep efficiency and solution efficiency.

Sweep efficiency reflects how uniformly the solution contacts the targeted area and can be described as the product of vertical and aerial sweep efficiencies $SE_{Vertical}$ and $SE_{Horizontal}$. The effectiveness of a solution is defined as $CE_{Solution}$. Combining these terms, the overall system efficiency can be defined as:

$$SystemEff. = SE_{Vertical} * SE_{Horizontal} * CE_{Solution} \qquad 1$$

Recognizing that the product of the efficiencies will almost always be less than one, some of the targeted material will almost always be left in place, even under the condition of cycling multiple solution pore volumes.

Mobilization of Targeted Compounds

The inclusion of chemicals to an aqueous flush can enhance the transport of the targeted organic compound(s) through a variety of mechanisms including:

- Physical displacement of non-aqueous phase liquid (NAPL)
- Solubilization of NAPL
- Desorption of sorbed compounds
- Matrix modification

While each of these are separate mechanisms, it is important to note that they are not mutually exclusive. Relative to each of these mechanisms, with the exception of matrix modification, a lot of literature is available describing the processes. For the purpose of this document, only a brief introduction is presented, and references for rigorous reviews are cited.

Physical Displacement

NAPLs become entrapped as discontinuous ganglia within porous media, as described by Wyatt (1992):

- Fluid-fluid interactions such as interfacial tension between NAPL and water

- Fluid-matrix interfacial properties that define the wetability and adsorption
- Physical properties of the NAPL, such as density and viscosity
- The geometry of the porous matrix which, with interfacial tension and wetability, affects the capillary forces
- The pressure gradient

Common approaches to chemically enhanced displacement include:

- Addition of surfactant to reduce interfacial tension, thereby allowing discrete NAPL ganglia to elongate under the forces present and pass through restricting pore throats
- Addition of an alkaline agent to reduce fluid-matrix interactions, making the matrix more water wet
- Addition of polymer such that the displacing fluid and the displaced fluid have similar mobilities. This results in more efficient displacement of NAPL ganglia at a pore scale and a more uniform sweep of the identified target.

A primary advantage of displacement processes is that initially large amounts of NAPL can be removed independent of either solubility or mass transfer limitations. The primary limitation of displacement processes is that they will only reduce, not eliminate, the forces entrapping NAPLs. Therefore, some entrapped NAPL will likely remain.

Solubilization of NAPL

Entrapped dens, nonaqueous phase liquid (DNAPL) can also be removed by adding chemicals, that enhance the solubility of the targeted NAPL. A review of these processes can be found in West and Harwell (1992). Mechanistically enhanced solubilization occurs through the formation of surfactant or alcohol micelles. As aqueous surfactant or alcohol concentrations increase, a critical concentration is reached at which surfactant molecules become arranged into structural units (micelles). Subsequently, hydrophobic organic liquids adsorb into the interiors of the micelles increasing the apparent solubility of the organic liquid in the aqueous phase.

The primary advantage of dissolution is that lower residual NAPL concentrations may be achieved than through NAPL displacement processes alone. The limitations of dissolution processes are that even with enhanced solubility, a large number of pore volumes will be required, and mass transfer from the NAPL to the aqueous phase can significantly limit the rates of recovery.

Desorption

Soil/water partitioning of organic contaminants, and the associated limitations in contaminant mass transfer from the sorbed to the aqueous phase is a phenomenon that affects a number of remediation techniques. The use of surfactants for desorption of organics from soil has probably been studied more for use in other remediation approaches than for in situ soil flushing. Much of this work has been performed in applied bioremediation research, particularly with respect to slurry bioreactors. Sorption of compounds such as PCBs and polynuclear aromatic hydrocarbons (PAHs) is seen as a key limitation in the cleanup level achievable in slurry bioreactors.

A number of studies have been conducted with the objective of determining the efficacy of surfactant addition for contaminant desorption and increasing the rate of biodegradation (e.g., Liu et. al., 1995). Results have been mixed. Some have concluded that surfactant addition holds promise, while others have found that it has provided no benefit. One may conclude that the use of surfactants for desorption of sorbed organics is not currently understood as well as it is in NAPL displacement and solubilization applications.

Matrix Modification

Almost all work with chemically enhanced recovery has focused on granular soils in which total porosity and intrinsic permeability are effectively constants, independent of the compounds present in the fluids occupying the pore space. Recognizing that many low permeability soils have high clay contents and that many clays are sensitive to aqueous chemistry, it follows that management of water qualities could lead to enhanced hydraulic characteristics of low permeability soils.

Examples of modified soil permeabilities due to fluid chemistry include:

- Flocculation of clays due to the replacement of sodium with calcium
- Desiccation of clay liners due to contact with non-aqueous phase chlorinated solvents

While this idea seems plausible, the authors know of no research in this area.

Limiting Factors

While chemically enhanced recovery offers many tantalizing opportunities to overcome the limitations of existing technologies, it is also subject to a number of limitations and concerns:

- Although many favorable reactions can be achieved, adverse reactions may also occur including enhanced vertical migration of DNAPLs and enhanced solubility of residual compounds of concern due to residual surfactant remaining in the matrix.
- Although mass reduction can almost certainly be achieved, it is unclear whether long-term site management requirements can be significantly altered. A case study describing 130-foot by 130-foot test cell indicates that 96 percent removal of DNAPL initially present left 3,000 gallons of DNAPL in place.
- When qualifying success as eliminating the long-term site management requirements posed by the compounds of concern, the authors know of no successful field demonstrations of chemically enhanced recovery.
- The overall complexity of mixing, delivering, recovering, and treating chemical solutions is high. Logically, it follows that overall cost associated with chemically enhanced recovery can be substantial.
- In many states, current regulations will not allow delivery of chemical solution to shallow groundwater systems.

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

Potential for Mobilization

The first step in considering chemically enhanced recovery is to define the approach and chemical solution to be used. Typically this analysis is completed in a laboratory where both fluid-fluid and fluid-matrix interactions can be evaluated. In addition to enhanced recovery, other factors that need to be considered include:

- Using a chemical system that can readily be treated after recovery, optimally separating out the targeted compound and reusing the chemical solution
- Applying a chemical system that will not result in adverse migration of the compounds of concern
- Using chemicals that in themselves are mobile within the matrix and pose no risks

While a high correlation between results obtained in the laboratory and those obtained in the field is not guaranteed without preliminary laboratory data, the likelihood of success in the field is greatly diminished. An example of such a laboratory study is described by Pitts et al. (1993).

Fluid Delivery-Recovery

The second step considered in assessing chemically enhanced recovery is to evaluate how fluids can be cycled through the targeted area. Factors that should be considered include:

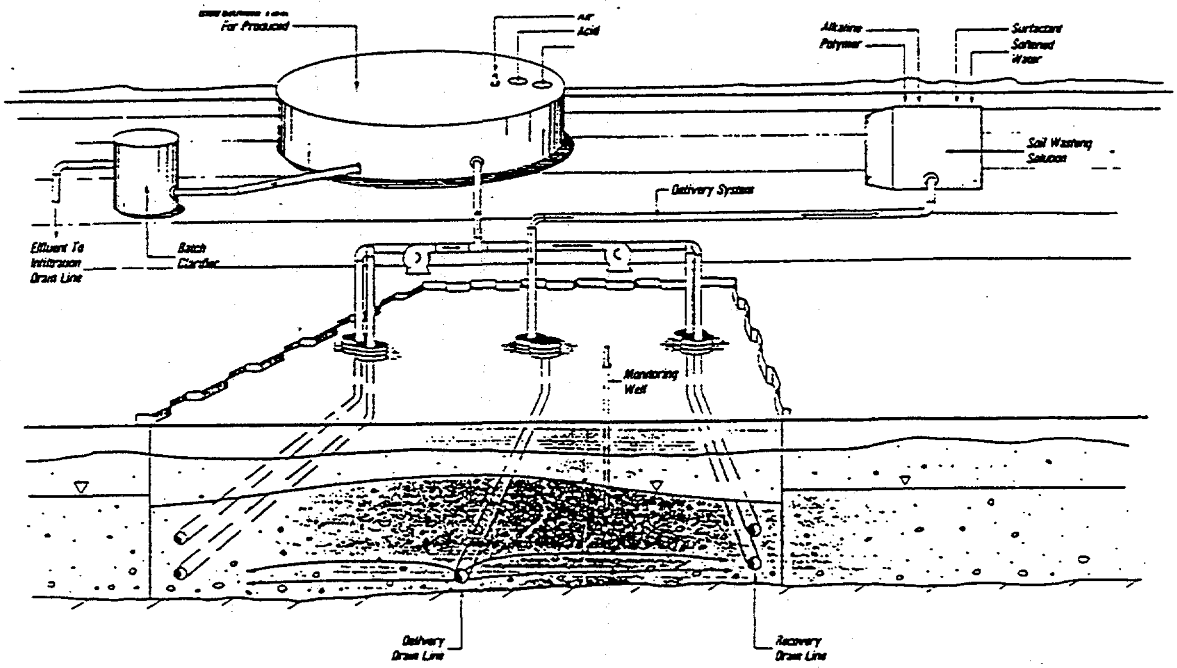
- The target must be contacted efficiently
- Fluids should only be delivered to areas from which they can be recovered
- Fluid production from outside the area of concern needs to be minimized to constrain costs associated with treatment of produced fluids

Figure 1 presents fluid delivery and recovery approaches reported by Pitts et al. (1993) and Abdul et al. (1992). In the first case, the approach is that of horizontal fluid cycling using drainlines for delivery and recovery and sheet pile walls for isolation. In the second case, vertical fluid flow through the unsaturated zone is employed with recovery using an underlying well.

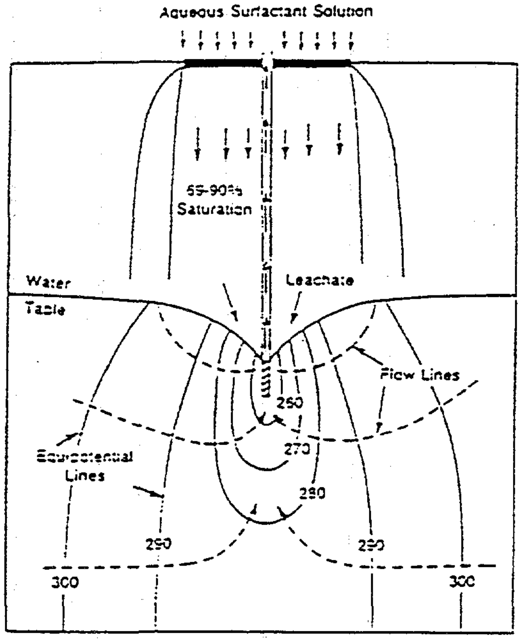
Setting

Recognizing that chemically enhanced recovery involves systems to mix, deliver, recover, and treat fluids, consideration needs to be given to compatibility with current land use. In general, costs to implement chemically enhanced recovery will be lowest at inactive facilities and will generally increase as a function of the constraints associated with land use.

Relative to hydrogeologic setting, the time to cycle a fixed volume of chemical solution is a function of the uniformity of the sweep, the spacing between recovery and delivery systems, and capacity of the sediment to transmit the solution (constrained by both permeability and the achievable driving force).



Chemically Enhanced Recovery of Waste Wood-Treating Oil as Reported by Pitts (1993).



Chemically Enhanced Recovery of PCBs as Reported by Abdul (1992).

Figure 1. Fluid Delivery/Recovery Approaches.

In general, the feasibility of chemically enhanced recovery will be at an optimum in uniform coarse sediments in which fluids can be readily cycled. In contrast, in heterogeneous low permeability sediments, where target compounds are present in both high and low permeability flow paths, chemically enhanced recovery will be less effective.

Operation and Maintenance Considerations

In that numerous simultaneous process operations are involved with chemically enhanced recovery, overall operations and maintenance will be greater than that associated with current remedial technologies such as pump and treat or soil vapor extraction. In all likelihood, operations and maintenance would involve:

- Assuring that delivered solutions meet specifications
- Monitoring formation plugging within the interval through which fluids are being cycled
- Maintaining containment of delivered fluids and mobilized target compounds
- Treating produced fluids

Waste Streams

To assure containment of delivered solutions and mobilized target compounds, it is likely that overall rates of recovery will exceed rates of delivery. This may be true even where physical barriers such as sheet pile walls are used since physical barriers may leak.

Recognizing this condition, it is likely that a continuous waste stream will be generated during solution delivery and recovery. Furthermore, at the conclusion of chemically enhanced recovery it will likely be necessary to flush the target free of both mobilized compounds and the chemical solution used. With this goal, it will likely be necessary to cycle clean water through the target and discharge the entire produced fluids stream.

In addition to discharge of treated water, solid waste may be generated depending on the produced fluids treatment processes employed. Examples include spent activated carbon, sludge from biological treatment processes, and/or solids filtered from fluids prior to delivery.

Adverse Impacts and Other Risks

The primary concern relative to using chemical solutions to enhance recovery of targeted organic compounds is the potential to adversely affect either the nature or extent of contamination. As discussed by Fountain (1992), reduction of the interfacial tension between DNAPLs and water associated with the use of surfactants has the potential to cause enhanced downward migration of DNAPL.

A second consideration is the affects of residual chemical left in the formation. CH2M HILL (1990) reports 34 percent of delivered surfactant was lost to sorption by the sediments in the targeted zone. Since surfactants can increase recovery during remediation, they may also effect solubility after remediation. Specifically, surfactants remaining in place at the critical micelle concentration along with some fraction of targeted compound may increase apparent concentrations of dissolved target compounds above initial conditions.

Predictive Tools

Laboratory studies provide an estimates of the effectiveness of the in situ surfactant technologies (Sale et. al, 1989). These data, along with site information, can be used in numerical simulation for predicting the project performance under certain operating conditions. The site information needed includes data defining transport properties such as permeability and porosity and data regarding the extent and concentration of contamination. This type of data can be obtained from well tests and tracer tests. The laboratory study provides data on fluid-rock interactions such as surfactant adsorption, cation exchange capacity, solubilization and interfacial tension effects, etc. Currently, the most comprehensive numerical simulator for this type of prediction is UTCHEM, by the University of Texas at Austin. The simulator was originally developed for enhanced oil recovery in petroleum reservoirs, but has been recently adapted for remediation projects.

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

As described by McWhorter (1992), low permeability media consists of "a network of interconnected fractures of variable aperture and spacing superimposed on a porous matrix." While the fractures comprise only a minor portion (less than 1 percent) of the total matrix volume, they are typically the primary pathways for fluid migration due to their comparatively high permeability and low NAPL entry pressure.

Additional features of low permeability soil described by McWhorter (1992) include:

- Flow of NAPL only along fractures. Entry of the NAPL into the matrix blocks is typically precluded by the high entry pressure (corresponding to low permeability) of the matrix blocks.
- Due to the large concentration gradient between the NAPL filled fracture and the matrix block water, dissolved constituents rapidly diffuse into the low permeability matrix.
- With time, significant depletion of the NAPL in the fracture may occur through dispersion due to the small amount NAPL that can be stored in a joint.

Hypothetical Application of Chemically Enhanced Recovery

Further insight into chemically enhanced recovery can be gained through consideration of a hypothetical release of tetrachloroethene (PCE) and trichloroethlene (TCE) to a stratified soil. Key features include:

- A 3-meter thick clay of permeability 10^{-6} to 10^{-8} cm/sec with fractures spaced a few centimeters apart with apertures of 10 to 40 microns
- Sand layers above and below the clay with hydraulic conductivities of 10^{-3} cm/sec
- An effective porosity of 1 percent within the clay
- DNAPL (TCE and PCE) perched above the clay and trapped in the continuous and dead end fractures within the clay
- Dissolved TCE and PCE within the matrix blocks

The following describes a conceptual approach to applying chemically enhanced recovery to the above setting.

Design

The first step in developing a chemically enhanced recovery system is to design the chemical solutions and evaluate the number of pore volumes required to reach a prescribed level of mass removal. Typically, this would be done in a laboratory using site sediments, water, and NAPL. Considering the limited experience with chemically enhanced recovery and the potential sensitivity of recovery to site specific conditions, this would be a critical step. Following the work at the Borden Aquifer site in Canada, (Fountain, 1992), it is assumed the result of this activity would be the selection of a 1 percent nonylphenol ethoxylate mixed with 1 percent phosphate ester of nonylphenol ethoxylate. In actuality, this decision would need to be carefully reviewed since nonylphenol ethoxylate may be toxic to aquatic life and tends to be highly adsorbing.

The next step would be to decide how to flush the targeted area. Criteria to consider include:

- Developing as uniform a sweep as possible
- Maintaining an inward gradient to the target
- Minimizing production of fluids from outside the target

Considering the criteria and the limited lateral hydraulic conductivity of the clay, it would be most feasible to flush fluids vertically across the clay. Furthermore, sheetpile walls would likely be cost effective in terms of limiting excess inflow. Considering the potential for enhanced vertical migration of DNAPL with downward flushing, it would be best to flush fluids upward across the clay preventing downward migration of DNAPLs.

Specifically, upward delivery of surfactants could be achieved by extending the sheetpile wall through the clay and approximately 5 feet into the underlying sand. Surfactant could be delivered below the bottom of the clay using wells at a rate less than the upward flux across the clay. Using this approach, surfactant would remain in the immediate vicinity of the target.

Note: The assumption of upward flow requires a water table above the clay. If water levels were at the top of the clay, cycling of fluids through the clay could only be achieved by mounding produced fluids or by dewatering portions of the clay. The objective of either of these steps would be to generate a hydraulic head to drive the solution from delivery to recovery. Since mounding delivered fluids might lead to outward gradients, and dewatered portions of the target would be unaffected, neither of these options are considered reasonable. Recognizing this, it is assumed that the water table is at least 5 feet above the top of the clay. Five feet of upward head across a 10-foot clay (3 meters) would likely be sufficient to limit further downward migration of PCE and TCE, even if the interfacial tension between the fluids was reduced to zero.

From a process perspective, required facilities would include:

- Equipment for mixing and delivering the chemical solution
- An air stripper to separate the chlorinated solvent from the produced fluids

- Possibly a filter system to remove suspended solids from treated water being cycled back to the delivery system
- A biological treatment system to remove surfactants from excess water produced during flushing and final displacement of the chemical solution

Operation

The first step in system operations would be to cycle water with a tracer through the targeted area. During this activity, process equipment could be checked out, and the design could be validated in terms of sweep efficiency through the targeted area and overall containment of delivered solutions and mobilized target compounds.

The next step would be to cycle the chemical solution through the target. Throughout this process, produced fluids would be monitored for concentrations of target compounds, and a side stream of produced fluids would be treated and discharged. Surfactants would likely be added to the delivered solutions to make up for surfactant consumption by the formation.

Cycling the chemical solution would continue until mass recovery per pore volume became insignificant, time constraints were exceeded, or costs became unacceptable. Based on work at the Borden aquifer site, (Fountain, 1992) the number of pore volumes cycled would be on the order of 10 to 20. Considering at 5-foot upward gradient across the clay and the previously described hydrologic characteristic of the clay, 10 to 20 pore volumes could be cycled across the clay in approximately 100 days.

Post Delivery Flushing and Monitoring

The final step would be to flush surfactant and remaining mobilized target compounds from the targeted area. This could be achieved by cycling water through the system with treatment and discharge of produced fluids. Assuming this required another 10 to 20 pore volumes, this could take an additional 100 days.

Removal Effectiveness

Regarding DNAPL perched above the clay, it seems likely that the described approach could remove a large fraction, but not all, of the DNAPL present. This is based on work done at the Borden aquifer site (Fountain, 1992).

Within the clay, removal efficiency will likely be lower with overall effectiveness being a function of:

- The relative distribution of DNAPL in fractures versus dissolved compounds in the matrix blocks
- The uniformity of the fractures in terms of their apertures
- The percent of the target compound that is in deadend fractures

Assuming that all the chlorinated solvents are DNAPLs, that they are restricted to a vertical fracture system, that the fracture apertures are uniform, and that no dead-end fractures exist, almost all of the target compounds could be recovered. Depending on the variances from these ideal conditions, less of the target compounds would be recovered. Specific considerations include:

- Horizontal fractures that contain DNAPL would be flushed far less effectively than vertical
- Dissolved target compounds present within the matrix block would likely be uneffected
- Dead-end fractures would likely be unaffected since little or no flow would circulate through them
- Since flow through fractures is proportional to the cube of the aperture, most of the delivered fluids would flow through the largest apertures. For example, a 40 micron fracture will transmit 64 times more flow than a 10-micron fracture.

5.0 COST AND RELIABILITY CONSIDERATIONS

Considering a 40 by 40 meter area and the current state of knowledge regarding chemically enhanced recovery, Table 1 provides an order of magnitude cost estimate for completing the above described chemically enhanced recovery project. Based on this analysis, the cost for the described project, including initial bench scale work, design, installation, operations, maintenance, and post operation monitoring, is $576,000.

Figure 2 presents a time line identifying the sequence and duration of major activities. Based on this figure, the time to complete the entire project is approximately 2 years with the fluid recovery and delivery phase lasting approximately 9 months.

Given a larger site, significant economies of scale would be recognized if the site could be addressed in a modular fashion. Under this scenario, overall process system size could be minimized and delivery and recovery equipment could be reused at multiple locations.

The overall ability of the described technology to meet a 50 and 90 percent reduction in mass present (e.g., a reduction from 2,000 to 1000 milligram/kilogram [mg/kg] or 2,000 to 200 mg/kg) is a function of the distribution of the target compound. Considering that much of the mass may disperse into the matrix, it seems highly unlikely that 90 percent of the mass present could be recovered. Attainment of 50 percent recovery may well be attainable at a relatively uniform site.

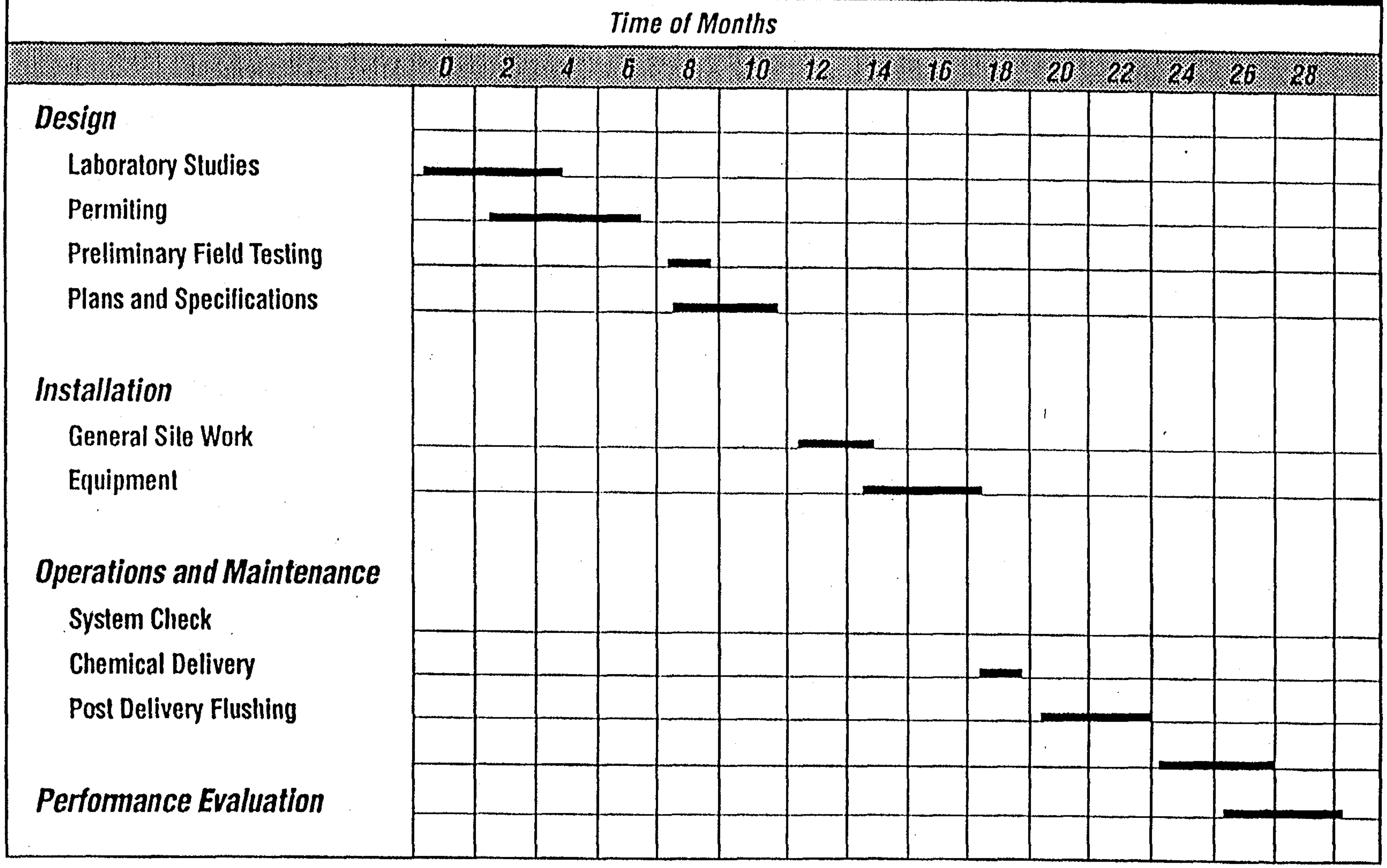
6.0 COMMERCIAL AVAILABILITY

Field applications of chemically enhanced recovery is limited to a handful of small scale field demonstration projects. For the most part, these projects have been conducted either by consultants working on the behalf of industry in attempts to develop technologies to meet regulatory cleanup goals or by universities conducting basic research. While several companies currently exist that specialize in chemically enhanced recovery, their experience is limited.

Table 1
Cost Opinion for Hypothetical Application of Chemically Enhanced Recovery

Design		
Laboratory Studies		$50,000
Preliminary Field Test		$15,000
Permitting		$10,000
Plans and Specifications		$25,000
	Subtotal	$80,000
Equipment (Installed)		
General Site Work		$5,000
Building for Equipment		$5,000
Mix Systems		$20,000
Delivery Systems		$10,000
Sheetpile Wall		$140,000
Delivery Wells		$10,000
Recovery Trenches		$20,000
Air Stripper with Atmospheric Discharge		$5,000
Recovery Systems		$30,000
Filter		$10,000
Biological Treatment		$10,000
Performance Monitoring Wells		$6,000
	Subtotal	$266,000
Operations and Maintenance		
Labor		$70,000
Surfactants		$10,000
Residue Disposal		$10,000
Misc. Expendables		$15,000
Analytical		$80,000
	Subtotal	$185,000
Performance Evaluation	Subtotal	$25,000
	Total	**$576,000**

Figure 2
Time Line for Implementation of Hypothetical Enhanced Recovery Project



At present, the greatest limitation associated with chemically enhanced recovery is uncertainty regarding how the technology should best be applied and what benefits can be achieved through its application. This is largely a reflection of the limited number of field applications that have been conducted. Further advancement of the technology is most likely to occur as additional field demonstrations are completed. Through the knowledge gained, current uncertainties will be reduced.

7.0 CASE HISTORIES

Documented field applications of chemically enhanced recovery include work at a wood-treating oils facility in Wyoming, at the Borden aquifer site in Canada, and at a PCB site. The following provides a brief overview of the first two projects. Details regarding the third are presented by Abdul (1992).

Tie Plant

From 1987 to 1990 a suite of in situ remedial technologies were field tested at a former wood-treating facility in Wyoming where a shallow alluvial aquifer had become contaminated with creosote based waste wood-treating oils (density 1.03 g/cm^3). A primary component of these studies was the analysis of chemically enhanced recovery of the oils. This involved laboratory testing followed by a small scale field demonstration in 1988 and a large scale field demonstration in 1989.

The large-scale pilot test was performed in the area in which waterflood oil recovery had been applied in 1988. Sheet-pile walls were driven to isolate a test cell with the dimension of 130 by 130 feet. Chemical solutions were delivered to a central 120-foot delivery drainline. Fluids were produced from two 120-foot recovery drainlines spaced 60 feet from and parallel to the delivery drainline. During the 235-day pilot test, approximately 7,400 pounds of polymer, 39,700 pounds of surfactant, and 81,900 pounds of alkaline agents were delivered to the subsurface.

Through the delivery of chemicals and subsequent flushing of mobilized oil, and residual chemicals, an equivalent of approximately 23,600 gallons of oil was produced. The corresponding reduction in soil contaminant concentrations was from an initial concentration of approximately 25,000 mg oil/kg soil to a final concentration of 4,000 mg oil/kg dry soil. Oil concentrations prior to waterflood oil recovery were approximately 100,000 mg/kg. Final concentrations ranged from 290 to 11,000 mg oil/kg dry soil, reflecting the impact of preferred flow paths within the contaminated interval.

While large amounts of mass were removed from the site, it was also recognized that remaining subsurface alluvial contamination, together with the contamination in the underlying bedrock, would act as a long-term source of groundwater contamination. Groundwater approaching equilibrium with this remaining contamination would contain dissolved PAHs at concentrations near the concentrations present under the initial conditions. Thus, it was recognized that implementation of in situ soil flushing would likely not eliminate or reduce the need for continuation of current groundwater containment practices in place at the site.

During the in situ soil flushing process, fluids were generated that were characterized by stable oil emulsions, high contaminant concentrations, high organic content, elevated pH, high alkalinity, and high salinity. These characteristics make the fluids very difficult to treat. The need for an effective and efficient process for treatment of the fluids is evident through consideration of the volume of fluids that would be generated in full-scale application of the soil flushing method. Based on extrapolation of the 1989 in situ soil flushing pilot test, approximately 275 million gallons of fluid with these characteristics would be produced. Considering effluent recycle and chemical reuse, fluid discharge, and residuals management, no complete process was identified for the treatment of fluids produced during in situ soil flushing.

Full-scale applications of the chemically-enhanced recovery technique would require an extensive piping network and large amounts of fluids and chemicals. Based on extrapolation from the 1989 pilot test, full-scale in situ soil flushing would require more than 125 million gallons of soil flushing solution containing more than 1 million pounds of polymer, nearly 10 million pounds of surfactant, and approximately 16 million pounds of alkaline agents. Based on the limited risk reduction achieved, unresolved technical issues, and implementation costs on the order of $500,000 per acre, this technology is no longer being considered at the site.

Borden Aquifer

The following describes work conducted at the Borden aquifer, quoting directly from Fountain (1992). Additional information regarding this topic is presented in Wunderlich (1992).

> "In a field test conducted at Canadian Forces Base Borden in collaboration with the Waterloo Center for Groundwater Research, a 3-meter by 3-meter test cell was constructed by driving sheet piling walls into a 4-meter-thick unconsolidated sand aquifer. Approximately 231 liters of tetrachloroethylene was added in a controlled release by B. Kueper, who then excavated the top meter to study the DNAPL flow. The cell was then refilled with clean sand and a blend of 1 percent nonylphenol ethoxylate, and 1 percent phosphate ester of nonylphenol ethoxylate was pumped through the 3-meter-thick contaminated section of the cell to evaluate surfactant-enhanced remediation.
>
> The surfactant was injected in five wells on one side of the cell and extracted from five wells on the other side. The wells were screened over the entire contaminated zone, which was kept saturated throughout the experiment. The concentration of tetrachloroethylene (PCE) in the effluent increased from its aqueous solubility of about 150 parts per million (ppm) to over 4,000 ppm when the surfactant was added. The increase in concentration illustrates the efficiency of the surfactant process. The surfactant solution used provides a solubility of PCE of about 12,000 ppm; values in excess of 11,500 ppm were observed in several sampling points on the five multilevel monitoring wells in the cell. This illustrates that the surfactants provided the same solubilization power in the field as predicted in the laboratory.
>
> The system performed as expected, solubilization was high, surfactant breakthrough was indistinguishable from that of a conservative tracer indicating sorption was very low (the aquifer has no significant clay or organic content) and the air stripper separation was effective. Several modifications had to be made to the air stripper, however, to prevent foaming; very low air velocities were eventually employed.
>
> The concentration of PCE in the multilevels dropped to a few ppm within 14 pore volumes, except for the multilevel ports right on the aquitard. These data indicated

that the DNAPL had been removed over nearly the entire aquifer. This was confirmed by analysis of cores taken prior to the start of the experiment, after seven pore volumes had been circulated, and after 14 pore volumes had been circulated. These analyses showed that:

1. Nearly all the PCE was removed by 14 pore volumes.
2. The layers of high PCE concentration, which represent perched lenses of PCE, remained at the same height throughout the experiment indicating the lenses did not drop because of vertical mobilization.
3. The persistence of PCE along the aquitard indicates that complete removal would require an extended treatment time.

We have now circulated almost 20 pore volumes of solution and elevated concentrations of PCE still occur in the multilevel at the top of the aquitard.

The base of the aquifer has slightly dipping layers of sand and silt. The PCE is apparently concentrated in the sand layers. Cleaning of the layers is retarded by low horizontal flow rates resulting from the low hydraulic conductivity of the silt layers. Similar hard-to-clean low-flow zones can be expected in any aquifer."

8.0 SUMMARY

Extensive laboratory scale research has been performed illustrating that rates of contaminant removal from porous media can be increased using chemical solutions. Primary mechanisms of removal include physical displacement of NAPLs, dissolution of NAPLs, and desorption of sorbed contaminants. Considering that "experience over the past decade has shown that restoration to drinking water quality may not be achievable due to the limitations of available remediation technologies" (EPA, 1993), chemically enhanced recovery presents a promising alternative.

While chemically enhanced recovery holds promise, its current level of development is limited to laboratory studies and a handful of small scale field demonstrations. In progressing from laboratory to field scale application, a number of issues become critical including:

- Can the targeted area be uniformly contacted?
- Will delivery of a chemical solution result in an adverse condition that may aggravate the risk posed?
- Can sufficient mass be recovered to significantly alter the requirements for long-term care of a site?
- Are the costs associated with the relatively complex process of mixing, delivering, recovering, and treating a chemical solution commensurate with benefits achieved?

While significant issues need to be resolved before large scale applications of chemically enhanced recovery occur, significant progress has already been achieved through a number of projects, including pilot tests at a former Tie Treating Plant and at the Borden aquifer. In both cases, mass removal exceeding 90 percent of initial in-place mass was achieved.

Unfortunately, in both cases sufficient contaminant mass remained to act as a long-term source of dissolved groundwater contaminants.

Relative to low permeability soils, lower recovery efficiencies are anticipated than those noted at the former Tie Treating Plant or the Borden aquifer, both of which are high permeability sites. Primary factors reducing recovery in low permeability soils are the presence of dissolved mass in the matrix blocks, variations in flushing rates along joints, and limited contact with targeted compounds in dead-end fractures.

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PNEUMATIC FRACTURING OF LOW PERMEABILITY MEDIA

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Remediation of DNAPL in Low Permeability Media Project

1.0 DESCRIPTION OF THE TECHNOLOGY

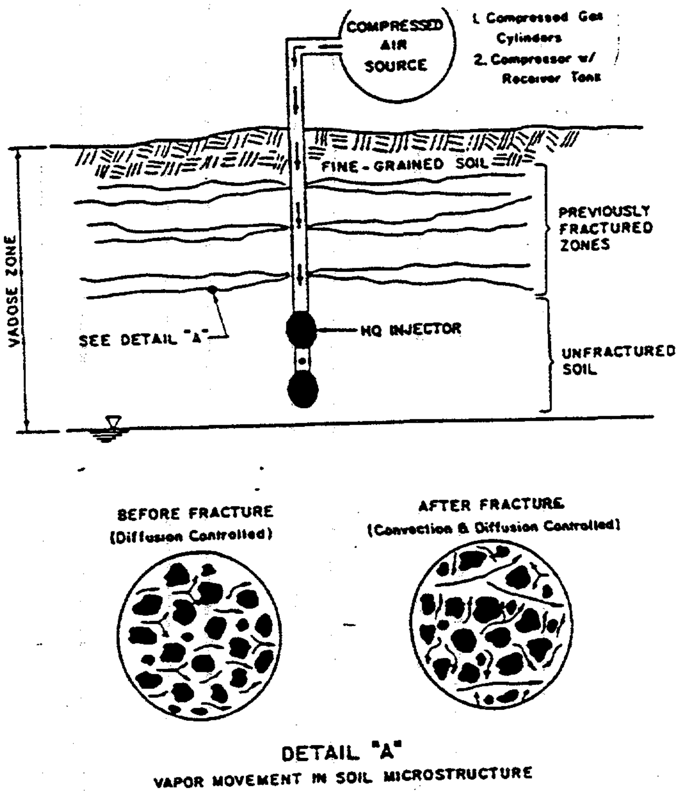
a. Introduction: Pneumatic fracturing is an innovative technology that enhances the in situ removal and treatment of contaminants from low permeability soil and rock formations. The process may be generally described as injecting air (or another gas) into a contaminated geologic formation at a pressure that exceeds the natural in situ stresses and at a flow rate that exceeds the permeability of the formation. This causes failure of the medium and creates a fracture network radiating from the injection point. Once established, the fractures increase the permeability of the formation, thereby increasing the flow rate of vapors and liquids for more efficient contaminant removal or treatment.

The principal objectives of pneumatic fracturing are reduction of treatment time and extension of available technologies to more difficult geologic conditions. Pneumatic fracturing is designed to be integrated with other in situ treatment technologies such as vapor extraction, bioventing, thermal injection, and pump and treat. Initial applications focused on enhancing treatment of the vadose zone, but recently the technology has been extended into the saturated zone. The pneumatic fracturing system has also been modified to deliver granular or liquid supplements (e.g. nutrients, innoculum, and reactive media) directly into the fractured formation to enhance in situ technologies such as bioremediation and thermal treatment.

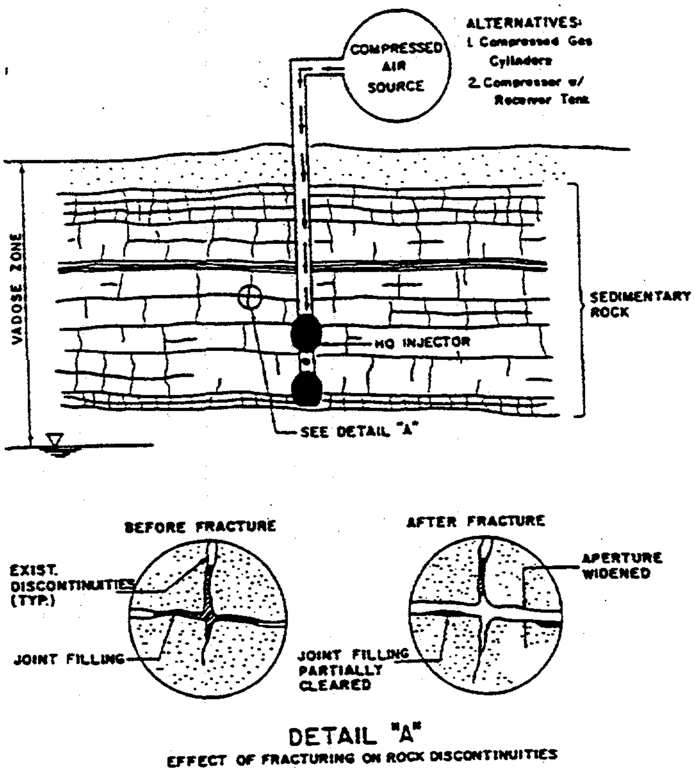
The effects of pneumatic fracturing on various formation geologies are shown conceptually in Fig. 1. For formations containing significant amounts of silt and clay, the process creates new convective pathways in the formation that increase permeability, and shorten diffusive distances (Fig. 1(a)). In sedimentary rock formations such as sandstone and shale, the process can dilate and extend existing discontinuities, thereby increasing permeability and improving interconnection (Fig 1. (b)). The pneumatic fracturing equipment can also be used in more permeable formations such as sand and gravel for rapid aeration and for injection of granular or liquid supplements.

Pneumatic fracturing is similar in concept to the hydraulic fracturing techniques applied in the petroleum industry and civil engineering for several decades. The principal difference is that pneumatic fracturing uses a gas to create the fractures, while hydraulic fracturing uses water, slurry, or other liquid agent. The theory and application of hydraulic fracturing are well established (e.g. Howard and Fast (1970) and Gidley, et al (1989)), and have been useful in understanding the new process of pneumatic fracturing. During the last several years, Murdoch (1989) has been developing hydraulic fracturing as an innovative delivery and recovery system for remediating contaminated sites.

The use of a gas as an injection fluid leads to some significant differences in the configuration of the equipment required to perform pneumatic fracturing, compared with hydraulic fracturing. The response of the geologic formation may also be different. These differences may be advantageous in certain situations since: (1) pneumatic fracturing does not need to introduce liquids into the formation which may tend to remobilize contaminants in the vadose zone; (2) pneumatic fracturing provides beneficial aeration and/or sparging during pneumatic injection; (3) pneumatic fracturing causes less permanent ground deformation, which may be of concern when fracturing in the vicinity of structures and utilities; and (4) pneumatic fracturing has a potentially greater production rate since the viscosity of the injection fluid is less.



(a) **Fine-grained Soil Formations**



(b) **Sedimentary Rock Formations**

Figure 1. Pneumatic Fracturing Concept.

The application of pneumatic fracturing involves two main considerations: (1) the mechanics of formation fracturing; and (2) contaminant transport through fractured media. An understanding of the first is essential to control and optimize the fracture network in the geologic formation. The latter aspect becomes important after the formation has been fractured, and it is desired to remove and/or treat the contaminants within the fractured network. These aspects are briefly described in Sections b. and c. which follow.

b. Mechanics of Pneumatic Fracturing: Fractures can be formed in geologic formations if air is injected at a pressure which exceeds the natural strength, as well as the in situ stresses present. The air must also be injected at a flow rate which exceeds the natural permeability of the formation so that sufficient "back" pressure can be developed. The orientation of the pneumatic fractures can be predicted by considering the direction of the major principal stresses present in the formation. Hubbert and Willis (1957) established in their study of hydraulic fracturing that fractures will tend to propagate perpendicularly to the direction of least principal stress. It follows that in overconsolidated formations where the least principal stress is vertical, horizontal fractures are favored. Conversely, in normally consolidated or underconsolidated formations, vertical fractures should result.

Since most surficial formations are overconsolidated due to past geologic events (e.g. overburden stress relief, desiccation, tectonic forces), horizontal fracturing may be expected to predominate. The tendency towards horizontal orientation is further accentuated in stratified formations, due to natural weaknesses along the bedding planes. Horizontal fractures at shallow depths may tend to curve upwards, however, as they extend outward (Nanendran and Cleary, 1983). Field observations are generally consistent with these theoretical considerations, since pneumatic fracture propagation has been predominantly horizontal. Some upward inclination has been observed in shallow recent fills, apparently owing lack of stratification and consolidation in these formations. In some cases, the inclined fractures have intersected or "daylighted" the ground surface.

The potential for downward migration of contaminants must be considered at DNAPL sites. Based on our present understanding of the mechanism of pneumatic fracturing in geologic formations, the risk of creating downward vertical fractures in small. This is consistent with field tests to date which have not shown any evidence of downward fracturing. Vertical fracturing has been limited to the immediate vicinity of the injection zone, ore in the overburden above the injection zone. Nevertheless, plume control below the fracture zone should be considered as a precautionary measure if it is not already in operation.

The amount of pressure required to initiate pneumatic fractures is a function of the cohesive strength of the formation, as well as the thickness of overburden. An expression for predicting pneumatic fracture initiation pressure has been developed by considering the geologic medium to be brittle, elastic, and overconsolidated. Assuming the formation has an effective unit weight, γ^1, and an apparent tensile strength, t_a, the fracture initiation pressure, P_i, at a depth, z, may be estimated by:

$$P_i = C\,\gamma^1 z + t_a + P_o$$

Where C is a coefficient (ranging from 2 to 2.5), and P_o is the hydrostatic pressure. Substituting typical values for clay soil and shale bedrock at a depth of 20 feet, the above expression yields initiation pressures of 50 psi and 150 psi, respectively. Fracture pressures are therefore relatively modest at shallow depth (where most of the contamination occurs), and are easily attainable with standard industrial compressed air equipment. This equation is for estimation purposes only, since a wide variation may be expected due to formation heterogeneities.

Injection flow rate is the parameter which largely determines the radial dimensions of pneumatic fractures. Once the fracture has been initiated, it is the high volume air flow which propagates the fracture and supports the formation. Field observations indicate that pneumatic fractures reach their maximum dimensions in less than 20 seconds, after which continued injection simply maintains the fracture network in a dilated state (in essence, the formation is "floating" on a cushion of injected air). Apparently, pneumatically induced fractures continue to propagate until they intersect a sufficient number of pores and existing discontinuities so that the fluid loss rate (leak-off) into the formation exactly equals the injection rate. In some cases the fractures may vent to the ground surface, which also causes loss of injected air. Experience indicates that injection rates of 1000 SCFM or larger are required to create satisfactory fracture networks in low permeability formations.

c. ***Fractured Media Flow and Transport:*** After a geologic formation has been pneumatically fractured, the ability to treat and/or remove contaminants will depend on the flow and transport characteristics of the fractured medium. When pneumatic injection is terminated, the fracture network constricts and the formation settles. Closure of the fractures is only partial, however, since most formations will exhibit a behavior known as "self-propping." This is attributed to both the asperites present along the fracture plane, as well as the block shifting which takes place during injection. The ability of a formation to self-prop will depend on the nature of the medium and the depth of fracture. Brittle geologic materials will prop better than more ductile geologic materials. Fracture injections at greater depths will exhibit less self propping, due to higher overburden pressures. For this reason, propping agents are commonly used in the petroleum industry for hydraulic fracturing of deep deposits.

The open, self-propped fractures resulting from pneumatic injection are capable of transmitting significant amounts of fluid. An approach for investigating the flow potential of individual fractures is the "parallel plate analogy" (e.g. Harr, 1962 and Ziegler, 1976). Using this approach, the functional relationship between flow, Q, and fracture aperture or thickness, b, can be represented by:

$$Q \propto b^3$$

where $\propto$ is the sign of proportionality. This relationship is known as the "cubic law". It emphasizes the high flow potential for even small fractures, since flow rate is proportional to the cube of the aperture. This accounts for the significant permeability increases which have been observed in pneumatically fractured formations.

This high flow potential is the principal reason why propping agents have not been routinely used with the pneumatic fracturing system to date. If the fracture is filled with a porous proppant, flow proportionality reduces to an area function, and there are higher friction losses. It can be easily shown with computations that a small "hairline" open fracture will have the same air flow potential as a much larger sand-filled fracture. Another disadvantage of using propping agents is the high viscosity of the injection fluid (typically water and sand slurry), which requires higher injection pressures. If desired, however, the pneumatic fracturing system can inject granular media into the fracture network for propping or other purposes.

Once a fracture network is established in a low permeability formation, aqueous and residual products in the vicinity of the fracture are more easily accessed, and in the case of vapor extraction, they are removed rapidly through volatilization. It is expected that fracture distribution in a formation will not be totally uniform, however, due to the heterogeneities present in all geologic formations. Unfractured matrix blocks will remain between adjacent fractures, and will contain residual and absorbed contaminant which can only be removed by diffusion. Since diffusive distances are shortened by pneumatic fracturing, contaminant removal will proceed more rapidly than if the formation had not been pneumatically fractured. Contaminant transport out of the matrix blocks will continue as long as air flow is maintained through the fracture network, and vapor concentrations at the fracture and matrix interface are kept low enough to cause outward diffusive gradients. The spacing of the pneumatically induced fractures will vary according to geology, but should generally be produced on the order of one to two feet.

It is noted that highest contaminant concentrations usually occur within and adjacent to existing structural discontinuities in the formation (e.g. joints, cracks, bedding planes). Since pneumatic fracturing dilates and interconnects existing discontinuities, direct access is provided to a majority of the contaminant mass. It is speculated that in these situations the diffusive processes in the matrix blocks will become less important, and it may be possible to meet target concentrations without cleaning the blocks completely.

2.0 GENERAL TECHNOLOGY CONSIDERATIONS

a. ***Types of Soil/Rock Treatable:*** The texture and structure of the geologic formation is the most important consideration in the application of pneumatic fracturing. The technology has been successfully demonstrated in several different low permeability formations to date (See Section 6.0,. "Case Histories," for more details). Based on the results of these tests, the types of soil and rock listed below are considered treatable with the technology.

Silty Clay/Clayey Silt
Sandy Silt
Silty Sand
Clayey Sand
Cemented Sands
Shale*
Siltstone
Sandstone
Limestone*

* Tests have not yet been conducted in these formations, but it is anticipated that pneumatic fracturing could be successfully applied.

Notes:
(1) Most of the formations listed above are typically stratified, and/or overconsolidated. The predominant fracture direction is therefore expected to be horizontal.
(2) When the pneumatic fracturing system is used for rapid aeration or injection of biological supplements, permeable formations such as sand and gravel are also considered treatable, although they are not listed above.

The amount of permeability increase observed in pneumatically fractured formations to date has varied from 3 to more than 1000 times. A review of the data indicate that soil grain size and formation structure are the most important factors in determining the degree of improvement. In general for soils, the observed permeability increases have been inversely proportional to grain size. A probable explanation is the existence of an upper permeability limit for pneumatically fractured formations. Hence, a massive silty clay will exhibit a dramatic permeability increase simply because it has a very low initial permeability.

Conversely, the potential increase for a silty sand is less, since it already has a moderate permeability.

Pre-existing fractures in a formation can affect the propagation of pneumatic fractures. In rock formations, the principal effect of pneumatic fracturing is dilation of existing fractures, since the injection pressures are not sufficient to fracture intact rock. Therefore, the frequency and orientation of existing discontinuities will largely control fracture patterns. In soil formations, the presence of existing fractures is probably less important since the solid soil matrix can be easily fractured by pneumatic pressures. Thus, in soil formations, the direction of the principal stresses and the fracture depth are more significant in the determination of fracture direction.

To evaluate a site for pneumatic fracturing, exploratory borings with continuous sampling or coring should be drilled. The following geotechnical evaluations should be performed as applicable:

Soil Formations:

- Detailed visual examination of sample to assess structure including stratification, friability, secondary cracking, and inclusions
- Grain size analysis
- Natural moisture content
- Location of water table and perched water zones
- Plasticity testing - Atterberg limits
- Cohesion testing - unconfined compressive strength
- In situ permeability testing, e.g., slug, vapor extraction, pumping (highly desirable and often available from past site evaluations)

Rock Formations:

- Detailed visual examination of sample to assess lithology, joint frequency and orientation, joint filling, natural bedding and degree of weathering
- Location of water table and perched water zones
- In situ permeability testing, e.g., slug, vapor extraction, pumping (highly desirable and often available from past site evaluations)

If the geotechnical evaluation indicates the technology is applicable, a pilot test should be performed to establish actual fracture behavior in the formation.

b. Effect of Soil Water: Pneumatic fracturing has been performed in the vadose, perched and saturated ground water zones. Field testing, coupled with laboratory analysis of soil samples, has led to the following observations on the effects of soil water:

1) Dry to moderately moist soils - These soils seem to respond well to pneumatic fracturing (e.g. Pisciotta et al., 1991 and Schuring et al., 1991). Such soils behave brittlely when subjected to rapid pneumatic injection, and post-fracture subsurface air flows are significantly higher than pre-fracture air flows. For soils containing clay, brittle fracture behavior may be expected at moisture contents near or below the plastic limit of the soil.

2) Stiff silty and clayey soils with high moisture contents - Experience indicates that these soils can be successfully fractured. However, post-fracture air flows in soils nearing the saturation point will be retarded by moisture in the pores and fractures. Pneumatic fracturing can be used to control the perched water zones frequently encountered in low permeability formations, since the fracture network creates an efficient drainage path.

   In fully saturated formations, significant increases in water pumping rates have been observed, indicating that fractures can remain viable under the water table in stiff soils. Further evidence of viability was provided during a long term study performed in a stiff clayey silt formation exposed to a natural cycle of saturation (Schuring and Chan, 1992). Air flows measured in the fracture network after the saturation and drying cycle were similar to those observed before saturation. Data on pneumatic fracturing applications in saturated soils are still limited, and further research and testing are necessary.

3) Soft silts and clays with high moisture contents - There has been minimal experience with pneumatic fracturing in soft, saturated clays and silts. These soils will behave very plastically, and relatively rapid fracture closure and healing could be a problem. In addition, these soils are not self-stable and preclude operation in an open borehole. The single experience in this type of soil showed an airflow increase of approximately three times as a result of fracturing.

4) Rock formations, unsaturated and saturated - The presence of moisture in consolidated rock formations does not appear to affect the pneumatic fracturing process: A siltstone formation was fractured within a saturated, perched water zone, and excellent results were recorded (U.S. EPA 1993). Once fractured, the treatment zone was quickly dewatered owing to its enhanced permeability, and vapor extraction was applied to the newly formed vadose zone.

c. ***Depth Range:*** The effective depth range of pneumatic fracturing with present process equipment is estimated at 3 to 60 feet. Minimum depth is controlled by the ability to form a top seal during injection, and also by the tendency of fractures to intersect or vent to the ground surface. Whether or not shallow fractures will vent is related to the compaction history. For example, fractures created in a stratified clayey silt formation remained horizontal and did not intersect the ground surface at injection depths as shallow as 3 feet. In contrast, fracture injections made at a 6 foot depth in fill materials formed inclined fractures (upwards at 10 to 25 degrees from horizontal) that vented at the ground surface at some locations.

There is no theoretical maximum depth limit for initiating pneumatic fractures, as long as sufficient pressure and flow can be delivered to the fracture zone. Considering the required pressure and depth gradient to initiate fractures, the depth limit with the present system is approximately 60 feet. Higher capacity equipment is planned for the future.

An important consideration for deeper applications will be fracture closure due to excessive overburden stress, since proppants are not presently used in the pneumatic fracturing process. To date, the deepest application has been 40 feet, which yielded substantial increases in post fracture permeability. The practical depth limit for pneumatic fracturing is not known at this time, and will likely vary with geological conditions.

d. ***Effective Radius:*** The radial extent of fractures has been monitored by: (1) air communication with outlying monitoring wells; and (2) ground surface heave. Available field data indicate that the effective radius of pneumatic fractures with the present system have typically ranged between 10 and 25 feet measured from the point of injection.

"Effective radius" refers to the radial distance at which significant enhancement in permeability was observed, even though the fractures may actually have extended further. The radius of pneumatic injections will vary according to geology and moisture conditions. In general, rock formations have exhibited larger radii than soil formations, which is attributed to their differing stiffnesses. Soil behaves more plastically resulting in local yielding around the injection point. Rock is more rigid and tends to extend the radius of fracture.

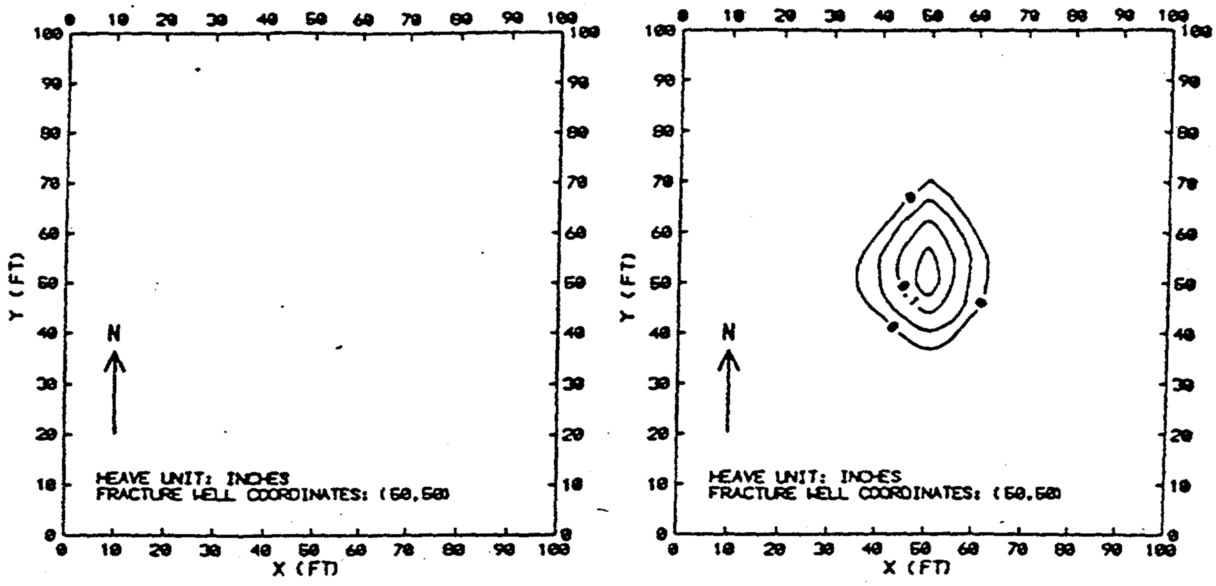
When a fracture pattern is examined in plan view, most fracture planes exhibit an elliptical shape. A typical series of surface heave contours recorded by electronic tiltmeters for a pneumatic injection in a siltstone formation are shown in Fig. 2 (U.S. EPA 1993). At this particular site the fractures exhibited a slight preference along the geologic strike of the formation (formation strike is perpendicular to the bedding dip). The figure also indicates that maximum radius was achieved in less than 20 seconds. Most sites have displayed some directional preference that is apparently related to site geology. Other factors that can affect fracture direction are surface structures and buried utilities.

More experience is required before fracture direction can be adequately predicted. Field tests with a directional nozzle which "forces" fracture propagation in a specific direction have been successful. It is also possible to steer fractures by positioning a surface load adjacent to the injection hole. At this stage in development, a field pilot test is necessary to determine fracture behavior at a particular site.

e. ***Contaminants Treatable:*** Since pneumatic fracturing is an enhancement technology, the types of contaminants that are treatable depend on which other technologies are being used. For example, vapor extraction is applicable to volatile and semivolatile organic compounds, while bioremediation is theoretically capable of degrading any organic compound. Integration of pneumatic fracturing with these technologies will not change their basic applicability, but it may extend the range of contaminants treatable. For example, pneumatic fracturing may make thermal injection feasible at a vapor extraction site by improving the heat flow and transfer characteristics of the formation. As a result, compounds with lower vapor pressures would become treatable with vapor extraction. Similarly, the ability to inject biological solutions containing microbes and nutrients directly into a geologic formation may extend the range of organic contaminants treatable with bioremediation.

f. ***Fracture Longevity:*** Studies are being conducted at several sites to assess the long term viability of pneumatic fractures. Since pneumatic fractures are open and self-propped in most applications, it is possible that they can constrict over a period of time, thereby reducing their effectiveness. A study performed in a siltstone formation showed that the enhanced permeability due to pneumatic fracturing was still present after 29 months. The site was located in a parking lot that was subjected to heavy truck traffic throughout the study period.

A longevity study 52 weeks in duration was performed in a clayey silty soil formation. After experiencing some initial partial closure, fractures still remained viable at the end of the study period with permeabilities measuring 19 times greater than pre-fracture values. It was further observed that air flow through the fracture network was inversely proportional to moisture content.



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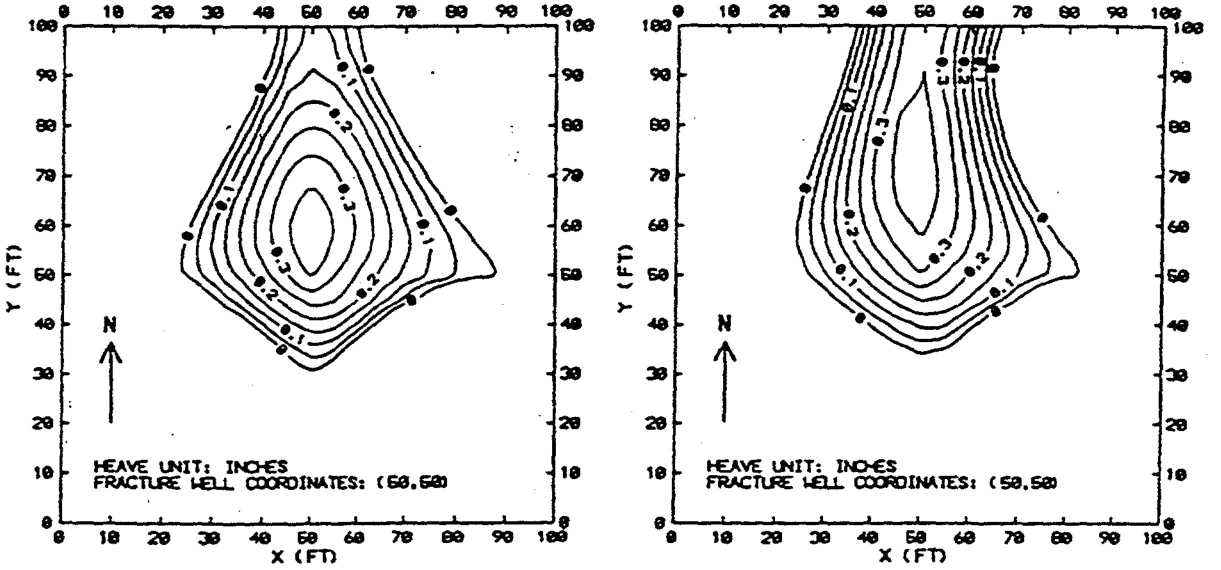
TIME = 1.5 SEC



TIME = 9 SEC

TIME = 14 SEC

FIRST FRACTURE INJECTION
DEPTH: 9.0 TO 11.2 FT
DURATION: 20 SECONDS DATE: 8/20/92

Figure 2. Surface Heave Contours for Pneumatic Injection in Siltstone.

Based on the results of these and other ongoing tests, it appears that fracture viability is related to: (1) the texture and plasticity of the geologic media; (2) moisture variations in the formation; and (3) the type of remedial process being integrated with the fracturing. At some sites, a single pneumatic fracture injection event will suffice. At other sites, depending on the duration of the remediation, one or more repeat injections may be necessary to optimize the removal and/or treatment of contamination.

g. ***Applicability Near Structure and Utilities:*** Pneumatic fracture injections cause deformation and heaving of the geologic medium under treatment. Peak ground surface heave observed during the actual injection event (which lasts about 30 seconds) have ranged from 1/8 inch to 2 inches. These values are typically observed at the injection point, and heave magnitude tapers to zero with increasing radius. The "residual" heave recorded after termination of the injection typically ranges between 10% and 20% of the injection heave (Schuring and Chan, 1992). The presence of residual heave indicates that the structure and density of the formation have been altered and is the principal reason why pneumatic fracturing is effective in increasing subsurface permeability.

The magnitude of ground surface heave will depend on the depth of injection, as well as the formation geology. Since soil and rock are deformable media, the actual fracture dimensions are larger than the observed surface heave, as some heave is absorbed by the formation as elastic strain. Elastic theory indicates that the observed surface heave should vary as the inverse square of the depth. At shallow depths, however, the formation does not behave as a totally elastic medium, and less attenuation with depth may be expected.

The potential effects which pneumatic fracturing can have on nearby structures and utilities depends on the type of construction and the magnitude of ground deformation. To date, only a limited amount of fracturing has been conducted beneath or adjacent to structures and utilities. Caution is recommended when applying pneumatic fracturing in close proximity to critical facilities until more experience is gained.

3.0 REMEDIATION CAPABILITY: NATURALLY FRACTURED MASSIVE TIGHT SOILS

This section speculates on the ability of pneumatic fracturing to remediate a naturally fractured massive tight soil. The site scenario is described as follows:

- Clay stratum 30-50 meters thick, areally extensive
- Water table depth 1-3 meters
- Upper 2 meters of clay is highly weathered due to desiccation
- Natural fractures spaced 1-100 centimeters, primarily vertical
- Natural fractures have 10-40 micrometer apertures
- Clay blocks between fractures are saturated (i.e. there are no continuous air pathways)
- Effective air-filled porosity is <1%
- DNAPL contamination

a. ***Removal Effectiveness:*** This is a challenging geologic formation to remediate in situ, and standard technologies would likely be ineffective without permeability enhancement. Pneumatic fracturing has demonstrated a capability to fracture tight clay formations, and increase subsurface air flow substantially. At this site, pneumatic injections should be capable of creating new fractures in the clay blocks, as well as dilating existing natural fractures. The overall effectiveness at this site will depend on whether horizontal fractures can be adequately initiated and propagated at the relatively shallow depth of contamination. It is possible that existing vertical fractures will cause surface venting in the vicinity of the injection point, resulting in limited fracture radii. Orientation of pneumatic fractures will depend on the direction and magnitude of the geostatic stresses, as well as the existing fractures of the soil. A careful examination of soil cores extracted from the site would be helpful in assessing soil structure. Final prediction of soil fracture behavior could only be determined by a field pilot test.

Pneumatic injections in this formation are expected to dilate existing continuous fractures, as well as connect and dilate discontinuous fractures. This will improve access to DNAPL trapped in the natural fractures, thereby increasing removal rate. Removal of contaminant that has diffused into the matrix blocks is more difficult, since transport will be diffusion-controlled. The shortened diffusive distances resulting from the new pneumatic fractures should accelerate contaminant removal. Diffusion rates will also benefit from an overall increase in air flow through the formation. Dual extraction (vapor and water) from wells will be necessary, since the enhanced fracture network will release perched water from the clay.

b. ***Complementary Technologies:*** At this site, pneumatic fracturing could be integrated with any of several in situ technologies. In fact, it is important to proceed aggressively with removal and/or treatment activities immediately after fracturing, to avoid possible spreading of contamination. One approach might be to fracture the formation, and then apply vapor extraction with forced injection of hot air. The heated air would encourage additional drying which could further crack the clay matrix blocks. It may be necessary to provide an impermeable cover over the site to prevent short-circuiting of the vapor extraction system. Long-term treatment with bioventing may also be feasible at this site. In this case, pneumatic fracturing could be used not only for permeability enhancement, but also to inject biological supplements directly into the formation. It would also be possible to inject reactive media such as powdered iron into the fracture network.

4.0 REMEDIAL CAPABILITY: CONTINUOUSLY STRATIFIED LOW PERMEABILITY SOILS

This section speculates on the ability of pneumatic fracturing to remediate a continuously stratified low permeability soil formation. The site scenario is described as follows:

- Stratified layers ranging from medium sand to silt
- Water table depth 3-4 meters
- Soil is relatively dry with continuous pathways in both the silt and sand
- Sand behaves like a porous media
- Silt has some preferential pathways (obviously the sand, also)
- Total porosity is 0.3; effective air-filled porosity is 0.2 (33% saturation)
- DNAPL contamination

a. ***Removal Effectiveness:*** Pneumatic fracturing is expected to be effective in this formation. The soils will behave brittlely due to their low moisture content, and fracture patterns should be predominantly horizontal owing to the stratified nature of the formation. The resulting fracture nets should improve access to the contaminants, and shorten diffusive paths. New fractures in the low permeability silt zones would accelerate removal of trapped aqueous product. The high pressure injection may also cause some shifting and disturbance of the sand, resulting in air flow improvement in the coarser zones. The ability to remove residual and absorbed product should be enhanced owing to increased formation air flow, although pneumatic fracturing will not affect these phases directly. Improvement of contaminant removal from isolated lenses would depend on how close they are to the injection point, and whether or not they have been intersected by fractures. Even if the isolated lenses are not fractured, they should benefit from the overall increase in formation air flow.

b. Complementary Technologies: At this site, pneumatic fracturing could be integrated with any of several in situ technologies. In fact, it is important to proceed aggressively with removal and/or treatment activities immediately after fracturing to avoid possible spreading of the contamination. Vapor extraction with vertical wells could be effective, especially if combined with air injection to accelerate air flow. Thermal injection may provide significant benefits, especially if the contaminant has a low vapor pressure. Bioventing could also be applied at this site, with pneumatic fracturing used not only for permeability enhancement, but also to inject biological supplements directly into the formation. Reactive media such as powdered iron could also be injected into the fracture network.

5.0 COMMERCIAL AVAILABILITY AND COST

a. Commercial Status: Pneumatic fracturing has been pilot tested at several sites over the last 3 years, including a U.S. EPA SITE Demonstration performed in August 1992. While the concept has been successfully demonstrated in the field, pneumatic fracturing is considered to be an emerging technology in the early stages of commercialization. Pneumatic fracturing has been recommended in several clean-up plans, and has been applied on a production basis at three contaminated sites. Pneumatic fracturing is a patented process, and the assignee is the Hazardous Substance Management Research Center at the New Jersey Institute of Technology.

At present, there is one company licensed to perform pneumatic fracturing: Accutech Remedial Systems, Inc. (ARS) of Keyport, N.J. It is a non-exclusive license, and discussions are underway with other potential licenses. Accutech has incorporated the technology into their remedial process known as Pneumatic Fracturing Extraction (PFE). A fully mobile, production version of the PFE system is presently available, with equipment capable of up to 20 pneumatic injections per day. A considerable amount of commercial activity and research is planned with the PFE system over the next 12 months.

A pilot test is always recommended to determine the effectiveness of the pneumatic fractures for a particular site. The test provides critical site specific data which are necessary to design the full scale remediation. Accutech offers a turnkey pilot test throughout North America for costs ranging from $35,000 to $45,000.

For future information on the PFE system, contact:

Mr. John J. Liskowitz
Accutech Remedial Systems, Inc.
Cass Street at Route 35
Keyport, N.J. 07735
Phone: 908-739-6444
Fax: 908-739-0451

b. Production Considerations: Pneumatic fracturing is a productive process that is easily integrated with other remediation activities. It will most often be applied as pretreatment to increase formation permeability during the initial stage of a clean-up. Common applications are expected to include: (1) pre-fracturing of new extraction and injection wells during their construction; (2) stimulating flow in existing wells; and (3) improving the uniformity and direction of formation flow. In some cases, it may be necessary to refracture the formation at a later time, depending on formation geology and projection duration. Repeat injections may also be appropriate at bioremediation sites for periodic replenishment of biological supplements.

The actual process of pneumatic fracturing is relatively rapid, and good field productivity is achievable. An individual pneumatic injection is accomplished by: (1) positioning a proprietary device known as an "HQ Injector" in the fracture well which seals off a discrete one to two foot interval; (2) application of pressurized air for approximately 30 seconds; and (3) repositioning the HQ Injector to the next elevation and repeating the procedure. A typical cycle takes between 10 and 15 minutes, depending on the amount of time to move the injector vertically within the same hole and horizontally from hole to hole. A production rate of 20 fractures per day is considered attainable with one rig, although pilot studies typically proceed at a slower rate to allow time for more precise measurements.

c. Estimated Time and Cost to Remediate a 100' x 100' x 15' Site:

Situation

Consider a hypothetical site 100' x 100' x 15' in stratified fine-grained media containing TCE which has diffused into the low permeability matrix blocks at concentrations of 1000 ppm. The concentration must be reduced to 200 ppm.

Production Time and Cost

Assume that wells will be installed on a 20 ft. grid, for a total of 25 wells. The primary extraction method will be vapor extraction supplemented with hot gas injection. It is presumed that each well will be pneumatically fractured during its construction at 2 ft. intervals ranging from depths of 3 to 15 feet. The following is an estimate of the *incremental cost of pneumatic fracturing in excess of primary remediation.*

No. of Pneumatic Fracture Injections = 25 wells X 6 injections X 1.5 (to allow for multiple injections at selected levels)

Injections per well = 225 injections

Production Time = 2 days mobilization + $\dfrac{\text{225 injections}}{\text{20 injections per day}}$ + 1 day demobilization

= 15 days (assumes one rig) = 3 weeks

Production Cost = 3 weeks x $13,200 per week

= $39,600

Unit Cost = $39,600/(100'x100'x12')/27 = $8.91 per cubic yard

Notes: (1) Weekly cost includes $7,200 for equipment and $6,000 for labor.
(2) Monitoring will be performed for operational purposes only.

Reduction in Remediation Time

The actual reduction in remediation time for this site resulting from pneumatic fracturing is difficult to estimate since a full production clean-up has not yet been completed. The time savings will obviously be related to the amount of permeability and mass removal enhancement observed after fracturing, which is estimated to be in the range of 10 to 100 times for fine-grained sediments. The actual proportion of time saved will likely not be as dramatic, owing to the diffusion-controlled contaminant release from the unfractured portions of the matrix blocks. Significant reduction in treatment time compared with standard methods should still be realized, however, which will reduce operating costs.

Additional cost savings will be realized since pneumatic fracturing will reduce the number of extraction wells required, compared with the no-fracture alternative. Also, power and pumping requirements will be reduced, resulting in lower operating costs.

6.0 CASE HISTORIES

6.1 Case No. 1

Location: ECRA Site, Hillsborough, N.J. (U.S. EPA SITE Demonstration)

Geology:
- Triassic sedimentary beds: Siltstone and Shale, moderately fractured
- Vadose zone with perched water

Contaminants: Primary: Trichlorethylene (TCE) Secondary: Other chlorinated solvents and benzene

Technology:
- Enhancement of vapor extraction and thermal injection
- One central vapor/fracture well and seven peripheral monitoring wells

Duration: Periodic testing throughout a three week period. Maximum continuous extration 3 days.

Fracture Depth Range: 9.0 to 16.4 ft.

Permeability: Config. 1: Permeability increased 8 times (all peripheral wells sealed)
Config. 2: Permeability increased 175 times (four peripheral wells opened for passive inlet)

Mass Removal: Config. 1: TCE mass removal increased 8 times (all peripheral wells sealed)
Config. 2: TCE mass removal increased 25 times (four peripheral wells opened for passive inlet)
Note: Permeability and mass removal values were averaged over 8 hours

Fracture Dimensions: Monitoring wells confirmed that effective fracture radius was at least 20 feet. See Table 1 below for summary of vaccum influence and permeability tests for each monitoring well. Electronic tiltmeter data showed up to 35 foot radii based on ground surface heave measurements.

Comments: A review of the tiltmeter and monitoring well data showed that fracture orientation was predominantly horizontal, with a slight directional preference along the geologic strike of the formation. Direct examination of the pneumatically induced fractures with a borehole video camera showed that permeability enhancements were largely due to dilation of existing geologic discontinuities, although some new fractures were formed. Analysis of extracted effluent after fracturing showed unusually high concentrations of other VOCs that had only been detected in trace amounts before fracturing. This suggested that pathways were opened to new pockets of contamination.

Table 1 - Summary of Monitoring Well Results

Monitoring Well No.	Distance To Fracture Well (ft.)	Geologic Orientation	Vacuum Influence (in. H_2O)			Extracted Air Flow (SCFM)		
			Pre-fracture	Post-fracture	Change Ratio	Pre-fracture	Post-fracture	Change Ratio
FMW-1	10	Strike	7.5	92	+12.3	0.62*	5.2-6.4	8.3-10.2
FMW-2	10	Off Strike & Dip	4.5	93	+20.7	0.62-0.88	5.2-7.0	5.9-11.3
FMW-3	10	Dip	23	92	+4.0	0.62*	5.1-9.4	8.2-15.1
FMW-4	10	Strike	14	92	+6.6	0.62*	5.7-8.1	9.2-13.1
FMW-5	20	Strike	0	77	(+77)	0.62*	5.5-7.5	8.8-12.0
FMW-6	7.5	Dip	44	90	+2.0	0.88	4.8-7.1	5.5-8.1
FMW-7	20	Dip	0	81	(+81)	0.62*	1.9-2.0	3.1-3.2

Notes:
1. All values are for 136 in. H_2O (10 in. Hg) vacuum applied at pump.
2. (*) denotes flow gage was at minimum reading. Actual pre-fracture flow was less.
3. Data for vacuum influence taken 30 minutes after start-up.

6.2 Case No. 2

Location: AT&T Richmond Works, Richmond, Va.
Abandoned Tank Farm

Geology:
- Miocene marine sediments: Silty Clay (CH-MH)
- Vadose zone

Contaminants:
- Methylene Chloride ($MeC1_2$) and Trichlorethane (TCA)

Technology:
- Enhancement of vapor extraction
- One central extraction well and four peripheral monitoring wells. Separate fracture well.

Duration: 3 days

Fracture Depth Range: 7 to 11 ft.

Permeability: Vapor well: Permeability increased 1000+ times (pre-fracture flow below gage sensitivity)

Mass Removal: Vapor well: Peak concentrations increased approx. 200 times.

Fracture Dimensions: Max. Radius 12+ ft. (fractures extended beyond monitoring wells and heave sensors)

Comments: Concrete slab and containment wall located over injection area. Minor widening and extension of existing cracks noted in concrete.

8.3 Case No. 3

Location: ECRA Site, Roseland, N.J.

Geology:
- Fill overlying glacial fluvial sediments: Clayey and Silty Sands, trace gravel
(SC, SM-SC)
- Interface of vadose/saturated zone

Contaminants: - DCA, DCE, and TCA

Technology: - Enhancement of vapor extraction

Duration: one month

Fracture Depth Range: 4 to 7 ft.

Permeability: Vapor well: Permeability increased 2+ times (flow gage pinned)

Mass Removal: Vapor well: Total VOC's increased 25+ times (flow gage pinned)

Fracture Dimensions: Max. Radius 27 ft. Some fractures daylighted the ground surface.

Comments: A fracture injection was made 9 feet away from a one story warehouse building. The building was monitored for movement and damage but none was observed. Surface heave data showed fractures reflected away from the structure.

6.4 Case No. 4

Location: Frelinghuysen Township, N.J.

Geology:
- Glacial lacustrine: Clayey Silts and Sandy Silts (CL-ML)
- Vadose and saturated zone

Contaminants: - "Clean" Site

Technology: - Enhancement of vapor extraction. Various well configurations.

Duration: Periodic testing up to present. A seven month study performed to examine fracture longevity.

Fracture Depth Range: 3 to 9 ft.

Permeability: Fracture wells: Permeability increased 50 to 200+ times depending on test conditions
Vapor wells: Permeability increased 1.4 to 50+ times depending on test conditions
Note: (+) denotes that flow gages were pinned. Actual maximum flows were larger.

Fracture Dimensions: Range of radius: 7 to 16 ft.

Comments: Most of the prototype developmental work was performed at this site. A seven month study was performed to examine fracture longevity, and assess the effect of rainwater infiltration. After experiencing some initial partial closure, fractures still remained viable after 27 weeks with permeabilities measuring 19 times greater than pre-fracture values. Fractures subjected to a saturation cycle due to a fluctuating water table during the study period regained their enhanced permeability upon drying. Air flow was found to be inversely proportional to moisture content.

6.5 Case No. 5

Location: New Jersey Institute of Technology Campus, Newark, N.J.

Geology: - Triassic sedimentary beds: Siltstone and Sandstone, moderately fractured
- Vadose zone

Contaminants: - "Clean" Site

Technology: - Enhancement of vapor extraction with single extraction/fracture well. No monitoring wells.

Duration: Periodic testing up to present. A eight month study performed to examine fracture longevity.

Fracture Depth Range: 9 to 17 ft.

Permeability: Permeability increased 5 to 14 times (sealed system with no passive inlets).

Fracture Dimensions: Max. radius: 10+ ft (fractures extended beyond heave sensors)

Comments: An eight month study was performed to examine the effect of fracture longevity. Fractures remained viable after 34 weeks with no detectable change in enhanced permeability. The site was located in a parking lot that was subjected to car and truck traffic throughout the study period.

7.0 SUMMARY

Pneumatic fracturing is an innovative technology that enhances the removal and treatment of contaminants in low permeability formations. The main advantages are reduction in treatment time and extension of available in situ technologies to more difficult geologic conditions. In low permeability formations, pneumatic injections create a network of open, self-propped fractures that increase formation air flow and shorten diffusive distances. The process can also be used for rapid aeration of high permeability formations and for injection of biological supplements. Injection flow rate is the most important system parameter which determines the extent of fracture propagation.

This technology is applicable to a variety of fine-grained soil formations and sedimentary rock formations. Observed permeability increases due to fracturing have ranged from 3 to more than 1000 times. Fracture orientation has been predominantly horizontal, and effective radii have ranged from 10 to 25 feet. To date, pneumatic fractures have been initiated at depths ranging from 3 to 40 feet. Present equipment is capable of establishing fractures to a depth of about 50 feet. In certain geologic conditions, excessive moisture may affect fracture effectiveness and development of subsurface air flow. Experience with pneumatic fracturing in the vicinity of structures and utilities is still limited, and caution is recommended when applying the technology in close proximity to critical facilities.

Pneumatic fracturing has been successfully demonstrated at the field pilot scale in several different geologic formations, and the technology is now commercially available. Pneumatic fracturing has been incorporated into production clean-ups at a few sites, but the technology is still considered to be emerging. The actual process of pneumatic fracturing is relatively rapid, and good field productivity is achievable. Pilot testing is recommended to evaluate the effectiveness of pneumatic fracturing at potential sites.

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STEAM INJECTION FOR *IN-SITU* REMEDIATION OF DNAPLs IN LOW PERMEABILITY MEDIA

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Sponsored by
U.S. Department of Energy
and
American Petroleum Institute

Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

The potential for remediation of dense, nonaqueous phase liquid (DNAPL) contamination by steam injection is investigated, including the advantages and disadvantages of the technology. The primary advantage is the significant enhancement of removal rates through steam distillation. The disadvantages are related to the lack of field experience with the technology and difficulties related to steam override and channeling in heterogeneous soils. The problems related to steam injection in low permeability fractured clay are examined, and removal times and costs are postulated for a hypothetical DNAPL contamination scenario. It is concluded that steam injection has significant potential for remediation of DNAPL in fractured clay soils, but there is significant uncertainty in predictions of the performance of steam injection in these soils.

2.0 INTRODUCTION

Steam injection was first used for tertiary petroleum recovery in 1933 (White and Moss, 1983), and is still widely used today, particularly for recovery of heavy oil from tar sands. In recent years steam injection has been identified as a promising technique for removing DNAPL contaminants from the subsurface (Hunt *et al.* 1988) but has not yet been widely used on a commercial scale for remediation. It is therefore instructive to examine the mechanisms and techniques of steam injection as applied to petroleum recovery, since there are many parallels between petroleum recovery and DNAPL remediation.

Steam injection assists in recovery of viscous oils primarily by reducing oil viscosity, allowing more effective displacement of oil toward recovery wells. In addition, production is increased by thermal swelling of oil, by steam distillation of light components of oil, by a gas drive resulting from the steam flush, and from a solvent dilution effect caused by the condensation of light ends in front of the steam zone (Butler, 1991). There are two primary modes of steam injection employed in the petroleum industry: cyclic stimulation, and steamflooding. In cyclic stimulation steam is injected into the reservoir for a period of weeks, to heat up the reservoir. The injection well is then pumped to remove the heated fluids. This process is repeated several times until recovery rates drop below the economic recovery rate. In steamflooding steam is injected continuously into the reservoir from one or more wells, and the oil is pushed horizontally to extraction wells. One of the shortcomings of this method is the tendency of steam to rise, leading to steam override and bypassing of the target zone. The steam assisted gravity drainage process was developed to avoid the steam override process. In the steam assisted gravity drainage process steam is injected close to, but above, a production well. The injected steam rises, creating a steam zone that expands upwards and outwards. Heated oil and condensed steam flow downward, and are captured by the production well.

The DNAPL remediation process differs from the petroleum recovery process in a number of ways. Complete DNAPL removal is required for groundwater remediation, rather than an incremental increase in oil recovery. Remobilization of DNAPL, leading to increased groundwater contamination, is not an acceptable consequence of DNAPL remediation. DNAPLs tend to be located near the ground surface at low, discontinuous saturations. In addition, most DNAPLs have viscosities near that of water, and many have relatively low boiling points. These factors must be considered when examining the important mechanisms in DNAPL remediation by steam injection.

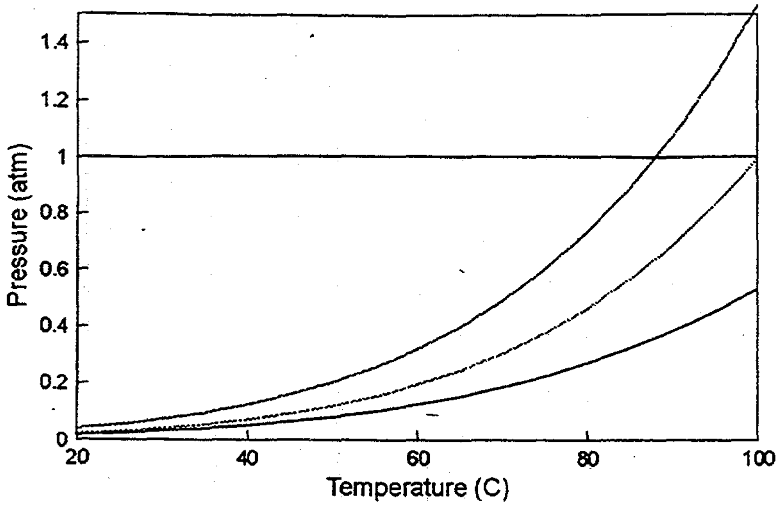

Figure 1. Variation of Vapor Pressure with Temperature for Water and PCE.

3.0 DESCRIPTION OF THE TECHNOLOGY

Steam injection enhances removal of both LNAPLs and DNAPLs primarily through steam distillation (Hunt *et al.* 1988). When steam is injected into soil the steam initially condenses and gives up latent heat to raise the temperature of the soil and pore fluids. As the temperature of the soil increases the vapor pressures of the pore fluids are increased. If steam is being injected into the vadose zone this results in an increase in the vapor phase concentrations of water and of other liquids, such as organics, present in the soil. If the steam is being injected into liquid-saturated soil a vapor phase is formed at a particular location when the sum of the vapor pressures of the liquid phases present exceeds the in situ liquid pressure. The composition of the vapor phase formed with steam injection will be a function of temperature and of the fluids present. The total gas phase pressure, P_g, is the sum of the partial pressures, P_i, of the n_c individual compounds present:

$$P_g = \sum_{i=1}^{n_c} P_i$$

An example of the variation of water and PCE vapor pressures with temperature is shown in Figure 1.

The partial pressure of a compound in a multicomponent liquid phase is often assumed to be related to the mole fraction, x_{ip}, of the compound in the liquid phase(water or organic) by:

$$P_i = x_{ip} P_i^v$$

where P_i^v is the pure component vapor pressure.

The gas phase mole fraction, x_{ig}, of a compound is given by:

$$x_{ig} = \frac{P_i}{P_g}$$

Thus, compounds that have higher vapor pressures at steam injection temperatures will have higher mole fractions in the vapor phase and will be preferentially stripped from the liquid phases present in the soil, in the same way as more volatile compounds are preferentially removed by soil venting. The efficiency of steam injection for mobilizing a particular organic compound through volatilization is thus a function of the compounds volatility. Volatile compounds may be volatilized effectively, while compounds with lower vapor pressures will be volatilized at much lower rates. Table 1 gives a list of a few organic compound's, their vapor pressures, and the gas phase mole fractions that would be expected in a steam injection operation with an *in situ* temperature of 100°C.

When steam is injected continuously into the subsurface, volatilizing water and organic compounds, a steam zone is formed, with a propagating condensation front. In the steam zone the amount of water remaining in the soil pores depends on the injected steam quality, temperature and pressure. At the condensation front a bank of condensed DNAPL forms and moves ahead of the steam front towards an extraction well. Although the DNAPL may have originally been distributed at residual saturation levels, and was thus immobile, the DNAPL saturations in the DNAPL bank will generally be above residual levels, and the DNAPL bank will be mobile. This raises concerns about vertical remobilization of DNAPL. One can easily visualize a scenario where DNAPL is immobilized on a fine grained lens, is displaced laterally off the lens by steam, and sinks below the steam zone to cause contamination at deeper levels in the aquifer. In order to avoid this vertical remobilization it is necessary to ensure that the steam zone extends to a significant depth below the contaminated DNAPL zone. In addition to the distillation mechanism discussed above, steam injection may affect DNAPL movement in the subsurface by changing temperatures, which in turn changes fluid densities, viscosities, and interfacial tensions. As temperatures are raised both water and DNAPL densities decrease. Most organic compounds have greater coefficients of thermal expansion than water, and the ratio of organic to water density decreases as temperature increases. Organic and water viscosities both decrease as temperature increases, so that steam injection may make very viscous organic compounds easier to displace hydraulically. Organic-water interfacial tensions also decrease as temperature increases. PCE-water interfacial tensions decrease by about 10% as the temperature is increased from 10°C to 90°C. Since entry pressures are proportional to interfacial tensions (given by the Laplace-Young equation), this entails a 10% decrease in entry pressures, allowing

Table 1. Mole fractions of Organics in Air and Steam

Compound	Vapor Press (mm Hg)		Mole Fraction in Air at 20°C	Mole fraction in Steam at 100°C
	20°C	100°C		
Carbon Tetrachloride	139.02	1870.32	0.18	0.71
1,1-Dichloroethane	182.49	2591.53	0.24	0.77
1,2-dichloropropane	38.25	840.99	0.05	0.53
Perchloroethylene	13.90	405.82	0.02	0.35
Trichloroethylene	58.14	1099.24	0.08	0.59
Chlorobenzene	8.91	294.71	0.01	0.28
Anthracene	0.00	0.35	1.68909E-06	0.00046

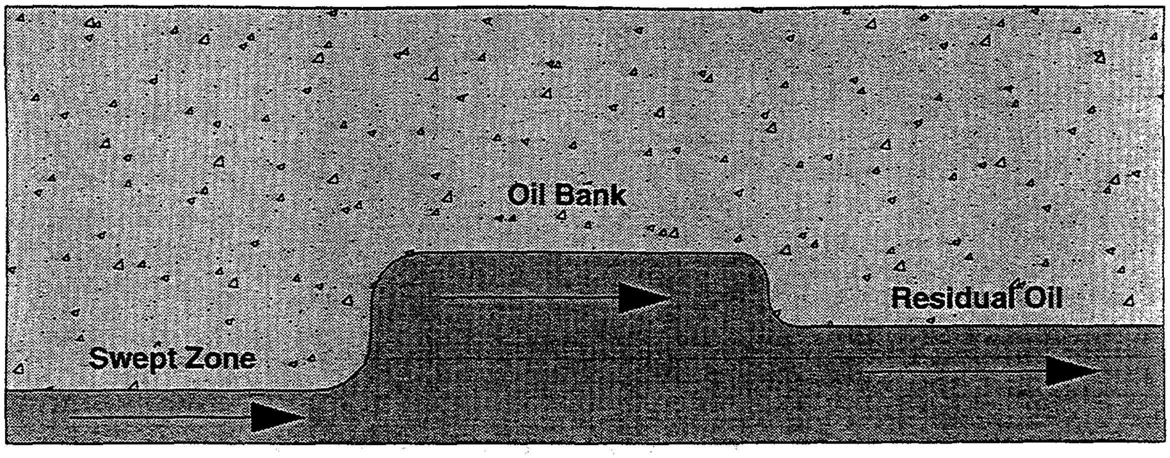

Figure 2. Oil Bank Formation in Steam Injection

DNAPL to penetrate finer grained lenses at higher temperatures than at typical subsurface temperatures. The ratio of viscous to capillary forces is called the capillary number. DNAPL trapped by capillary forces can be displaced hydraulically if the critical capillary number, a function of the fluids and the soil structure, is exceeded. Decreasing interfacial tensions increases capillary numbers, while decreasing water viscosity decreases capillary numbers. In the case of water displacing DNAPL, raising the temperature, decreases the water viscosity more quickly than the interfacial tensions, so that overall raising the temperature decreases the capillary number. Thus steam injection does not lead to any direct enhancement of hydraulic displacement of residual DNAPL. Some swelling of the DNAPL occurs on heating, but this does not result in significant DNAPL mobilization.

As the steam zone expands and the condensation front moves towards the extraction well heat is transferred through the soil with fluid flow (advection) and also by conduction, as a result of temperature gradients. Heat conduction occurs in both the longitudinal and transverse directions with respect to the direction of flow. Since steam is much lighter than water, the steam zone tends to rise as it travels horizontally. This steam override, or gravity segregation can be a significant problem in designing a steam injection program. In addition to the low density, steam also has a much lower viscosity than water, and channeling can also be a significant problem. Transverse heat conduction is an important mechanism in damping steam channeling in heterogeneous soils.

The main advantage of steam injection over ambient temperature technologies is the enhancement of organic removal that occurs due to steam distillation. The concentrations of organics in the recovered vapor and condensate stream will be much higher than would be achieved in ambient techniques such as soil venting. In addition, steam injection can be used below the water table, without occurrence of the extreme channelling characteristic of air sparging. The weaknesses of the technology are the requirements for steam generation, the difficulties associated with steam override, and the limitation to semi-volatile compounds. In addition, unlike bioremediation techniques, the contaminants are not destroyed, but must be disposed of after removal from the subsurface.

4.0 GENERAL TECHNOLOGY CONSIDERATIONS

Steam injection is primarily geared to *in situ* groundwater contamination. It is most effective for removing separate phase DNAPL, rather than dissolved phase DNAPL. Steam injection is equally suited to remediating petroleum and chlorinated hydrocarbons. The most important characteristic of the compound is its vapor pressure over the temperature range typical of steam injection.

Steam injection can be used to access contamination under buildings provided that there is no danger of steam and organic vapors entering the building. This would likely be the case if the soil zone to be cleaned was an adequate depth below the bottom of the building. This would also avoid problems with steam short-circuiting through permeable soil layers that are usually placed below building foundations. In addition, the building must be small enough to allow adequate spacing of injection and extraction wells, unless directional drilling technologies are used. Pavement does not pose any special problems for steam injection and may aid the process by preventing breakthrough of steam and organic vapors at the ground surface.

Steam injection can theoretically be used at any depth. It is used at depths as great as 3,000 feet for tertiary petroleum recovery. The deeper the steam is injected the greater must be the pressure and temperature of the steam, entailing higher costs for steam production as well as higher equipment costs.

4.1 Utility, Operation and Maintenance Requirements

A steam injection program requires a boiler for steam production, injection wells, extraction wells, vacuum extraction equipment, condenser equipment, and treatment trains for off-gas and condensate treatment. A source of feedwater for steam generation is required, and a feedwater treatment system may be required for pretreatment of feedwater to remove dissolved solids, and prevent excessive scaling of the boiler tubes. In most cases the boiler would be fired by natural gas. In the case of steam injection in the vadose zone, vacuum extraction is required to remove vapors. This necessitates the use of vapor extraction equipment. The vapors and condensate recovered from steam injection operations are normally passed through a condenser to condense water and organic vapors. The remaining noncondensible gas fraction will require treatment with activated carbon. The water and organic fractions of the condensate can be separated gravimetrically. The water fraction will require treatment to remove dissolved organics before disposal.

4.2 Secondary Waste Streams

At the extraction wells associated with steam injection heated organic fluids and water will be produced before steam breakthrough, and water and organic vapors will be produced after steam breakthrough. The produced fluids and condensed vapors may be separated into organic and water phases. The organic phase may be pure enough to be recycled. The water phase will be saturated with organic compounds and will require further treatment before it can be disposed of. The volume of water produced will be much lower than that produced by conventional pump and treat techniques since the recovery rates of DNAPL will be much higher with steam injection by virtue of the steam distillation removal mechanism.

4.3 Environmental Risks

The steam injection process produces heated organic vapors, which in the case of some contaminants may lead to fire or explosion hazards. It is important to control the migration of the steam and organic vapors when remediating near surface DNAPL contamination to avoid steam breakthrough at the ground surface at unexpected locations. In addition, as mentioned previously there is some concern about vertical remobilization of DNAPL leading to increased groundwater contamination.

4.4 Models

Several models of steam injection for petroleum recovery have been developed. These models are not generally applicable to modeling DNAPL remediation by steam injection. Most of the models neglect dissolution of organics in the water phase, and neglect capillary pressures. Falta *et al* . (1992) described a one-dimensional model for simulation of steam injection in NAPL remediation. The model, which included three-phase flow and transport of a single component organic phase, was compared favorably to laboratory steam injection experiments conducted by Hunt *et al*. (1988). Sleep (1993) presented a three-dimensional three-phase multicomponent model for steam injection.

5.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

In low permeability formations a number of factors influence the effectiveness of steam injection. Lower permeabilities require much greater pressures to get the same rate of steam zone propagation, and this entails higher temperatures to produce steam. This is particularly the case for steam injection below the water table, where liquid water is displaced. Butler (1991) recommends that steam injection not be used for petroleum recovery in formations with permeabilities below 100 m/d.

In fractured low permeability soils preferential channeling of steam along the fractures will occur. In formations with primarily vertical fracturing it will be quite difficult to get horizontal steam movement, since the tendency of steam to rise will lead to vertical channeling of the steam up the fractures to more permeable zones above. This steam channeling in fractured media is exploited in the steam assisted gravity drainage oil recovery process.

In stratified soils, or fractured low permeability soils in which steam channels along the high permeability pathways, contaminants in the low permeability zones will only be recovered when they diffuse into the high permeability zones through which the steam is flowing. However, as steam moves along the high permeability layers, heat will be transferred by conduction from the high permeability zones to the low permeability zones (See Figure 2). The rate of conduction will depend on the thermal conductivity of the soil and fluid and on the temperature difference between the high and low permeability zone. If the low permeability zones are water saturated the temperatures will eventually become high enough to allow the steam zone to expand into these zones. At this point distillation of organic liquids trapped in the low permeability zones will take place. Once thermal and hydraulic equilibrium are reached between the low and high permeability zones vapor phase diffusion will be the dominant mechanism moving contaminants into the high permeability flowing zones.

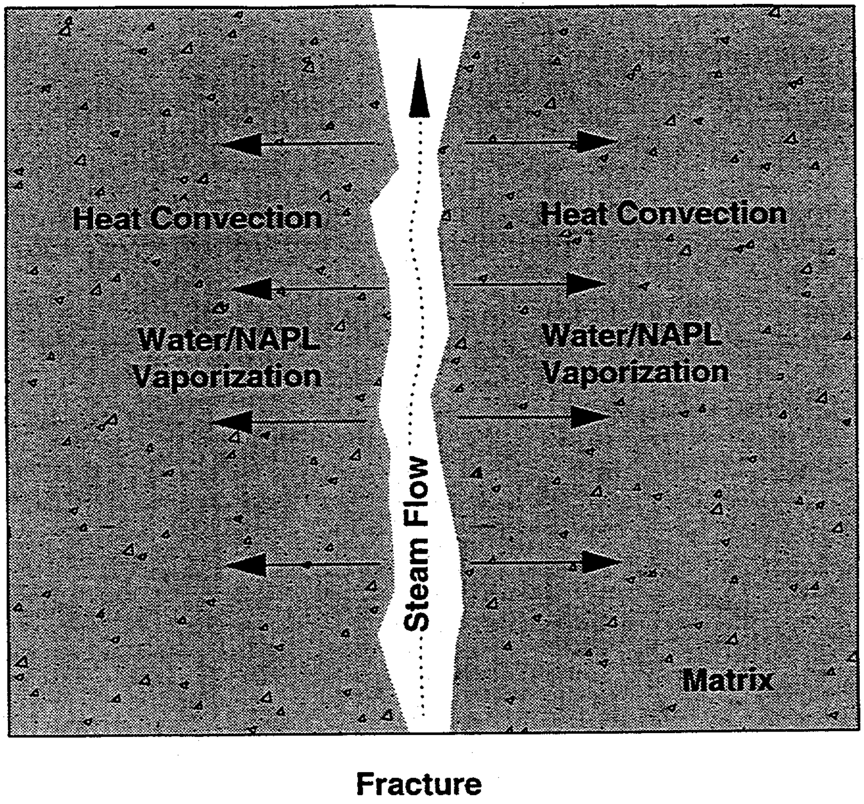

Figure 3. Steam flow and heat transport in fractured media

The time for substantial heating of the low permeability zones to occur depends on the thermal conductivities of the soils and fluids, the temperature of the steam, and on the thickness of these zones. Closely spaced fractures, or thin low permeability layers will lead to much shorter heating times and lower overall steam consumption.

5.1 Effect of Soil Water Content on Contaminant Removal

Steam injection can be used in any range of soils from dry to completely saturated. The energy requirements are higher with higher degrees of saturation, since more energy is required to raise the temperature of water and to vaporize the water than is required for an equivalent volume of air. Better hydraulic control of the expanding steam zone can be maintained in the vadose zone than can be maintained in the saturated zone. In the vadose zone the steam is primarily displacing air, and there are not great differences between the viscosities and densities of steam and air, as there are for steam and water. Thus gravity override and viscous channeling are not as important for steam injection in the vadose zone as they are for the saturated zone.

Effective vapor phase diffusion coefficients are a function of the gas filled porosity. One commonly used model for the effective vapor phase diffusion coefficient in partially saturated soils is the Millington-Quirk (1961) model:

$$D_{eff} = \theta_g^{7/3} / \theta^2$$

where θ_g is the gas-filled porosity, and θ is the soil porosity. Thus, as water contents increase and the gas-filled porosity decreases the effective diffusion coefficient decreases.

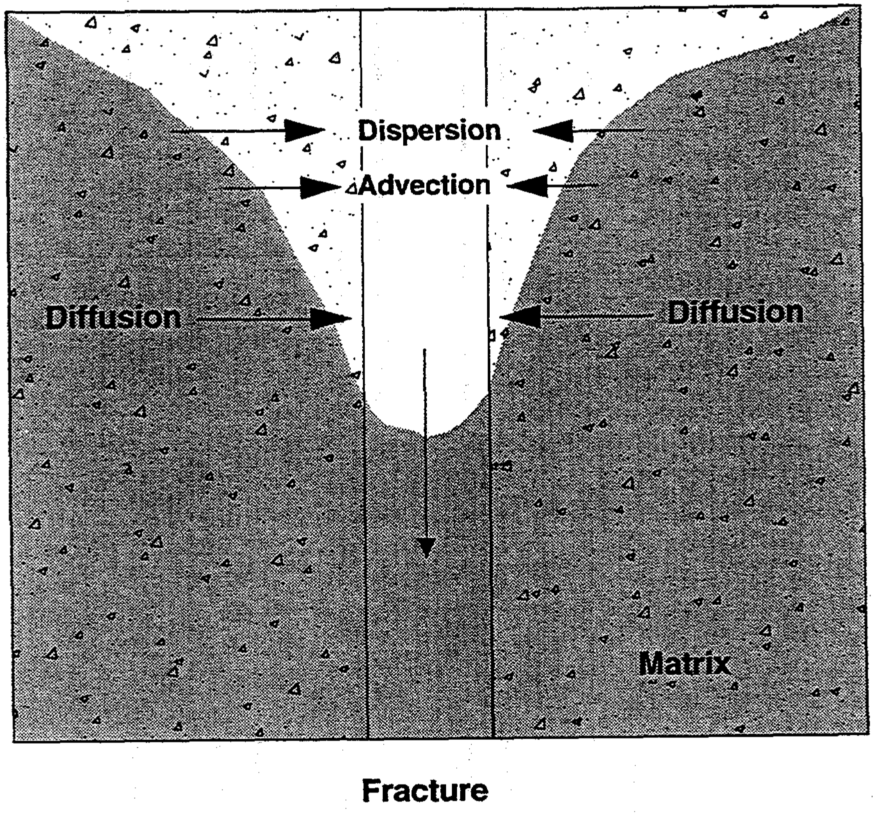

Figure 4. Diffusion from matrix to fracture

5.2 Hydraulic Control of the Water Table

Since steam injection may be used above or below the water table, hydraulic control of the water table is not necessary. If contaminants are located below, but near, the water table, steam injection near the water table may be difficult to control due to short circuiting of the steam into the vadose zone. For this reason, it might be advantageous to lower the water table before commencing steam injection, provided this did not result in unacceptable vertical redistribution of contaminants.

5.3 Remediation Scenario

In the scenario considered, TCE and PCE have leaked into a sand aquifer, contaminating an area 40 m by 40 m. At the bottom of the sand aquifer is a 3 m thick clay aquitard, containing 10 to 40 micron fractures, spaced a few cm apart, assumed to be primarily vertical in orientation. A sand aquifer underlies the clay layer. TCE and PCE are assumed to be pooled on the top of the clay layer. Since the entry pressure for PCE is approximately 60 cm of PCE for a fracture aperture of 10 microns, and 15 cm of PCE for a 40 micron fracture (based on PCE-water interfacial tension of 45 dynes/cm and PCE specific gravity of 1.6) it is possible that PCE and TCE will have entered the fractures. In addition, dissolved PCE and TCE will have diffused into the clay matrix. Based on a TCE water solubility of 1100 mg/l, a porosity of 0.4, and a bulk clay density of

1,600 kg/m^3, there is approximately 2100 kg of dissolved TCE in the porewater in the clay and 13,300 kg of TCE in the liquid phase or adsorbed to the clay. If all the TCE (specific gravity 1.4) was in the fractures, and the fracture porosity was 1%, then the average TCE saturation in the fractures would be 20%. Given the depth of fractures, it is quite likely that there is sufficient head of TCE in the fractures to exceed the clay matrix entry pressures at lower depths. Thus, there is likely free phase TCE in the clay matrix also. The cleanup target of 200 mg/kg represents an average dissolved TCE concentration of 800 mg/l, just below the solubility of TCE. Thus, the target may be achieved primarily be removing the free phase TCE from the clay.

For the purposes of the current remediation design it is assumed that the DNAPL did not reach the sandy aquifer below the fractured clay. The water table is at the top of the clay layer. For fracture apertures of 10 to 40 microns the corresponding range of fracture hydraulic conductivities is 0.01 cm/sec to 0.16 cm/sec. If the hydraulic conductivity of the matrix blocks is between 10^{-6} cm/sec and the fracture spacing ranges from 5 cm to 10 cm, the effective vertical clay hydraulic conductivities range from roughly 2×10^{-6} cm/sec to 3×10^{-5} cm/sec. Since the fractures are primarily vertical the effective horizontal permeability of the clay layer will be in the range of 10^{-6} cm/sec to 10^{-8} cm/sec. Thus the ratio of vertical to horizontal hydraulic conductivities in the clay layer will range from 2 to 3000, depending on the combination of fracture aperture, fracture spacing and matrix hydraulic conductivity.

The remediation approach recommended for the above contamination scenario is to inject steam above and below the clay layer and apply vacuum extraction above the clay layer to recover vapors produced by steam injection. It is recommended that the injection and extraction wells be installed in a five spot pattern above the clay layer, with extraction wells surrounded by steam injection wells. The outermost layer of injection wells should be outside the limit of contamination to ensure that no contamination is driven beyond the treatment zone, causing additional contamination of the subsurface. The extraction and injection wells should be screened just above the top of the clay layer with an interwell spacing of roughly 10 m to ensure that steam flows along the top of the clay layer to maximize heat transfer to the clay layer. A low permeability, heat resistant flexible membrane liner should be placed on the ground surface to prevent vapor losses to the atmosphere and to minimize induction of air flow from the atmosphere. Below the clay layer the wells should be screened over short sections close to the bottom of the clay layer. The purpose of these wells is to provide heating of the clay from below. It is assumed that a regular grid pattern with 10 m interwell spacing would be adequate. Since the steam is less dense than water, it is expected that the steam will flow up through the fractures in the clay to the sand aquifer above. Since the fractures are closely spaced heat transfer from the fractures to the matrix blocks should be reasonably efficient. It is expected that a steam zone will develop below the clay layer and that this steam zone will expand upwards through the clay layer, vaporizing water, PCE and TCE in both the fractures and matrix blocks. If the fracture spacings and apertures are relatively uniform across the clay layer, it is expected that the entire clay layer can be heated to steam temperature from the combination of heat conduction from the sand layers above and below and from steam flow through the fractures and heat conduction from the fractures to the matrix.

As a result of the high permeabilities of the fractures, steam would be expected to break through the fractures in a few days at most. It is difficult to estimate the time to cleanup to a level of 90% removal, but on the basis of the field studies described below, two to three months would be expected to be sufficient. The total volume of soil to be heated, assuming that the heat zone extends from 1 m below the clay layer to 2 m above the clay layer is 9600 m^3. Assuming an average porosity of 0.4, a fully saturated clay layer and lower sand layer, and 30% degree of saturation in the upper sand layer this represents approximately 3 x 10^6 kg of water and 2 x 10^7 kg of soil to heat. Minerals have a heat capacity of roughly 1 kJ/kg-K (Butler, 1991), while water has a heat capacity of roughly 4.2 kJ/kg-K. At 100°C water has a heat of vaporization of 2250 kJ/kg. If the aquifer was originally at 20°C, and 70% of the water was vaporized, the heating requirements would be approximately 2.6 x 10^9 kJ to bring the temperature to 100°C, and a further 6.8 x 10^9 kJ to vaporize the *in situ* water, for a total of 9.4 x 10^9 kJ. If this energy is provided primarily by the latent heat of steam then approximately 4.2 x 10^6 kg of steam are required to create the steam zone. If the spacing between adjacent injection wells is 10 m then a total of 50 wells would be placed at the site. At steam injection rates of 100 kg/hr/well of 100% quality steam (6 times the rate used in the steam injection program used by Udell and Stewart, 1988) the total steam injection rate would be 5000 kg/hr. Given the heterogeneous nature of the site and the inefficiencies in heating the clay layer from above and below, it is unlikely that heating efficiencies would exceed 50%. With the injection rate of 100 kg/hr/well and a heating efficiency of 50% heating the clay layer to steam temperature would take approximately 70 days.

Once the clay layer reached steam temperature, and a vapor phase formed in the clay matrix, the primary mechanism for removal of contaminants from the clay matrix would be vapor phase diffusion. Udell and Stewart (1988) achieved a removal rate of contaminants (aromatics and chlorinated solvents) of approximately 500 mg/kg-day from a contaminated site. Since vapor diffusion from the clay matrix is expected to be the rate limiting step in low permeability fractured clays, the removal rate would certainly be smaller. If the rate was 50 mg/kg-day it would take approximately 40 days to remediate from 2000 mg/kg to 200 mg/kg. If it is assumed that most of the contaminant removal occurred after the clay layer was heated to steam temperature then the total time for heating and contaminant removal would be approximately 110 days. Once the clay layer was heated to steam temperature steam injection rates could be reduced, to reduce water and fuel demands. If the rate was reduced by 50% to 50 kg/hr/well for the last 40 days the total steam injection would be 7 x 10^6 kg of steam with a heating demand of approximately 1.6 x 10^{10} kJ.

6.0 COST

The costs for the remediation scheme outlined above are:

1. Well Installation:		
16 Vacuum extraction wells and 50 steam injection wells at \$3000/well:		\$198,000
2. Fuel:		
1.6 x 10^{10} kJ (Natural Gas, \$2.00/10^6 kJ):		\$ 32,000
3. Treatment System for Gas and Condensate Streams		
Pumping, Phase Separation and Carbon Adsorption:	Capital:	\$ 70,000
(API, 1986)	Operating:	\$ 10,000
4. Monitoring System:		
	Capital:	\$ 50,000
	Operating	\$ 20,000
5. Total		\$380,000

Design costs, capital for steam generation, condensor equipment, boiler water, cooling water, and manpower are not included.

7.0 RELIABILITY

Steam injection has not been extensively field tested. In particular, tests have been conducted in fractured clay systems. The estimates of removal rates and times to cleanup are therefore highly speculative. Factors such as fracture spacing, fracture aperture, spatial distribution of DNAPL in the clay, changes in fracture and matrix properties on heating, chemical interaction between clay and contaminant, and excessive steam channeling will all reduce the contaminant removal rates. In addition, caution must be exercised to avoid remobilization of the DNAPL downward through the fractures into the underlying sand aquifer.

8.0 COMMERCIAL AVAILABILITY

The use of steam injection for groundwater remediation is still in the early stages of development. The majority of published studies have been conducted in one-dimensional, homogeneous sandfilled laboratory columns (Hunt *et al.*1988a, 1988b, Stewart and Udell, 1988). Design procedures for determining the optimal well configurations, injection temperatures and pressures, contaminant removal rates, and achievable cleanup levels for varying hydrogeological conditions are not yet well developed. The most comprehensive field scale experiment of steam injection was conducted at the Lawrence Livermore National Laboratory Site (Ramirez *et al.* 1993). With the exception of the group conducting the studies at LLNL there are no vendors with experience in using steam injection in the field. There have been no field scale trials of steam injection in low permeability fractured soils, and the experience with steam injection for DNAPL removal, even in homogeneous, sandy soils, is limited. Thus, in contrast to vapor extraction, the commercial availability of steam injection is quite limited.

Future enhancements to the technology may include the development of improved understanding of the strengths and limitations of the technology and the formulation of procedures for varying hydrogeological conditions. Further development of soil fracturing with steam injection and steam assisted soil mixing processes being developed by Novaterra (La Mori, 1993) may lead to enhancements of the effectiveness of steam injection.

As previously described, steam injection is often combined with soil vacuum extraction to recover vapors. For low permeability soils, combination of steam injection with hydraulic or pneumatic fracturing may improve access to low permeability zones. High pressure steam injection has been used to create fractures to improve petroleum recovery by steamflooding (Butler, 1991).

9.0 CASE HISTORIES

Udell and Stewart (1989) reported on field experiments of combined vacuum extraction and steam injection for remediation of a mixture of organic solvents, including xylenes, ethylbenzene, 1,2-dichlorobenzene, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, and acetone. The organic contamination was below a cement pad in the unsaturated zone. The contaminated zone was confined at the bottom by a clay layer at a depth of 6 m from the ground surface. Six steam injection wells were placed in a circle of radius 1.5 m around the contaminated area, with steam injection at 5 m depth. A single recovery well was placed in the center of the contaminated zone to recover contaminants. Vacuum extraction was first applied for 40 hours, during which time 100 kg of VOCs were recovered. Subsequently, steam was injected through the 6 injection wells at a pressure of 41 kPa, with a total flow of 110 kg/hr. Breakthrough to the recovery well occurred after 32 hours. Monitoring of *in situ* temperatures showed that zones of low permeability in the treatment zone lead to nonuniform steam and water flow and steam channeling, resulting in the early breakthrough. The test was continued up to a time of 140 hours, at which time 148 kg of contaminant vapors and 97 kg of condensed contaminants were recovered. Assuming a treatment zone of 6 m depth, radius of 1.5 m, and bulk soil density of 2000 kg/m^3, this yields a removal rate of approximately 500 mg/kg-day.

Nunno *et al.* (1989) reported the results of field tests of steam injection conducted in a vacuum bell of size 2 m by 2m. The soil consisted of layers of sand, slag, clay, bog, and another sand layer. Four steam lances were used to inject steam at temperatures of 130 to 180°C. Removal rates for BTEX varied from 20% in clay, to 99.5% in sand. Napthalene removal varied from 60% in clay to 99.9% in sand. Removal of other PAHs varied from 35% in bog to 97% in sand, while phenol removal varied from 20% in clay to 80% in sand.

Lord *et al.* (1989) conducted laboratory studies of steam injection in a 36 cm square box, using a variety of mixtures of sand and silt, ranging from 100% sand to 100% silt. They placed a high transmissivity geotextile and a flexible membrane liner on the top of the soil and applied a vacuum below the liner. Steam was applied at the bottom of the test box. The vacuum drew steam up through the contaminated soil, removing volatile compounds. Gasoline removal from sand was almost complete, while removal from a 50% sand, 50% silt soil mixture only reached 80%. Similar results were obtained for other hydrocarbons, with lower removal rates achieved for less volatile compounds.

10.0 SUMMARY

Steam injection is a relatively new technology that has not been widely tested for DNAPL remediation. Steam injection has significant potential for remediation of DNAPLs in low permeability formations. The steam distillation mechanism may result in much greater removal rates than may be achieved with ambient temperature remediation technologies. The ability to desaturate the clay matrix by heating porewater to the boiling temperature, so that contaminants are removed by gas phase diffusion, rather than aqueous phase diffusion, increases mass transfer rates in fractured systems. Issues such as gravity override and heat mass transfer limitations in fractured or stratified soils require additional investigation.

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SOIL VAPOR EXTRACTION WITH DEWATERING

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

The physical treatment technology of soil vapor extraction (SVE) is reliable, safe, robust, and able to remove significant amounts of mass at a relatively low cost. SVE combined with a pump-and-treat system to create a dewatered zone has the opportunity to remove more mass with the added cost of treating the extracted groundwater. Various limiting processes result in a significant reduction in the overall mass removal rates from a SVE system in porous media. Only pilot scale, limited duration SVE tests conducted in low permeability media have been reported in the literature. It is expected that the presence of a fracture network in low permeability media will add another complexity to the limiting conditions surrounding the SVE technology.

2.0 DESCRIPTION OF THE TECHNOLOGY

SVE is a physical treatment technology that involves the forced removal of soil gas from an unsaturated soil matrix in an attempt to remove the associated volatile phase of a non-aqueous phase liquid (NAPL). If the conditions are conducive, then this removal of soil gas results in a mass transfer from the pure phase NAPL, from the aqueous phase, and from the sorbed phase to the gas phase. The primary objective of such a technology is to reduce the following soil bulk concentration to some specified level

$$C_T = \rho_n \theta_n + C_w \theta_w + C_a \theta_a + C_s \rho_b \tag{1}$$

where C_T is the mass of contaminant per unit volume of soil; ρ_n is the mass density of the pure phase NAPL; θ_n, θ_w, and θ_a is the NAPL content, moisture content and air content respectively; C_w is the aqueous phase concentration; C_a is the air phase concentration; C_s is the mass of contaminant sorbed per mass of soil; and ρ_b is the bulk soil density. The forced removal of the air phase results in a reduction in C_a in (1) and produces a dis-equilibrium between the four phases. Since some mass is removed from the system, mass is transferred from the other three phases in an attempt to re-establish an equilibrium between all four phases. Ideally, this process results in a reduction of the soil bulk concentration C_T, and hence a step towards site clean-up.

The forced removal of soil gas is accomplished through the use of an air blower or pump in conjunction with a network of extraction and injection wells (either vertical or horizontal) or trenches to create a suitable air phase pressure gradient. The utility of such a system allows for the enhancement of air flow through the subsurface zones of highest contamination.

The basic components of a typical in-situ SVE system using only extraction wells and an impermeable ground cover to control air flow are shown in Figure 1.

The success or failure of an SVE system depends on numerous variables that relate to:

- site characteristics, such as
  - spatial distribution of NAPL
  - depth to the water table
  - infiltration zones

- soil properties, such as
  - air conductivity
  - soil moisture content
  - porosity
  - sorption capacity (organic carbon content)
  - degree of heterogeneties
- chemical properties, such as
  - NAPL composition
  - solubility
  - sorption potential
  - air/water partition relationship
  - NAPL/air partition relationship
- SVE design and operation parameters, such as
  - number and spacing of wells or trenches
  - passive vs active air injection
  - in-situ pressure gradients
  - site capping
  - control over extraction and injection well or trench configurations
  - intermittent operation (pulsed pumping)
  - variations in operating pressures and flow rates

In situations where water table fluctuations are quite large or when it is economically viable, the water table location can be hydraulically controlled. A significant lowering of the water table or dewatering of the saturated zone provides an opportunity to increase the contact between air and pure phase NAPL. If air phase pressure gradients can be established within this dewatered zone then mass removal from this zone will be achieved.

Dewatering may be achieved through the use of standard pump-and-treat technology, although dual purpose wells (water extraction along with air extraction) can be designed for effective use. SVE combined with dewatering is an effective combination of two technologies as illustrated in Figure 2. Clearly, a system of this nature has the opportunity to remove more mass with the added cost of treating the extracted groundwater. Also, if the dewatering system is properly designed, aqueous phase source control may be possible.

Limitations

SVE remediation programs have been shown to exhibit three distinct stages of performance that manifest into sudden slope changes in the overall system off-gas profile. The first stage is of relatively short duration and is characterized by high vapor concentrations. The second or transition stage is when the off-gas concentrations rapidly decrease to a very low level. The final or tailing stage produces very low off-gas concentrations.

The performance of SVE systems have been investigated from a number of different perspectives ranging from small scale laboratory experiments, through pilot and field scale systems, and into the realm of numerical computer simulation. Each of these investigations have shed light on the various and complex limitations surrounding the use of SVE technology.

Local Equilibrium Assumption

Evidence provided by laboratory studies suggest that equilibrium phase partitioning rules represent SVE of uniformly distributed NAPL residuals from homogeneous soils. Brusseau (1991) calls this the local equilibrium assumption (LEA). An SVE system is assumed to be in a state of equilibrium during the first stage of operation. Baehr *et al.* (1989) performed a number of laboratory studies investigating the removal of gasoline from columns and determined that the LEA was able to be employed to simulate the column experiments adequately. However, due to the multi-component mixture used in these experiments, tailing behaviour was observed due to the changing mole fractions within the liquid phase. This may have masked any non-equilibrium phase transfer behavior that occurred during the extraction. Column and box experiments performed by Benson (1990) using a single component NAPL fully supported the LEA; however, consideration must be given to portions of the mobile air stream that not pass through the residual zone. This dilution effect results in a reduction in the effluent concentration from saturated levels. Given that the spatial distribution of NAPL at field sites is generally heterogeneous (e.g., Poulsen and Kueper, 1992), very low effluent concentrations may be observed even when the LEA is valid and diffusional limitations are negligible. As the spatial distribution of the NAPL residuals diminish as clean-up progresses, the amount of contact of the NAPL residual zone with the mobile air phase will decrease, thereby giving rise to even lower effluent gas concentrations. This reduction in effluent concentration creates declining mass removal efficiency (mass of contaminant removal per volume of air passing through the treatment zone) and gives rise to non-ideal behavior.

Effective monitoring of such sites will allow for operational changes in the SVE system to maximize NAPL and air contact.

Diffusion Limited Mass Removal

Spatial variations in permeability, moisture content, and NAPL content give rise to preferential mobile air pathways and hence to non-ideal system behavior.

Ho and Udell (1992) reported on a sequence of box-experiments in which NAPL was trapped in a lower permeability layer overlain by a layer of higher permeability. For a permeability ratio of 1:100 or higher the mass removal efficiency decreased significantly due to gas phase diffusion limitations. At the field scale, Chambers and Hennier (1991) discussed the results of a pneumatic test performed in a multi-layer system and found little pressure response in a low permeability layer even when the extraction well was screened across that layer. This implies that the removal of NAPL trapped within relatively low permeability layers will be slow since variations in permeability result in a channelling of most of the air flow through the zones of higher permeability.

Even in situations that are much less heterogeneous than those described above, non-ideal behavior has been observed due to diffusion limited removal (McClellan, 1991; Rainwater *et al.*, 1991). Consider the schematic representation of a soil-water-air NAPL system shown in Figure 3. For mass to be removed from the lower NAPL zone, both aqueous phase and gaseous phase diffusion must occur; while for mass to be removed from the upper NAPL zone only gaseous phase diffusion must occur. The shift from high off-gas concentrations characteristic of the first stage of SVE operation to much lower concentrations is due in part to a change from an advective-dominated system to a diffusion-dominated system.

In an attempt to investigate the underlying processes that cause non-ideal behavior, two basic formulations of numerical models have been developed. The first type (e.g., Gierke *et al.*, 1992; Brusseau, 1991) are those that attempt to explain the processes by separating the soil into mobile and immobile zones (a dual porosity formulation), while the second type attempt to explain non-ideal behaviour using mathematical approximations, often first-order representations, (e.g., Rathfelder *et al.*, 1991). Gierke *et al.*, (1992) performed column experiments with sand and with an aggregated porous soil medium and used a dual porosity model to help describe the resulting diffusion limited removal. They concluded that, non-ideal behaviour could be expected to be an important factor when SVE is employed in soils with high inter-aggregate porosities. Unlike Gierke *et al.*, (1992), Brusseau (1991) considered a dual porosity model along with the effects of heterogeneties and non-equilibrium sorption. In general, the dual porosity model provided better simulations than the LEA model of laboratory column experiments. This suggests that even under laboratory conditions, physical heterogeneity and non-equilibrium sorption are important factors. Therefore, it is expected that the increased complexity of natural geological environments will cause even greater effects at the field scale.

Dewatering and Gravity Drainage

Dewatering of a DNAPL contaminated site may cause further migration of the DNAPL due to gravity drainage. If the fluid wetting sequence is assumed to be water-NAPL-air (most wetting to least wetting) then a reduction in the water phase pressure (reduction in the water table location) will give rise to a downward flow of DNAPL since NAPL-water contacts are replaced by NAPL-air contacts. This results in an overall further downward migration of the pure phase liquid that may not be favorable.

Water Table Upwelling

In some situations where the water table is located near the vapor extraction wells, water table upwelling may occur and reduce the amount of direct air and NAPL contact.

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

(a) ***Is the technology primarily geared to soil or groundwater contamination?***

SVE is primarily a technology that focuses on the remediation of unsaturated zone soils that may contain residual NAPL. Since mass transfer from the aqueous phase occurs during SVE there exists the possibility that some remediation of the transition zone or shallow groundwater zone may take place. If dewatering is employed as part of the SVE remediation effort then some of the residual NAPL located within the previously saturated zone may be removed. However, as stated previously, there exists a risk that gravity drainage may occur as a result of dewatering.

(b) ***To what extent is the technology suited to remediate petroleum as well as chlorinated hydrocarbons?***

SVE is suitable to remediate both petroleum and chlorinated hydrocarbons. In fact, the majority of SVE case studies reported in the literature involved hydrocarbon fuels such as gasoline, diesel fuel and jet fuel (JP-4). Some case studies of gasoline and JP-4 have observed that some of the mass removal was caused by aerobic biodegradation enhanced by SVE (Cook *et al.*, 1991; Downey and Elliot, 1990), since these systems supply oxygen to the subsurface. Moreover, due to their density, light non-aqueous phase liquids (LNAPLs) *float* rather than *sink* and thus are more susceptible to direct air contact than DNAPLs.

(c) *How well is the technology able to access under buildings or pavement?*

Due to its limited surface disturbance, SVE can easily access NAPL located beneath buildings or pavement. For such situations the use of passive or active injection wells should be employed to control the airflow.

Most foundation footings are placed on gravel pads to control water build-up; and hence these gravel pads provide a higher permeability zone for air flow channelling. In these situations it is expected that mass removal will be gas phase diffusion limited.

It is expected that the building or pavement may provide a good soil surface seal that will prevent short-circuiting; however, this may not be the case since pavement is rarely a good air seal (due to fatigue cracks and construction techniques), and building floors have utility conduit openings that may allow for air leakage.

(d) *What is the maximum depth of remediation?*

There appears to be no theoretical limit to the maximum depth that an SVE system can operate. Practical factors such as blower or air pump selection and depth of wells or trenches may be constraints.

(e) *What are the utility, operation and maintenance requirements?*

Once the SVE system is installed, the utility requirements are the power to run the blower or vacuum pump and that is used to treat the off-gas.

Operation and maintenance of an SVE system is essential. Routine monitoring of the systems performance should be undertaken by suitable field personnel to ensure that the system is constantly operating as designed. Operational changes may be required from time-to-time to optimize system performance.

(f) *Are secondary waste streams produced?*

Yes, an emission control system is required to treat the off-gas prior to discharge to the atmosphere. The most commonly used SVE off-gas treatment options are sorption on granular activated carbon and thermal destruction (flaring or incineration and catalytic oxidation). Depending on the off-gas concentration and local regulations, direct discharge has been employed.

(g) *Are there potential environmental impacts or safety risks associated with the use of this technology?*

Possibly. For example,

(1) in a situation where active air injection is employed and portions of the gas phase plume are directed off-site into otherwise un-contaminated areas.

(2) the off-gas is not treated to an acceptable level prior to release. The possibility of this occurrence can be substantially reduced with effective system monitoring and solid engineering design.

A properly designed and operated SVE system is safe; however, potentially explosive mixtures of extracted gas may occur at some sites and therefore, explosive-proof equipment should be employed.

(h) ***Are models available to predict performance in porous media and to what extent are they developed?***

Numerous models have been developed to predict the performance of SVE systems in porous media. Depending on the site characteristics and chemical complexity the choice of model could range from models employing simple analytical solutions to large numerical simulators. Analytical solutions such as those presented by Falta *et al.* (1993) and Johnson *et al.* (1990) were presented primarily as design aids and thus are limited to the analysis of simple situations. Generally, these types of models are unable to simulate heterogeneous domains and their utility is limited. More versatile and comprehensive analyses can be performed by numerical (finite element, finite difference, or control volume) models that solve the appropriate flow and transport equations in two or three dimensions as required. These models allow for the simulation of heterogeneous porous media, non-uniform NAPL distribution and in some cases non-equilibrium phase partitioning. The flow equations may involve the simultaneous determination of the air phase, water phase, and NAPL phase pressure distributions or just the air phase pressure distribution depending on the complexity of the problem under consideration. In the latter situation, flow models may be used with the parameters adjusted for gas flow if the assumption of incompressible flow is valid (Massman, 1989; Cho, 1991). The transport equations may be formulated for a single component analysis or perhaps for a more complicated multi-component analysis. The usual transport processes considered are: advection, hydrodynamic dispersion, diffusion, sorption and interphase mass transfer.

Recently, some non-isothermal models have been developed (e.g., Adenekan *et al.*, 1993) that allow for the simulation of temperature changes in the subsurface that may occur during SVE remediation. These changes in temperature may be the result of evaporative cooling, heat transported to the subsurface due to the SVE system, and general changes in the subsurface temperature due to variations in ambient temperatures (e.g., summer to winter).

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

(a) ***What is the effect of soil water content on contaminant removal?***

Soil water content or water saturation has a significant impact on the performance of an SVE system. An increase in water saturation produces the following complications:

(i) Air conductivity: an increase in water saturation in a portion of a porous medium reduces the gas saturation and hence reduces the ability for gas to flow through that portion of the porous medium. Although a linear relationship exists between water saturation and gas saturation, the air conductivity-gas saturation relationship is generally non-linear, for example,

$$k_{rg} = C(\ 1 - S_{Te}\ )^2 (\ 1 - S_{Te}\ )^{(\frac{2+\lambda}{\lambda})} \tag{2}$$

where C is the Klinkenberg factor, S_{Te} is the total effective liquid saturation, and λ is the pore size index. Figure 4 presents the normalized sensitivity coefficient with respect to the total effective liquid saturation for (2) with $C = 1$ and $\lambda = 2$. The normalized sensitivity coefficient represents the percent change in the air conductivity due to a 1% decrease in the total effective liquid saturation. For example, a 1% decrease in the total liquid saturation from an initial total liquid saturation of 0.8 would result in approximately a 10% increase in the air conductivity.

(ii) Diffusion limitations: Higher zones of water saturation throughout the subsurface above the capillary fringe can usually be associated with the presence of finer-grained and lower permeability lenses. These lenses act as a capillary barrier to DNAPLs as they pass through the unsaturated zones, and, hence, pools of DNAPL will collect on these lenses. This results in the NAPL becoming trapped within a zone of higher water saturation. To remove the NAPL from this zone using an SVE system, the following mechanisms must take place: mass transfer from the pure phase NAPL to the aqueous phase must occur, followed by aqueous diffusion to the water and gas interface, and finally mass transfer from the aqueous phase into the mobile and possibly non-mobile gas phase. For the contaminant within the non-mobile gas phase, gaseous phase diffusion is required for mass transport to the mobile air phase if this is an appropriate pathway. Since aqueous phase diffusion coefficients are approximately four orders of magnitude smaller than gaseous phase diffusion coefficients, the presence of higher water contents leads to aqueous phase diffusion limitations for mass removal.

Even if no NAPL exists within these zones of higher water saturation, aqueous phase diffusion limitations may still complicate mass removal since aqueous phase contamination must still be removed from these zones. Obviously, remediation of these zones should be much faster than those zones where pure phase NAPL exists.

Control of soil moisture can be achieved by the use of a surface seal to reduce infiltration. The use of hot air injection as an SVE system enhancement will aid in the reduction of water saturation; however, economic considerations should be addressed.

The capillary fringe is defined as the tension saturated zone, and by definition has no air content (except for entrapped air) and thus removal of DNAPL residual from within this zone is aqueous phase diffusion limited.

(b) *Is hydraulic control of the water table critical to success?*

Possibly. If water table fluctuations are minor, then no hydraulic controls are necessary. Large fluctuations in the water table location may be both advantageous and detrimental to an SVE system. A lowering of the water table may allow more pure phase NAPL to become exposed to the advective air flow (if possible). On the other hand, a rise in the water table will prevent direct air/NAPL contact thereby reducing the mass removal efficiency. Moreover, this rise in the water table may also lead to an increase in the quantity of water removed by the SVE system which may have to be treated as hazardous waste depending on the type and concentration of contaminants.

(c) *Can the porous media models be reliably adapted to predict performance in low permeability media?*

The site conditions for the scenario to be addressed are:

- stratified soil with layers ranging from a medium sand (1×10^{-3} cm/s) to a clay (1×10^{-6} to 1×10^{-8} cm/s)
- the 3-m thick single clay layer situated between two sand units contains natural desiccation fractures spaced a few centimetres apart with apertures of 10 to 40 mm
- effective porosity of clay is < 1%
- the water table coincides with the top of the clay layer

- piezometric head reduction in the lower sand unit due to pumping will dewater the natural fractures within the clay layer
- an underground storage tank containing TCE and PCE has leaked over several years and the pure phase product has pooled on the clay layer. Aqueous phase contamination of PCE and TCE exist throughout the clay layer due to aqueous phase diffusion.

If the desiccation fracture plane orientation within the clay layer is assumed to be hexagonal or even orthogonal (Harris *et al.*, 1994), and the fracture spacing is of the order of a few centimeters (say 2-4 cm) then the effective diffusion length (from fracture to center of matrix block) is of the order of 1-2 cm. Considering this small diffusion length, the assumption that this clay layer can be conceptualized as an equivalent porous medium (EPM) is valid for at least modelling simulation purposes. At the centimeter scale this EPM assumption is obviously not valid, but for the discretization employed in most numerical analyses it will be applicable. Therefore, porous media models, if properly employed, can be adapted to predict the performance of an SVE system for this scenario.

Dewatering of the lower sand unit may prove to be a difficult simulation task with the use of EPM models since a capillary pressure - water saturation relationship representative of the EPM clay layer would need to be derived. This relationship is necessary to allow the clay layer to dewater without an excess depression of the water table within the lower sand unit.

Mass Removal Effectiveness

- *Free Product Pooled on Top of the Clay Layer*

Without dewatering: The removal of significant mass from the zone of free product will take a considerable amount of time due to aqueous phase diffusion limitations within the capillary fringe.

With dewatering: Although this should allow more mass to be removed since the capillary fringe is no longer situated above the clay layer, this zone will still be characterized by higher water saturation values (decreasing over time), and, as previously discussed removal will be governing by aqueous phase diffusion limitations. If complete removal of this high water saturation zone is possible, and the NAPL pool depth is not sufficient to imbibe into the fractures, then complete removal of this pool is possible.

- *Separate Phase Product Trapped in Continuous Fractures*

Assuming that the continuous clay fractures have been dewatered, the removal of significant mass from these fractures is likely.

Due to the variable aperture characteristics of these fractures, complete removal due to mobile air coming in contact with pure phase NAPL is unlikely. Depending on the aperture distribution, complete mass removal will likely be limited by aqueous phase or gaseous phase diffusion.

- *Separate Phase Product Trapped in Discontinuous Fractures.*

If no airflow is possible, then mass removal from these dead-end or discontinuous fractures will be very slow due to aqueous phase diffusion limitations (assuming that these fractures are still water saturated).

- *Dissolved Phase Product Diffused into Matrix Blocks*

Assuming that all the pure phase NAPL has been removed or is not present in nearby fractures, and these nearby fractures contain mobile air, then SVE will deplete mass from the matrix blocks. Given the small diffusion lengths (≅ 1 to 2 cm) this should not pose a limitation for total site remediation.

5.0 COST AND RELIABILITY

Assume the following conditions for this analysis:

- a 40 m x 40 m areal zone in the clay layer in the scenario discussed in Section 4 contains a uniform TCE concentration throughout its 3 m thickness of 2000 mg/kg.
- complete dewatering of the 3 m clay layer will produce an effective air filled porosity of 1%
- all pure phase TCE is in direct contact with the mobile air phase
- vapor pressure for TCE of 0.077 atm
- saturated air phase concentration 420 g of TCE/m^3 of air
- bulk density of clay 2.7 g/cm^3

Clean-Up Rates

Based on the assumptions stated above, one pore volume of TCE saturated air contains 4.2×10^{-3} kg of TCE, and a unit volume of the clay porous medium contains 5.4 kg of TCE. Under ideal conditions and an air phase exchange rate of one pore volume per day, the time to reach 90% mass removal would be 3.2 years, and the time to reach 50% mass removal would be 1.8 years. The ideal clean-up throughout this period is constant at 1.5 mg/kg·day.

SVE System Design Considerations

To control the air flow within the clay layer, a dense pattern of air injection and extraction wells would have to be employed. This pattern would have to be altered frequently so that stagnation points are removed. In a situation like this, short-circuiting of air flow to the sand layers above and below this clay will dictate the number of wells and operational parameters (flow rates and pressures). The exact details will have to be determined as part of an extensive pilot test program.

Cost Estimates

In order to determine a cost estimate, a nominal SVE system consisting of 30 extraction and injection wells and above ground manifold piping will be assumed.

Pilot Study	$ 15,000
Well Installation and Manifold Piping	$100,000
Soil Gas Monitoring Probes (20)	$ 5,000
Air Blowers	$ 10,000

Monitoring (3 years)	
- off-gas	15,000
- in-situ soil gas	$ 20,000
- soil cores (5)	$ 10,000
Power	$ 20,000
Total Estimated Cost	$195,000

Confidence and Expected Reliability

The ideal mass removal rate stated above clearly will not be possible since numerous limitations as discussed in Sections 2 and 4 will inhibit this rate.

6.0 COMMERCIAL AVAILABILITY

Almost all of the components required for an SVE system are available. Numerous vendors are capable of the design and implementation of SVE systems. To the best of the author's knowledge, system components are highly reliable and are capable of operation for the stated design period.

Complementary technologies that may enhance cleanup include:

- air sparging to enhance mass removal within the capillary fringe
- hot air injection to increase vapor pressure and reduce water saturation levels

7.0 CASE HISTORIES

Due to the low permeability of clays, SVE has not been a technology of choice and therefore, only pilot scale, limited duration SVE system tests have been reported in the literature. The following outlines the relevant facts from two case histories.

1. The following details were extracted from Gibson *et al.*, (1993) which reports on a long-term field pilot test of an SVE system in clay soil used to remediate an LNAPL.

   Physical setting: A property associated with the General Motors Corporation is characterized by discontinuous pockets of clay between limestone outcrops. The treatment volume is approximately 18000 m^3 (1600 m^2 in plan and 11 m deep), and the water table fluctuates between 9 to 13 m below ground surface (bgs).

   Geology: The solvent exposed clay at this site has undergone physical changes to increase its permeability.

   The natural clay (unfractured) is homogeneous and strongly cohesive with a permeability of 1×10^{-10} cm^2 (hydraulic conductivity of 1×10^{-7} cm/s for water), a bulk density of 1.92 g/m^3, a porosity of 0.43, and a fraction of organic carbon by weight of 0.14%.

   The solvent exposed clay properties (fractured) show a loss of cohesiveness with 0.5 to 1 mm aperture fractures. Based on lab tests the water hydraulic conductivity is 1×10^{-6} cm/s, while venting tests indicate a water hydraulic conductivity 1×10^{-2} to 1×10^{-1} cm/s.

Contaminants: The contamination resulted from paint thinner leakage from a surface storage tank system. The paint thinner was comprised of a range of compounds with vapor pressures ranging from 8 x 10^{-3} atm to 1 x 10^{-4} atm. Thirty-five soil cores were used to determine the spatial variation of contamination. The following was determined from the core results: there was no product in the upper 3 m; 75% of the product was between 3 and 8 m bgs; the highest soil concentration was 5100 mg/kg; and the total mass estimate was 1780 ± 600 kg.

System Design: A single extraction well screened from 5 m to 10 m bgs connected to a 1.5 HP regenerative blower was employed. A partial surface seal (15 m x 18 m) was placed over the center of treatment area to direct air flow. An extraction rate 11.0 scfm was used throughout the 240 day test. The pressure in the extraction well was -0.12 atm (-91.2 mmHg, -1.24 m H_2O).

Performance Monitoring: More than 30 1" diameter multilevel monitoring wells were used to sample soil vapor and measure in-situ pressure

Mass Removal: Changes in in-situ soil gas concentration and composition were used to indicate clean-up levels. Overall, there was a 49% decrease in off-gas vapor concentration. A total of 336 kg of paint thinner was removed (19% of initial estimate).

Comments: The following are general comments about this SVE application: (1) no post soil cores to determine soil clean-up, (2) mass removal rate shows little decline until 180 days and little tailing observed.

2. As part of the EPA Superfund Innovative Technology Evaluation (SITE) Program, a field demonstration of SVE technology was conducted at the Groveland Wells Superfund site, in Groveland, Massachusetts. Although not specifically focused on the application of SVE to low permeability media, the documentation generated from this field demonstration (Michaels, 1989) discussed the use of SVE to remove volatile organic compounds (VOC) from a clay layer. The following focuses on the details of VOC removal from this clay layer.

   Physical Setting: A small metal manufacturing facility (e.g., screws and valves) that was placed on the National Priorities List in 1983 used various solvents as degreasing agents. The entire contamination zone is quite large and this demonstration only focused on a portion of this zone. Within this zone the water table fluctuates between 8 m to 16 m bgs.

   Geology: An 8 m unsaturated zone comprised of the following soil types in descending order: 0 - 3.7 m - a fine silty sand (10^{-4} to 10^{-5} cm/s); 3.7 - 5.8 m - a stiff wet clay layer with an air content of 15%, (10^{-8} cm/s); and > 5.8 m - a coarse sand and gravel (10^{-3} to 10^{-4} cm/s).

   No fractures were reported within the 2 m clay layer. A considerable amount of water was perched on the clay layer.

   Contaminants: The solvent used at this facility was mainly trichloroethylene (TCE), but perchloroethylene, 1,1,1-trichloromethene, trans-1,2-dichloroethylene were also used. Eight pre-test soil borings indicated that most of the contamination was confined to the zone above the clay layer; one core indicated TCE concentrations in the clay layer ranging from 200 to 1600 ppm. The total estimated mass of VOCs in the soil below and around the facility was between 1300 to 13000 kg.

System Design: The SVE system was placed near the edge of the highly contaminated zone. The test duration was 56 days. Four extraction well nests were installed to 7 m bgs and were connected to a 25 HP blower. Each nest consisted of a shallow screened interval (above the clay layer) and a deep screened interval (below the clay layer). Near the core that indicated TCE contamination within the clay layer, the vacuum in the shallow extraction well and in the deep extraction well were maintained at approximately 20 cm of H_2O and 25 cm of H_2O respectively.

Performance Monitoring: The off-gas was analyzed; 16 shallow gas probes were pre and post sampled; pre, intermediate, and post soil cores were taken and sampled.

Mass Removal: Based on the analysis of off-gas and flow rates, approximately 600 kg of VOCs were removed, of which 95% was TCE. Obviously, no breakdown of the contribution from the clay layer is possible.

Soil Cores: A post-test soil core, taken near the single contaminated clay pre-test core, showed considerable mass removal from the clay layer; for example, from 195 ppm to ND, from 220 to 60, and from 1600 to 2 ppm.

Comments: (1) placement of the SVE system may have biased results, (2) aqueous-phase diffusion limitations should have been apparent near top of clay layer, (3) given the little data collected from the clay layer, the claims made by Michaels (1989) regarding SVE application in clays are unfounded.

8.0 SUMMARY

SVE with dewatering has the following strengths and weaknesses for remediation of DNAPL's in low permeability media:

strengths
- low cost
- reliable, safe and robust
- able to remove a significant amount of mass
- significant experience base exists

weaknesses
- difficult to establish air flow in layered systems
- aqueous and gaseous diffusion limitations will dictate mass removal rates
- little data available from low permeability sites

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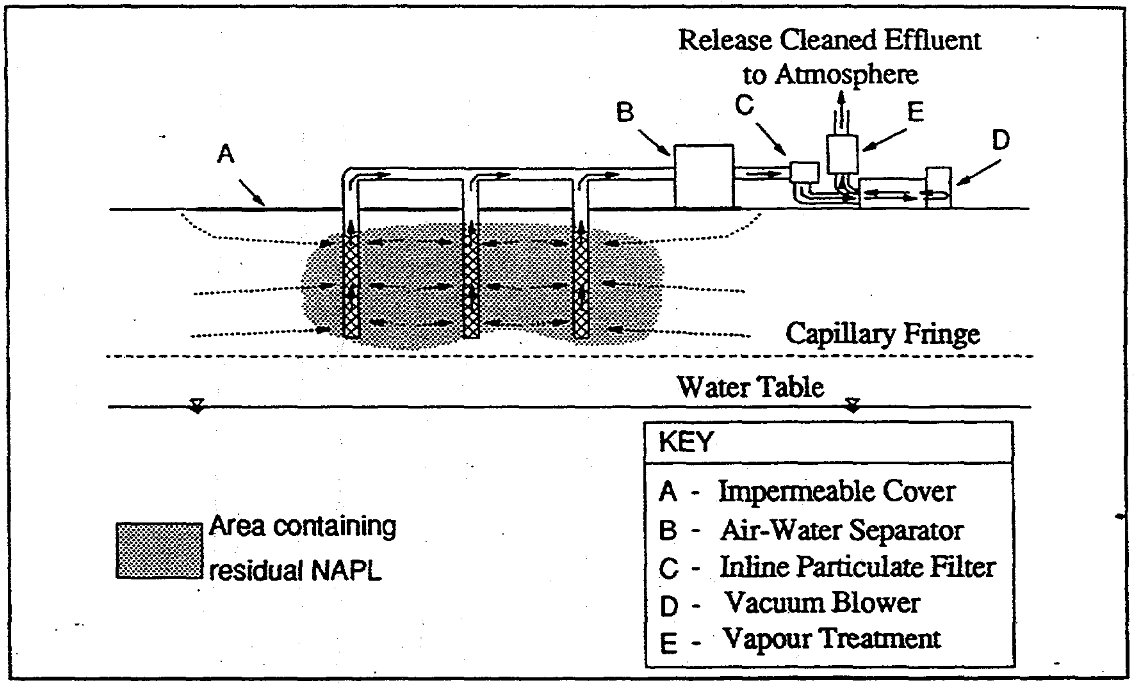

Figure 1. Schematic diagram of a soil vapor extraction system.

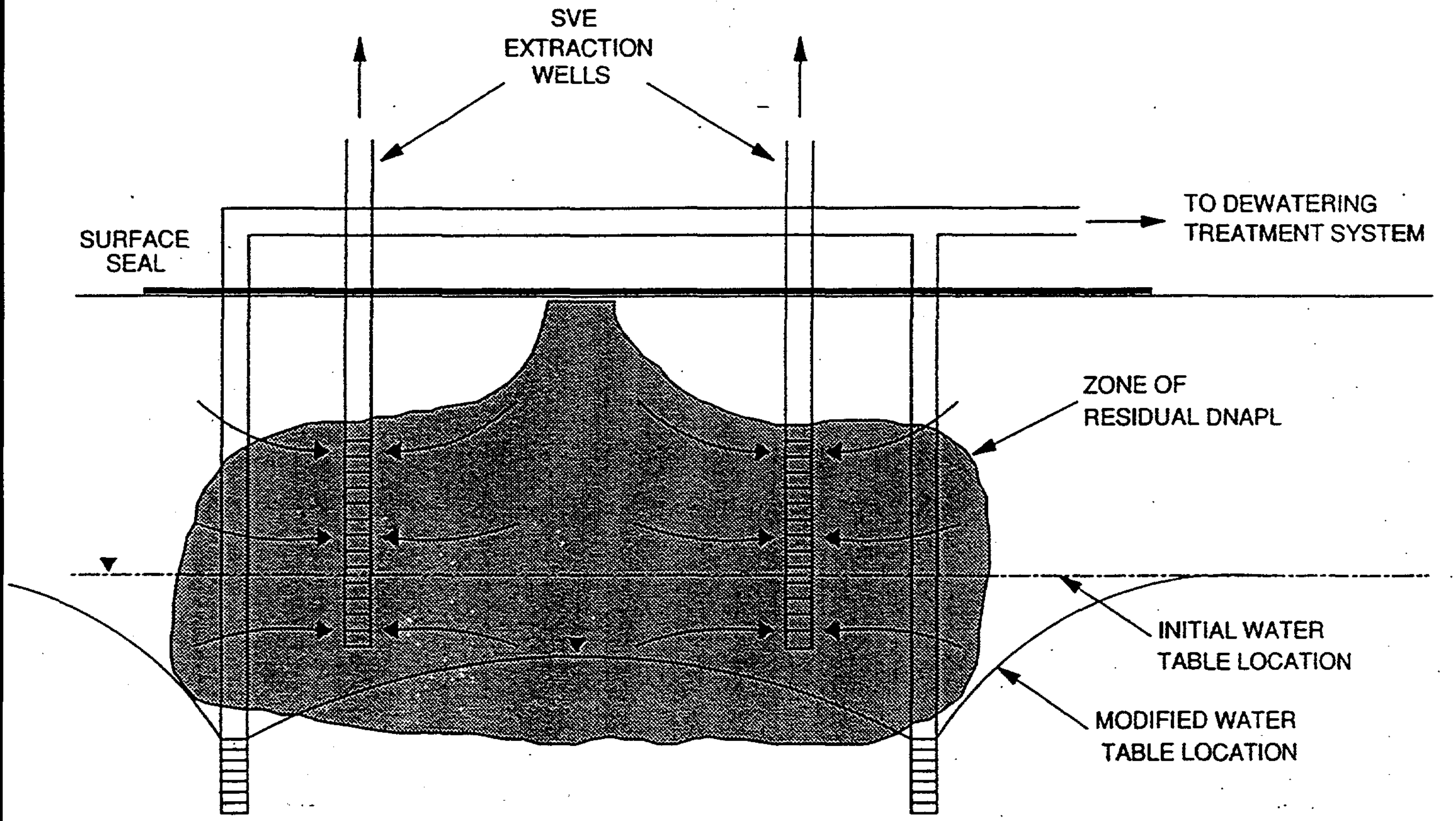

Figure 2. Schematic diagram of SVE combined with a dewatering system.

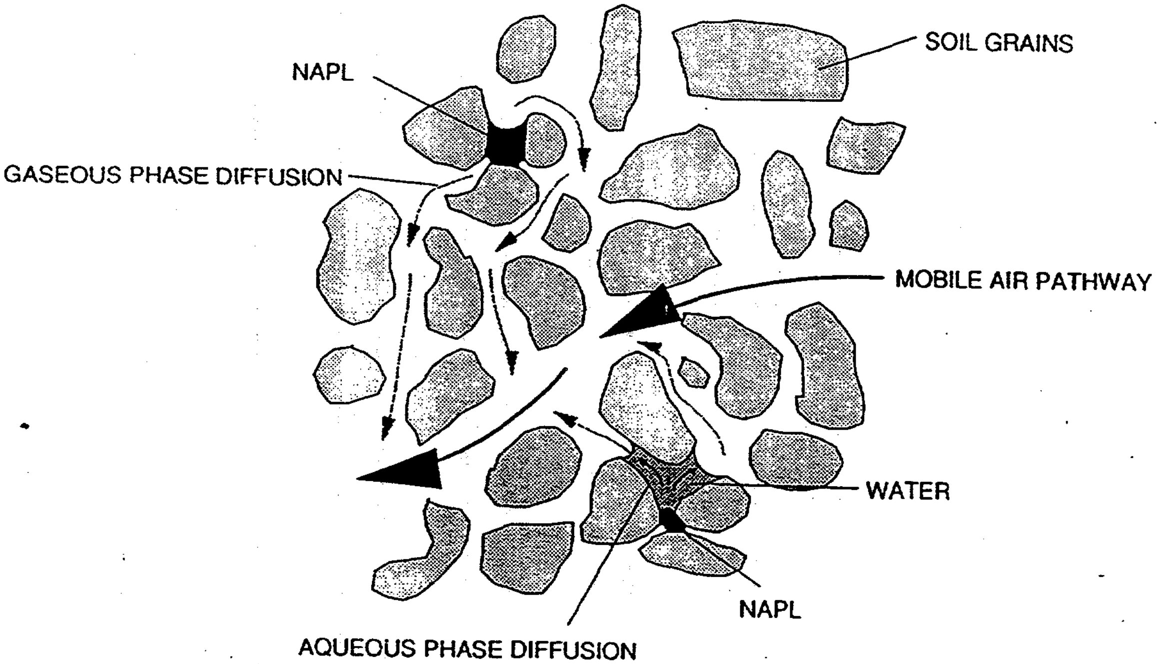

Figure 3. Idealized soil-NAPL-water-air system.

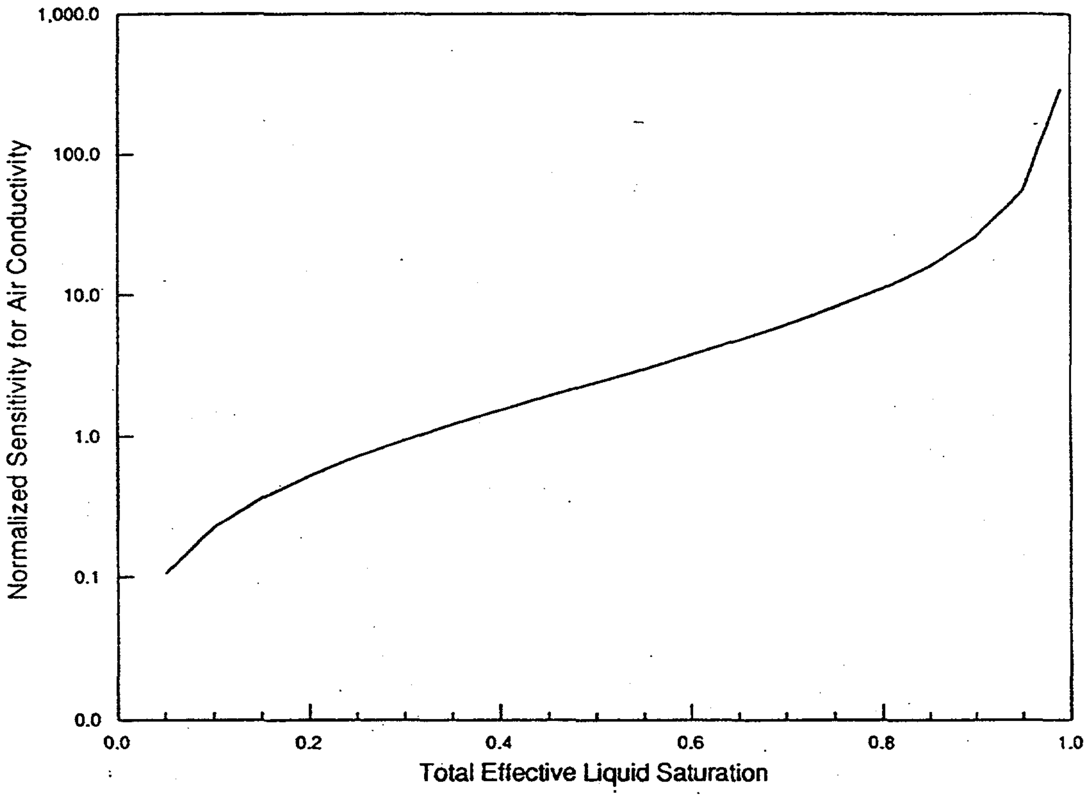

Figure 4. Normalized sensitivity for air conductivity with respect to total effective liquid saturation.

THERMAL TREATMENT OF LOW PERMEABILITY SOILS USING ELECTRICAL RESISTANCE HEATING

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Remediation of DNAPL in Low Permeability Media

1.0 ABSTRACT

The acceleration of recovery rates of second phase liquid contaminants from the subsurface during gas or water pumping operations is realized by increasing the soil and ground water temperature. Electrical heating with AC current is one method of increasing the soil and groundwater temperature and has particular applicability to low permeability soils. Several mechanisms have been identified that account for the enhanced removal of the contaminants during electrical heating. These are vaporization of liquid contaminants with low boiling points, temperature-enhanced evaporation rates of semi-volatile components, and removal of residual contaminants by the boiling of residual water. Field scale studies of electrical heating and fluid extraction show the effectiveness of this technique and its applicability to contaminants found both above and below the water table and within low permeability soils.

2.0 DESCRIPTION OF THE TECHNOLOGY

Electrical resistance heating is a thermal enhancement technology that is applicable to a wide range of media and contaminants. In practice, the technology would be combined with vacuum venting, groundwater pumping or both. In addition, there is evidence that increasing the temperature of the contaminated subsurface environment may accelerate biodegradation reactions. Electrical heating combined with vacuum extraction will tend to dry the subsurface media. As temperatures increase to the boiling point of water, electrical heating will cause boiling of the water within low permeability zones, enhancing the recovery rates of the contaminants found in those regions. For the treatment of volatile compounds, significant enhancement in removal rates are expected through heating to temperatures below the boiling point. However, interstitial water vaporization provides for convective transport of contaminant-laden vapors from low permeability zones, thus eliminating a large portion of the diffusive resistance that limits recovery rates.

The key physical processes exploited in thermal processes are increased solubilities of the contaminant in the aqueous phase, increased equilibrium concentrations in the vapor phase, desorption of contaminants due to an increase in temperature (Scheflan and Jacobs, 1953), and the stimulation of vapor mass flux from low permeability zones due to electrical heating. The trends of increasing electrical conductivity with an increase in temperature (Vaughan, Udell, and Wilt, 1993) or a decrease in permeability (correlated with clay content) mean that the highest energy dissipation rates (and thus a more rapid increase in temperature) will be found in low permeability zones. As the temperature rises in a given region, the energy dissipation rate continues to increase until the boiling point of water is reached. Thereafter, boiling of interstitial water in the low permeability zones occurs. This process effectively strips semi-volatile contaminants from the soils and water of the low permeability matrix through pressure gradient-induced flow of hot vapors towards the vapor extraction wells. For volatile compounds with boiling points below that of water (TCE, carbon tetrachloride, TCA), complete vaporization of the liquid contaminant will occur before the water begins to boil. The boiling of the liquid phases will lead to increased gas permeability and decreased liquid permeabilities during operation. These coupled effects make this technology particularly applicable to low permeability media contaminated with volatile contaminants when combined with vapor extraction.

The major weaknesses of the technology are associated with the high electric fields near the electrode wells and the real or perceived safety concerns. The high electric fields near the electrode wells lead to soil dry-out and thus loss of current since the soil electrical conductivity decreases dramatically with complete drying. By the injection of water (with or without ionic additives) at the electrode locations, and completion of the electrode wells using graphite packing, local electrical conductivities can be maintained at high enough levels to provide acceptable power rates to the subsurface. The safety concerns in many sites can be addressed through proper engineering, but electrical heating near underground utilities and below occupied buildings might be problematic.

The use of electrical heating techniques for the recovery of volatile and semi-volatile liquids from porous media is not new. A large body of research on electrical heating for enhanced oil recovery by viscosity reduction and distillation can be found in the petroleum literature (i.e., Chute and Vermeulen, 1987, 1988). However, the use of resistance heating for the in situ recovery of contaminants has a very short history. The process has been applied to pilot scale cleanup of TCE at Lawrence Livermore National Laboratory (LLNL) in 1992, (Buettner and Daily, 1994), a gasoline spill at LLNL in 1993, and a TCE contaminated site at Savannah River in 1993 (Gauglitz, et. al., 1994). Summary results of those projects are presented in this work.

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

To implement this technology, electrodes are placed at regular intervals, and voltages on the order of several hundred volts are applied to the electrodes. The power dissipation rate is proportional to the electrical conductivity (S/m) and the electric field (v/m) to the second power. Since the electric field drops as the inverse of the distance from the electrode, the near-electrode power dissipation drops as the distance from the electrode to the second power. The far-field power dissipation distribution can be controlled by the use of three-phase AC voltage to electrodes placed in a triangular pattern (the LLNL design) or six-phase power applied to a hexagonal electrode pattern (PNL design). In any case, well spacing becomes a critical parameter for uniform heating. For ER heating, the lower permeability soils tend to have higher electrical conductivities and thus present electrical current paths to the "injected" electrical energy. Therefore, ER heating has a natural applicability to low permeability soils. Also as the soil temperature increases, electrical conductivity also increases. Thus, for a given voltage difference applied across two electrodes, the current and the heating rate increase with time. However, as the temperature increases to the point where boiling of the interstitial water occurs, the current will begin to drop since the drying of the soil will decrease the electrical conductivity of the soil. Since the power dissipation is greatest near the electrodes, provisions for electrode cooling and soil moisture maintenance are needed. By water-cooling the electrodes, the electrical heating wells become, in essence, steam injection wells. Even without water injection, drying near the electrodes will produce an outward steam flux.

Recovery wells are required for the removal of volatilized hydrocarbons. The wells would be similar to those installed during vacuum extraction applications. Above ground vapor cooling would be beneficial. The technology can be applied to most types of soils, but higher water content, low permeability soils are most amenable due to their high electrical conductivities. Low moisture soils may be problematic since their electrical conductivities are also low.

The ability to remediate higher distillation range petroleum products using electrical resistance heating could be limited. Given the large power requirements to vaporize all the pore water, and the feature that dry soil is not a good electrical conductor, it is doubtful that the soil temperature can be raised above the boiling point of water except near the electrodes. However, the increase in temperature from ambient conditions to the boiling point of water will result in an increase in vapor pressures by factors of the order of 40 times. Thus electrical resistance heating to augment vacuum extraction will accelerate the cleanup by similar factors. Also, there may be an advantage in heating the soils to temperatures in the range of 40° C since biodegradation rates seem to be maximized there.

Electrical resistance heating is geared primarily to soil contamination, although groundwater remediation is possible using the technique. The mechanisms exploited during an electrical heating and fluid extraction process are equally applicable to both petroleum and chlorinated hydrocarbon contamination. Access to contaminated regions under buildings or pavement would be possible if extraction well and electrode installation can be accommodated. However, the technology may not be practical under buildings since the structure precludes the installation of wells at close enough spacing and the potential of current leaks through the building utilities would present a safety hazard. Underground utilities and other subsurface metal objects are also problematic since they present alternative paths of current flow. The risk of electrocution exists due to the high voltages and power levels. In the case of flammable contaminants, there may be a risk of spark-induced ignition of the liquid contaminant or explosion of vapors in air. However, as field experience with this technique expands, effective designs that avoid hazardous situations are evolving.

There is no intrinsic limit to the depth of remediation. However, condensation of hot gases on the walls of the extraction casing, and the resulting drainage of liquid contaminants back down the extraction well, would become more problematic as the depth increases.

The utility requirements for electrical heating are substantial. Field demonstrations have been carried out using 480 V / 3 phase line power (LLNL) and 1000 V / 6 phase power (Savannah River). Power rates of up to 1000 kW have been applied to the subsurface and are scaleable upward for larger sites. Operation is not complex and maintenance is minimal beyond that of vacuum extraction operation. The use of water injection to prevent electrode dryout is considered integral to the use of the technique in the vadose zone, and would require additional maintenance and operational effort. However, with appropriate design, the electrical heating component of the process can be controlled automatically.

The surface equipment would be similar to that of vacuum venting and/or groundwater pumping, with the addition of fluid cooling equipment installed on the vapor line (or possibly the fluid extraction line). Vapor cooling would be necessary for carbon adsorption vapor treatment to increase the adsorption capacity of the carbon. No cooling would be necessary for oxidation treatment of the off-gases. With cooling, a secondary waste stream of separate phase liquid contaminants from the vapor cooling equipment may result. However, such a stream would be relatively small, and can be inexpensively disposed of by recycling or incineration.

Analytical models have been developed to predict the performance of electrical heating in raising the soil temperature in a two-dimensional field. Such models can be adapted to describe the spatial variation in boiling rates and contaminant removal rates once steam temperature is reached. Numerical models are also being developed to account for second-order three dimensional effects and temperature dependent electrical properties. Ultimately, fully coupled electrical heating and fluid transport computer codes would be needed to fully describe the myriad of thermal and fluid interactions possible in a given site. Such codes are under development by several groups and are public domain for the most part.

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

Sufficient soil water content is needed to maintain electrical conductivity. As temperatures rise to values near the boiling point of water, the vapor flux out of preferentially heated low permeability zones will enhance volatile removal rates from zones otherwise inaccessible to fluid flow. Hydraulic control of the water table may be helpful in controlling vapor phase transport, but might not be necessary. There may be an advantage in keeping the fractures somewhat saturated to maintain electrical conductivity across those fractures.

The scenario presented could be modeled with a reasonable degree of accuracy. Without consideration of the fractures, there are analytical and numerical models available from LLNL, LBL, and UC Berkeley that could simulate the use of electrical heating in conjunction with fluid extraction for design purposes. More sophisticated simulators capable of fracture inclusion are being developed for research use.

An appropriate design of an electrical heating and fluid extraction system would involve a set of heating electrodes and extraction wells. The electrodes would be placed in the contaminated clay layer, and the extraction wells would be placed in the perched zone above the clay layer as shown in Figure 1. Electrodes would be cooled by low flow rate water injection. Operation of the electrical heating system would occur continuously for a period of time until temperatures begin to rise significantly. Extraction flow rates would be controlled so that the energy removal by pumping hot vapors is only a fraction of the electrical energy input. The goal is to bring the low permeability soil to the boiling point of water. Significant boiling of the separate phase liquid would be expected before this point is reached.

Thereafter, boiling of the interstitial water and vacuum extraction of the vapors will employ sufficient mechanisms to recover contaminants pooled on top of the clay, separate phase product trapped in continuous and discontinuous fractures, and dissolved product diffused into the matrix block. From energy, heat and mass transfer considerations, contaminant removal by interstitial water boiling would be more effective during the depressurization cycle of steam injection than would be expected by electrical heating. However, even with distributed electrical power dissipation to a steam-water-contaminant saturated porous medium, boiling of the interstitial fluids will greatly enhance contaminant recovery rates. If free product DNAPL is present in the fractures, boiling induced steam flux from the matrix will aid in the vaporization and removal of the DNAPL trapped in the fracture. For DNAPLs with boiling points less than that of water, DNAPL boiling would force the contaminant from the region. Boiling of the contaminated water in the matrix adjacent to a fracture could effectively decrease contaminant levels there. Depending on the initial concentration of contaminant in aqueous solution, its boiling point, its solubility in water at steam temperature, and its Henry's constant at steam temperature, uniform heating to 100 °C and subsequent boiling of as little as 4% of the pore water can reduce aqueous concentrations to drinking water standards (Itamura and Udell, 1994). Such a case would be typical of TCE contaminated soils. Compounds such as PCE would require significantly more effort to reach cleanup levels since liquid PCE would not boil before the boiling point of the water is reached.

The scenario presented of the removal of a mixture of TCE and PCE is predictable. Liquid contaminant boiling would occur to some extent by the time the soil reaches 100° C. One would expect that TCE would be recovered preferentially during the heating from 87 to 100° C. Thereafter, the rates of TCE removal would go down while the PCE rates would remain high. Whether or not the liquid PCE would have also disappeared with the TCE vapors will depend on the initial mixture composition. For small mass fractions of TCE in the mixture, contaminant boiling may not occur at all. The simulation of these processes is possible using simple semi-analytical methods, or numerical simulation using codes developed at UC Berkeley.

5.0 COST AND RELIABILITY

The cost to remediate a site of a plan area 40 m by 40 m, with a cross-section shown in Figure 1 would depend on the required number of extraction wells and electrode wells, access to adequate line power, and fluid treatment options. However, capital and operating costs of the order of $\$50/m^3$ might be expected based on similar field activity at LLNL. Thus, the cost may be estimated to be in the range of $250,000. A more detailed breakdown of costs can be made once a final design is available.

The time necessary to remediate the site is determined by the power input rate. Assume that electrical heating at a rate of 1000 kW can be maintained. From an energy balance, the time necessary to heat the 4,800 m^3 target to steam temperature is approximately 250 hours. To boil 10% of the interstitial water would take an additional 90 hours. The theoretical remediation rates could be of the order of 100 mg/kg-day. The question here is the effectiveness of electrical heating in providing uniform boiling throughout the fractured matrix. The spatial distribution of the electrical conductance of partially saturated fractures are largely unknown. Thus it would be difficult to assess the uniformity of the heating. However, the estimated time frame is very short. With a factor of 20 included to account for lower power rates, preferential current paths, and conductive cooling, a time scale of less than a year and remediation rates of 5 mg/kg-day are still attainable.

6.0 COMMERCIAL AVAILABILITY

Three phase electrical resistance heating has been demonstrated at LLNL using off-the-shelf equipment. Six phase heating as demonstrated at Savannah River requires a six phase transformer, but such equipment is readily available commercially. LLNL and PNL personnel are willing to work with commercial entities to implement this technology at specific sites. However, there is no commercial entity that is currently offering this technology on a commercial basis. The likely future enhancements might include water ionic additives in the water used to cool the electrodes (thus eliminating the loss of conductivity due to dryout) (practiced successfully by PNL), co-use of electrode wells as vapor recovery wells, and better designs evolving from additional field experience.

This technique is complementary to steam injection. Field work at LLNL at the gas pad using combined electrical heating and steam injection (Dynamic Underground Stripping) has shown that each of these techniques have strengths is areas where the other has weaknesses. Specifically, electrical heating occurs preferentially in the lower permeability regions where steam injection heats preferentially the high permeability zones (see LLNL Gas Pad case study). Although the results of the electrical heating at the LLNL Gas Pad were inconclusive, it is clear that significant heating rates and boiling rates can be achieved in low permeability zones using this techniques in combination with steam injection.

7.0 CASE STUDIES

Three field studies have been operated to examine the effectiveness of electrical heating and fluid extraction to recover contaminants from spill sites. The first site demonstration, conducted by LLNL on site, was a pilot study of small dimensions with TCE found in both the saturated and vadose zones. The second field demonstration, also conducted by

LLNL on site, was a gasoline spill with second phase liquid contaminants found both above and below the water table. The third demonstration was conducted at Savannah River by PNL using six-phase power. Details are presented below.

Lawrence Livermore National Laboratory, Site 300, Livermore, California

During the summer of 1992, electrical heating of an unsaturated zone contaminated with TCE was combined with vacuum extraction in a pilot scale field demonstration. A region of about 7 m diameter and 4 m in thickness was heated by six electrodes placed symmetrically around the periphery. The extraction well was placed in the center of the zone.

Three phase, 400 V power was supplied to the electrodes during the day; vacuum extraction was operated continuously. The electrical heating ran for 47 days with the temperature in the middle of the pattern increasing from 19° C to 44° C. The temperature continued to rise for several days in the center of the pattern to 54° C after heating was discontinued due to conductive heating from surrounding zones experiencing higher heating rates. A total of 9600 kW-hr of electrical energy was dissipated in the subsurface. Roughly 30% of the input electrical energy could be accounted for inside the pattern by the soil temperature rise.

Vapor concentrations increased by over a factor of 2 during heating as compared to stable rates obtained by vacuum extraction alone. Near the end of electrical heating, vapor concentrations in the extracted vapor decreased rapidly. At least 12 kg of TCE was removed. It is not known if the recovered TCE originated from inside or outside of the target zone. Also unknown was the extent of remediation. The highest pre-heating soil concentration was 100 ppb. Assuming a high soil density of 1600 kg/m^3, and a volume of 156 m^3, a maximum of 25 kg of TCE would be found in the target area. No post heating soil samples were taken. (See Buettner and Daily, 1994, for more details).

Lawrence Livermore National Laboratory, Gas Pad, Livermore, California

In a more recent study, electrical heating was combined with steam injection at LLNL in an effort to cleanup gasoline-contaminated soil within water-bearing zones. This project is referred to as Dynamic Underground Stripping. The site plan and hydogeologic section are shown in Figures 2 and 3, respectively. The subsurface geology was of alluvial origin, with layers of high permeability interspersed with clays and clayey silts. The horizontal correlation of the high permeability layers was moderate except for a thick gravel layer found below the water table from about 35 m (140 ft) to 42 m (150 ft). This gravel layer was found in each well surveyed. The gasoline was detected as a second phase in an area about 50 m (150 ft) in radius as shown in Figure 2. The vertical distribution ranged from 17 m (50 ft) to about 45 m (137 ft) in depth as shown in Figure 3, with significant spreading due to major ground water elevation fluctuations. Indeed, separate phase gasoline was found in the deep water-bearing zone nearly 8 m below the water table as shown. This situation rendered other technologies such as ambient temperature vacuum extraction to be impracticable and groundwater extraction to be time-prohibitive. There were two major flow zones at this site: the deep gravel layer and an upper unsaturated zone consisting of intermingled sands, silts, clays and gravels. A contaminated clay layer of variable thickness separated the two permeable zones.

Six combination electrical heating and steam injection wells were placed around the perimeter of the area contaminated by separate phase gasoline. Three additional heating wells were located in regions of contamination and three recovery wells were installed near the center of the plume as shown in the site plan of Figure 2. No electrodes were installed in injection well GIW-820. A total of 11 electrodes were emplaced (1 in each steam injection well, and 2 in the three electrical heating wells). The electrical heating electrodes in the injection wells were placed in the low permeability zone separating the upper and lower steam zones. The electrodes in the electrical heating wells were placed in the clay layer separating the steam zones and the clay layer above the upper steam zone. The injection wells were constructed to allow separate steam injection into the upper and/or lower permeable regions. The recovery wells were completed over the entire height of the contaminated zone. Also shown in Figure 2 are the placement of the 11 temperature observation wells.

Electrical heating was operated intermittently during the evenings and nights for a period of two months. Power rates of up to 1000 kW were achieved with a total energy input of 202 MW-hrs. Minimal vapor or groundwater pumping was done during electrical heating. Pumping of soil gases and fluids began with the initiation of steam injection. At the beginning of pumping the gasoline concentration in the water had risen to 150 ppm in comparison to historic values of 25 ppm.

During the first steam pass, steam was injected first into the lower gravel layer below the water table for two weeks. Steam broke through at the recovery wells about 10 days after injecting steam. After the first two weeks, steam injection into the upper zone while continuing steam injection into the lower zone at a lower rate. This lower rate did not provide sufficient energy into the gravel layer below the water table to maintain the steam zone. Thus the steam flow rate into the recovery wells dropped to zero until steam broke through to the recovery wells in the upper zone on the 23rd day from the initiation of steam injection. From day 21 to day 30, steam was injected only into the upper zone. From day 30 to day 37, steam was injected only into the lower zone. Steam broke-through again into the lower zone on day 32. Steam injection and fluid extraction ceased at the end of day 35 for a period of 3 months while higher capacity treatment equipment was installed. Steam injection resumed for a second pass on day 144 after 9 days of groundwater extraction and vacuum pumping. The steam injection schedule was periodic with periods of steam pressurization and de-pressurization. Steam was injected a total of 21 days during this 46 days of gas and groundwater extraction. Vacuum extraction and groundwater pumping resumed in October, and electrical heating occurred during November for a period of 50 days. No steam was injected during this final phase.

Temperature logs in each of the 11 temperature monitoring wells were obtained during electrical heating and steam injection phases of this demonstration. Sample temperature profiles inside the ring of injection wells near the ends of electrical heating, and the first and second passes of steam injection are shown in Figure 4. For reference, the lithology log is superimposed to show the correlation between the geologic features and the development of the temperature field. Electrical heating raised temperatures up to 70° C in low permeability zones in temperature monitoring wells near the heating wells. Indeed, electrical heating is shown explicitly to preferentially heat those zones that were ineffectively heated by steam (TEP-7). While the steam initially entered the highest permeability zones during the first pass, conductive heating brought the smaller lower permeability zones to steam temperatures by the end of the second pass. Uniform temperatures in the target zones were observed in TEP - 9 and TEP- 10 by the end of the second pass. However the lower permeability zone separating the two steam zones near TEP - 7 and TEP - 8 had not yet reached steam temperature by the end of the second pass. An interesting detail seem in each of the plots is the effect of groundwater pumping on the temperature profiles in the lower steam zone. Since the energy injection rate into the lower zone was less in the second pass than in the first pass, and the pumping rates were somewhat higher, convective cooling of the lower steam zone occurred due to the infiltration of cold water from unheated zones.

The recovery rates of gasoline are shown as a function of time in Figures 5-7. The process was operated continuously during three different intervals, with additional field work conducted in between during the down-time. During the 1st pass (figure 14), increases in recovery rates were observed in solution, in the gas phase, and as a separate phase liquid within the first few days of steam injection with the highest rate occurring on days coinciding with steam breakthrough into the lower interval of the extraction wells (2/15/93 and 3/3/93). Otherwise, gasoline recovery rates were limited by the use of the regenerated carbon gas treatment system with a capacity of less than 50 gallons gasoline per day. A total of approximately 1700 gallons of gasoline was recovered during the first phase. However, direct measurements of the volumes of the liquid gasoline removed from the condenser could not be made. Therefore those amounts are not shown in figure 14, except as a portion of the liquid imprecisely measured in the liquid megatorr which included the pumped free product. While a greater amount of displaced free product was expected before steam break-through in either the upper or lower zones, the recoveries were restricted by the limitations on liquid pumping rates imposed by the liquid treatment system and the intrinsic difficulty of capturing a free product bank with the two liquid pumping wells. Higher gas and liquid handling capacities in the surface equipment would have allowed increased recovery rates. After five weeks of operation, the system was shut down to install improved liquid gasoline measuring systems and higher capacity fluid handling equipment.

The recovery rates observed during the second pass were much higher as shown in Figure 6. The increased rates were due to higher capacity gas and water treatment systems, as well as the increased subsurface temperatures and cyclic steam enhancement. The recovery rates were highest before steam injection began. Thereafter, periodic peaks in the recovery rates were measured corresponding to times when steam injection ceased and depressurization began. A total of 4900 gallons of gasoline was recovered during the second pass. The second pass was terminated due to permitting restrictions on the boiler while recovery rates remained high and may have continued with additional cycles of steam injection. During the next 80 days, soil samples were collected, the steam boiler was taken from the site, and additional electrical heating wells were installed. The treatment system was shut down during this period.

The recovery rates during the final phase are shown in Figure 7. While significant rates of recovery were measured during the beginning of pumping, the rates fell with time, and the magnitudes were much less than those observed during the second pass. Some improvement in the recovery rates were achieved by converting upper zone injection wells into vapor recovery well. However, little could be done to increase recovery rates during the final few days of operation: including electrical heating. Power rates for the electrical heating during this phase reached 450kW with an average of 250kW. Increases in water condensation rates from the extracted vapors were observed during electrical heating, corresponding roughly to the electrical power divided by the enthalpy of vaporization. An additional 1000 gallons of gasoline were recovered in this final phase. The cumulative total of gasoline removed was 7600 gallons at the end of operation.

The soil concentrations found after the second pass, but before the final stage are shown in Figure 8. In general, gasoline was effectively removed from the hot steam-bearing zones and concentrations were significantly reduced in the low permeability zone separating the upper and lower permeable units. An estimate of 750 gallons of gasoline remaining in the soil after the end of the second pass was made from the soil concentrations shown in Figure 8; about 1000 gallons were recovered during the final vacuum extraction and ground water pumping phase.

Subsequent gas and water sampling showed decreasing concentrations of gasoline components with time, implying that there is no separate phase gasoline remaining at this site. Ethybenzene, toluene, and xylene concentrations in the water dropped to below MCL. Benzene concentrations continued to decrease. Hydrocarbon-degrading biological activity was found in the zones subjected to steam temperatures, indicating that the application of steam did not leave the site sterile. It is expected that no further treatment will be required. Details of all aspects of the Livermore field demonstration can be found in reports to follow (Newmark, ed., 1994).

Savannah River

Coinciding with the timing of the final phase of electrical heating at LLNL, electrical heating was used at Savannah River by PNL to remove PCE, TCE, and TCA from low permeability clays in the vadose zone. Six phase power was used to energize six electrodes emplaced in a hexagonal pattern, with a vapor venting well placed in the center. The electrodes were each 15 feet from the vent well.

The mean line to neutral voltage was near 1000 V over most of the operation. Power rates were in the range of 250 kW. A total energy input of 100 kW-hr was achieved. Soil temperatures rose to 100° C after 8 days of heating. Power was maintained for an additional 17 days with water condensate rates increasing to and remaining at 1,300 gallons per day. The energy required to produce that amount of condensate was about half the electrical power input. A rough estimate of the energy distribution is about 1/3 to bring the target area to the boiling point of water, 1/3 to boil interstitial and injected water, and 1/3 to surrounding soils outside of the pattern.

Slight increases in contaminant recovery rates in the air leaving the condenser were observed upon initiation of the electrical heating beyond that expected of vacuum extraction alone. However the location of the demonstration inside of a larger contaminated zone obfuscated the vapor concentration data presented by Gauglitz, et. al., 1994. The contaminant removal rates in the water condensate have not been reported. However, soil concentrations dropped on average by over 99% inside of the pattern, and by over 95% outside of the pattern in heated zones (Gauglitz, personal communication).

8.0 SUMMARY

Electrical resistance heating, combined with vapor extraction for *in situ* cleanup of DNAPL contaminants found both above and below the water-table in low permeability, fractured media is a promising technique. The primary mechanisms responsible for the effectiveness of this thermal technique are: acceleration of the vaporization of volatile and semi-volatile compounds, desorption of contaminant adsorbed to the solids, and enhanced removal of contaminants in the low permeability zones by water boiling. With proper design and operation, this method of soil and ground water remediation is expected to be relatively rapid, robust, and predictable. Field experience is limited, and no field demonstrations have yet shown the ability of this technique to remediate a site to meet drinking water standards. However, it is reasonable that this technique could reduce soil and groundwater concentrations in low permeability regions to extremely low levels (below 1 ppb) if uniform boiling of water occurs to a modest degree. Thus, there is great potential for this technology.

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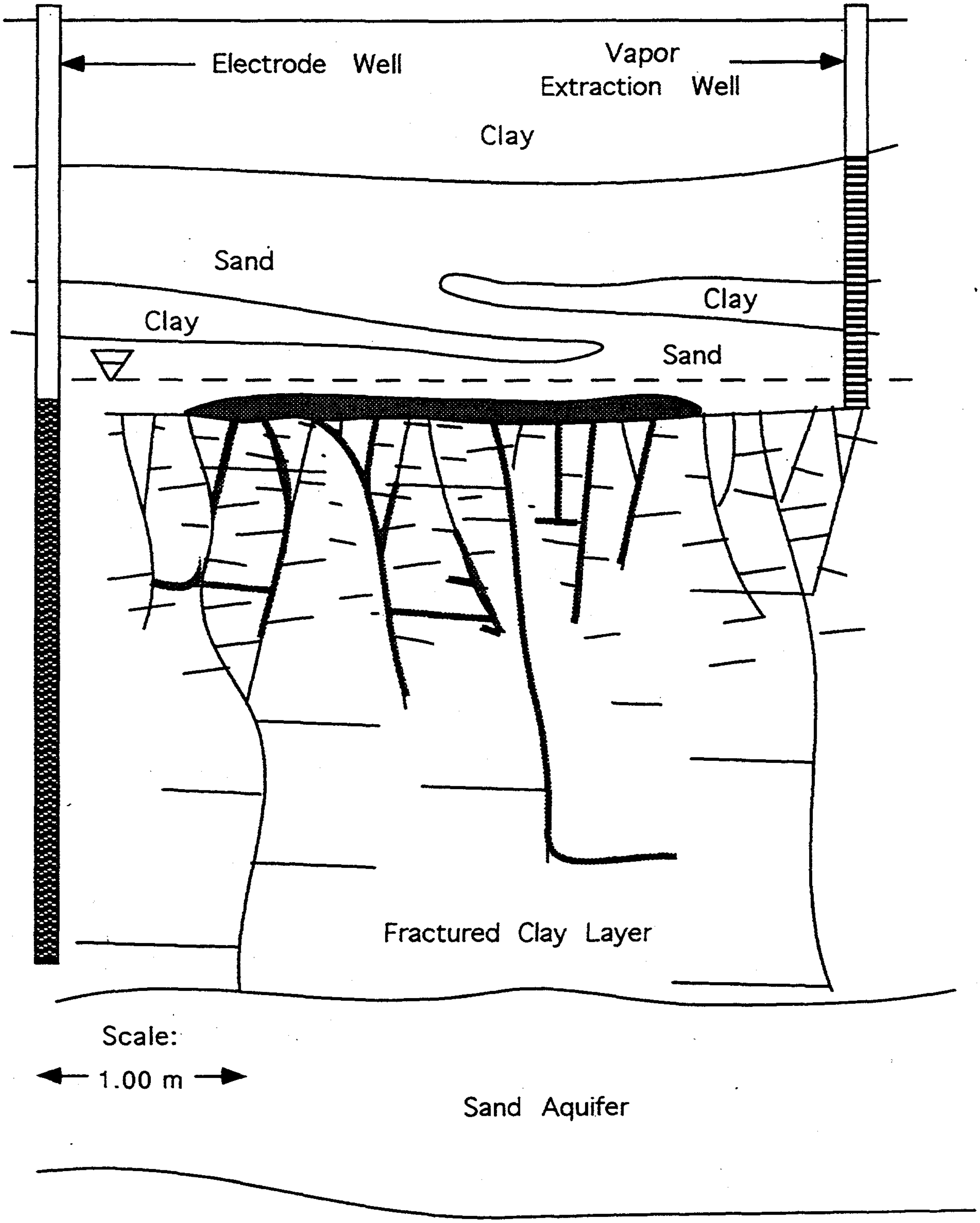

Figure 1. Schematic representation of scenario.

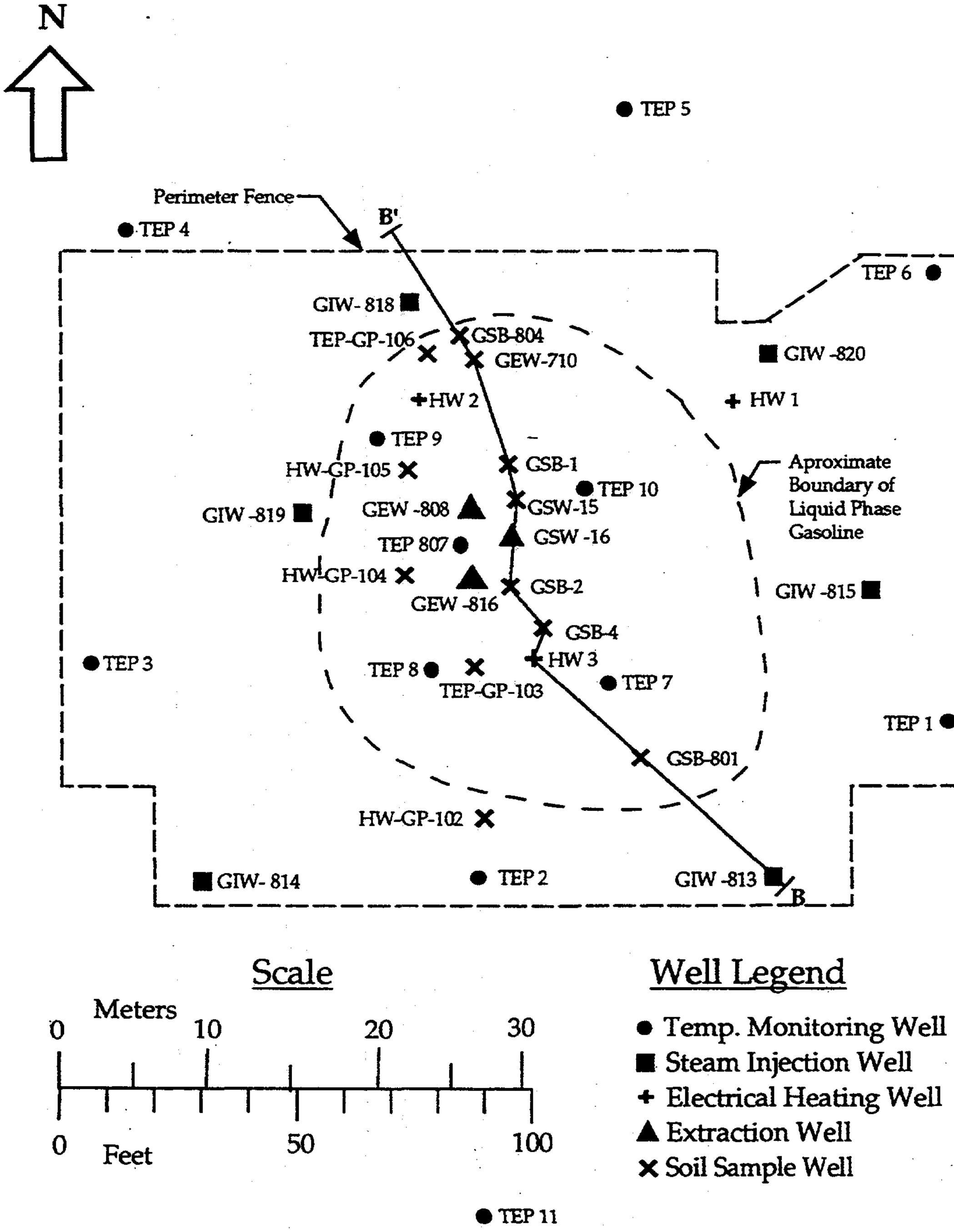

Figure 2. Site plan of the LLNL demonstration project.

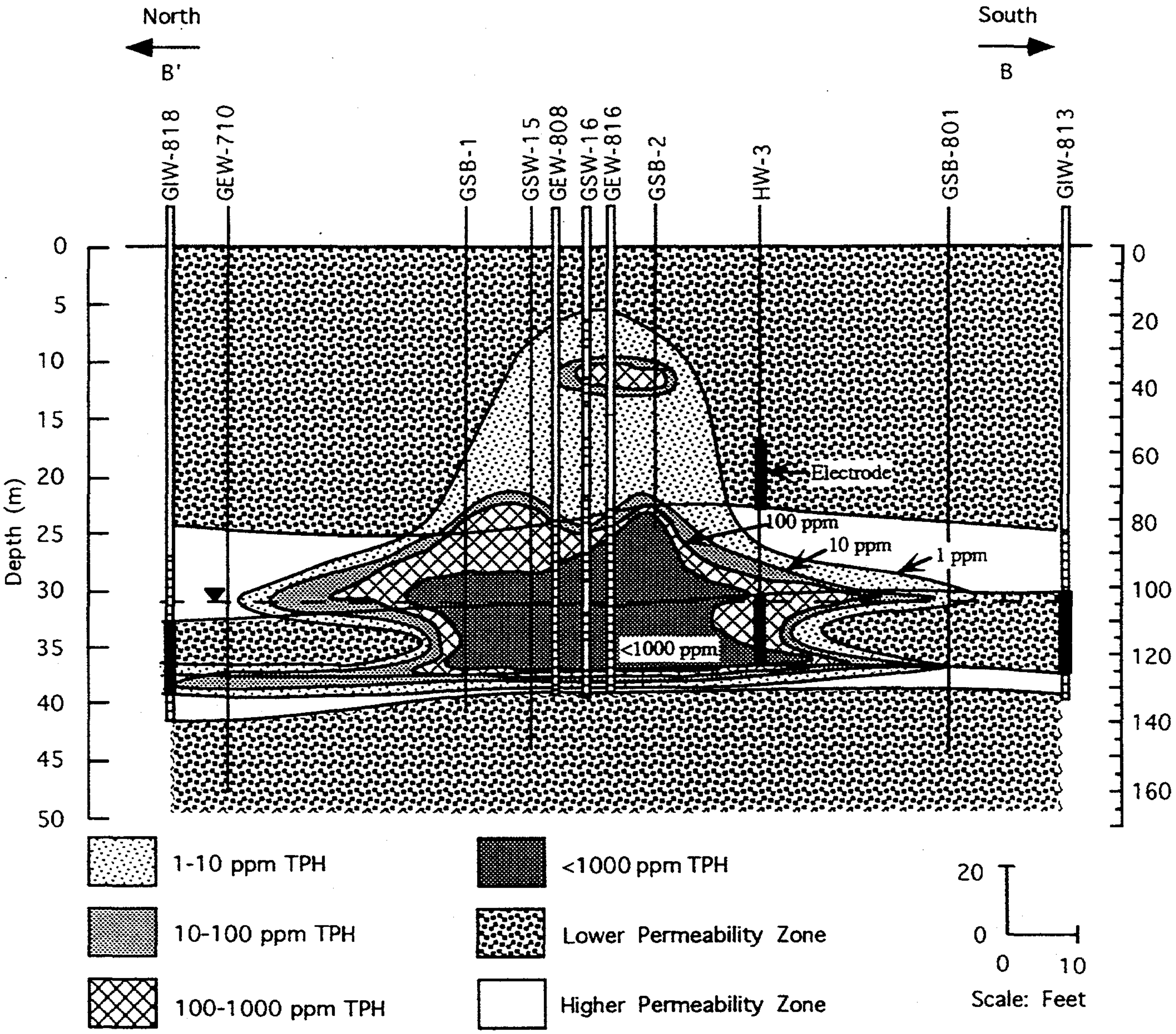

Figure 3 Simplified geologic cross-section showing approximate initial distribution of gasoline, the upper and lower steam zones, the injection and extraction well screened intervals, the electrode locations, and the water table elevation.

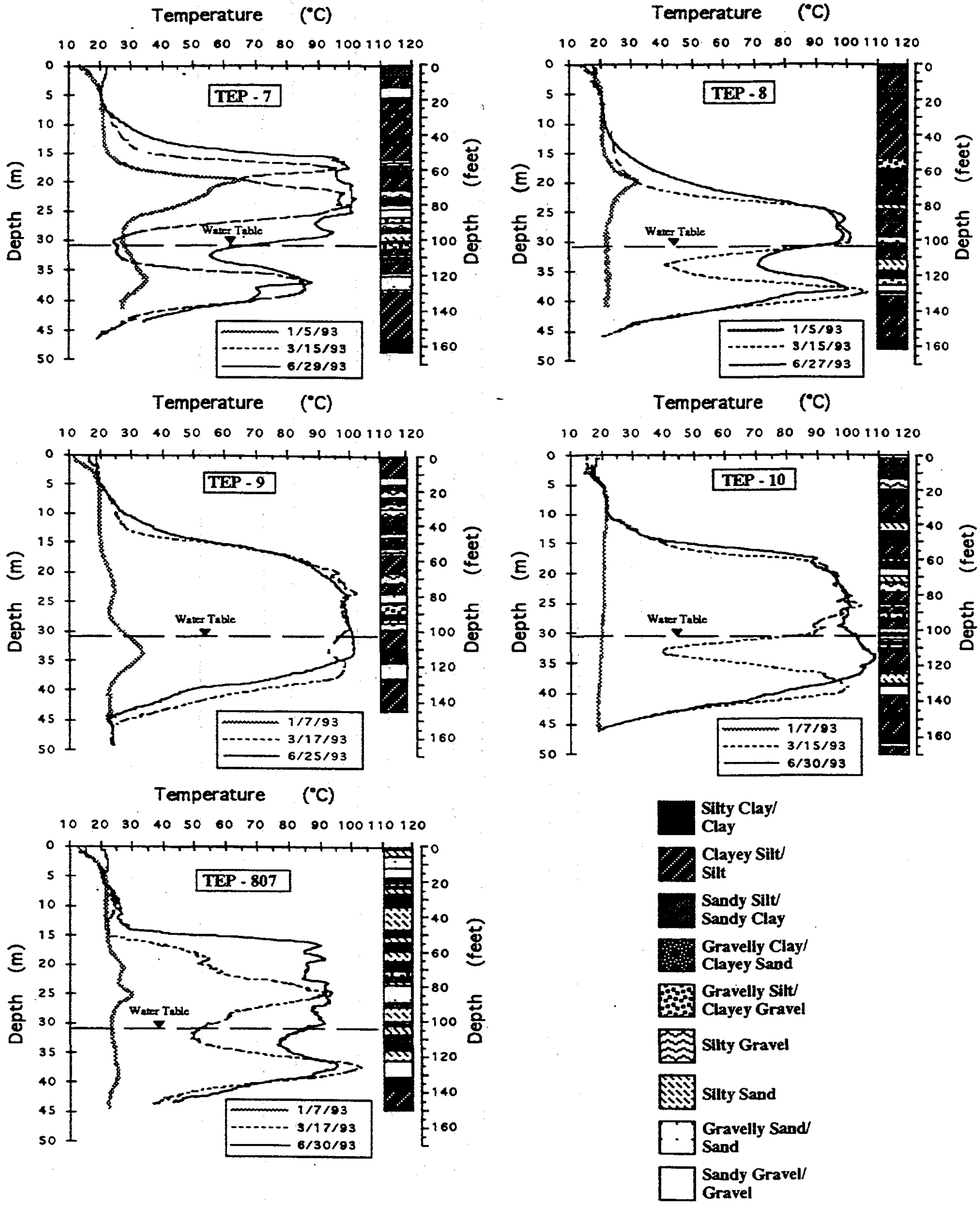

Figure 4 Temperature profiles in wells inside of steam injection ring. The gray lines are the temperature profiles near the end of electrical heating, dotted lines represent the temperature profiles near the end of the first pass, and the solid lines represent the temperature profiles near the end of the second pass. The subsurface lithologies are superimposed to show correlations between the subsurface geology and the development of the thermal field.

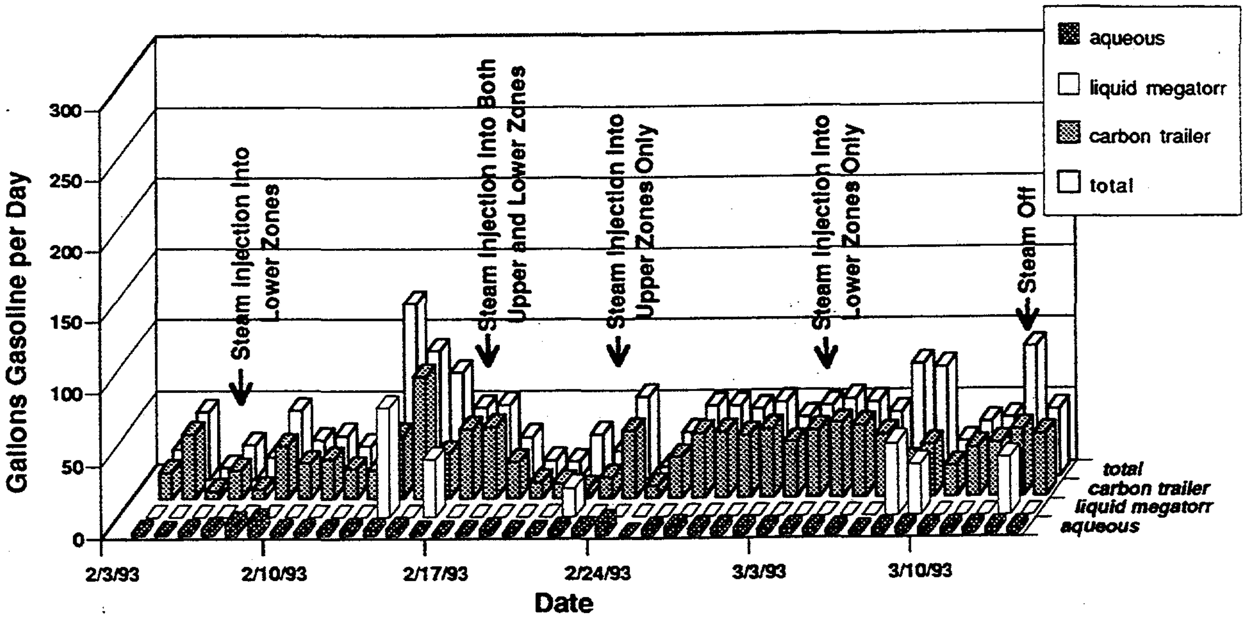

Figure 5. Recovery rates of gasoline from the extraction wells during the first pass.

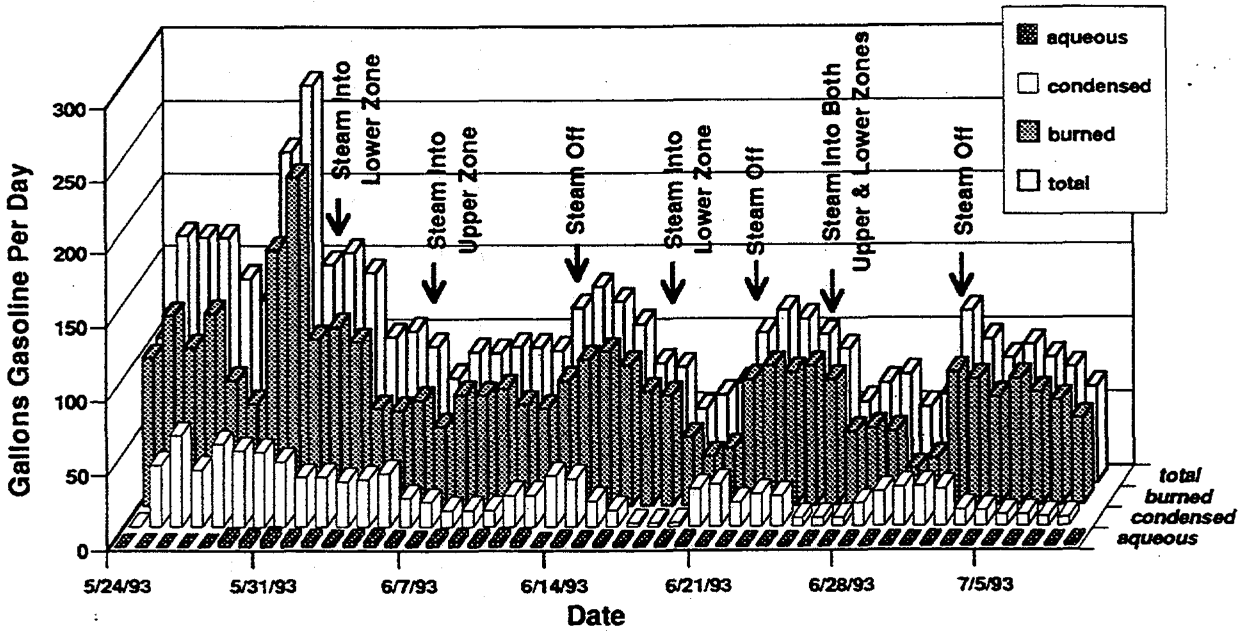

Figure 6. Recovery rates of gasoline during the second pass.

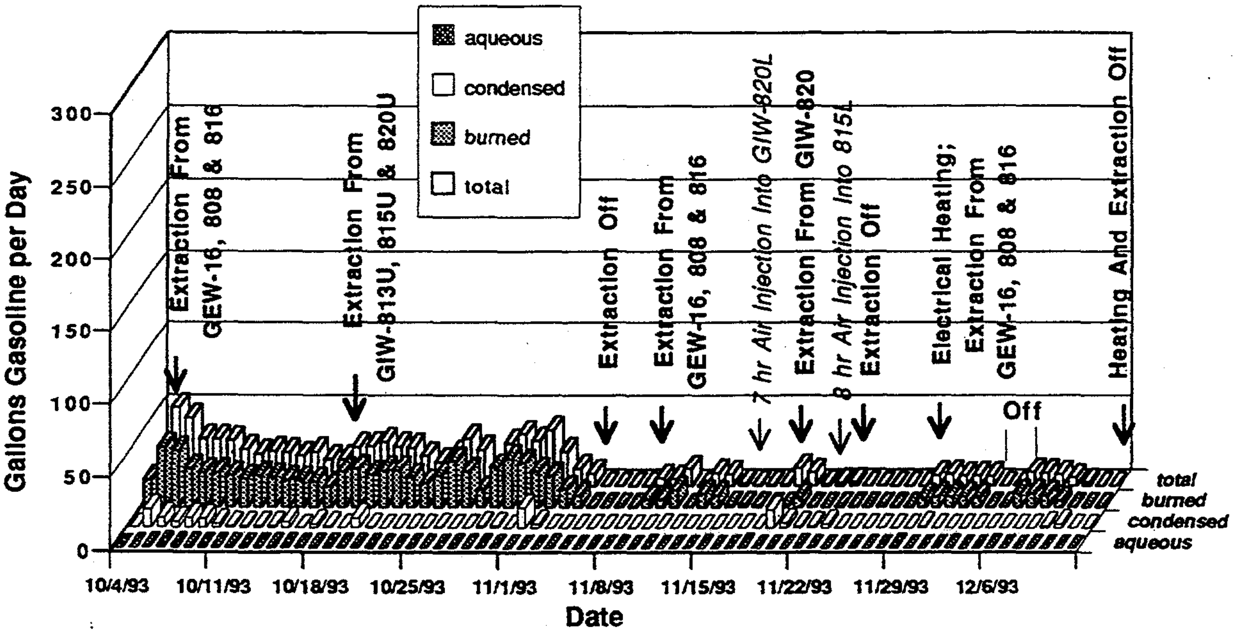

Figure 7. Recovery rates of gasoline during the final operation of pumping system.

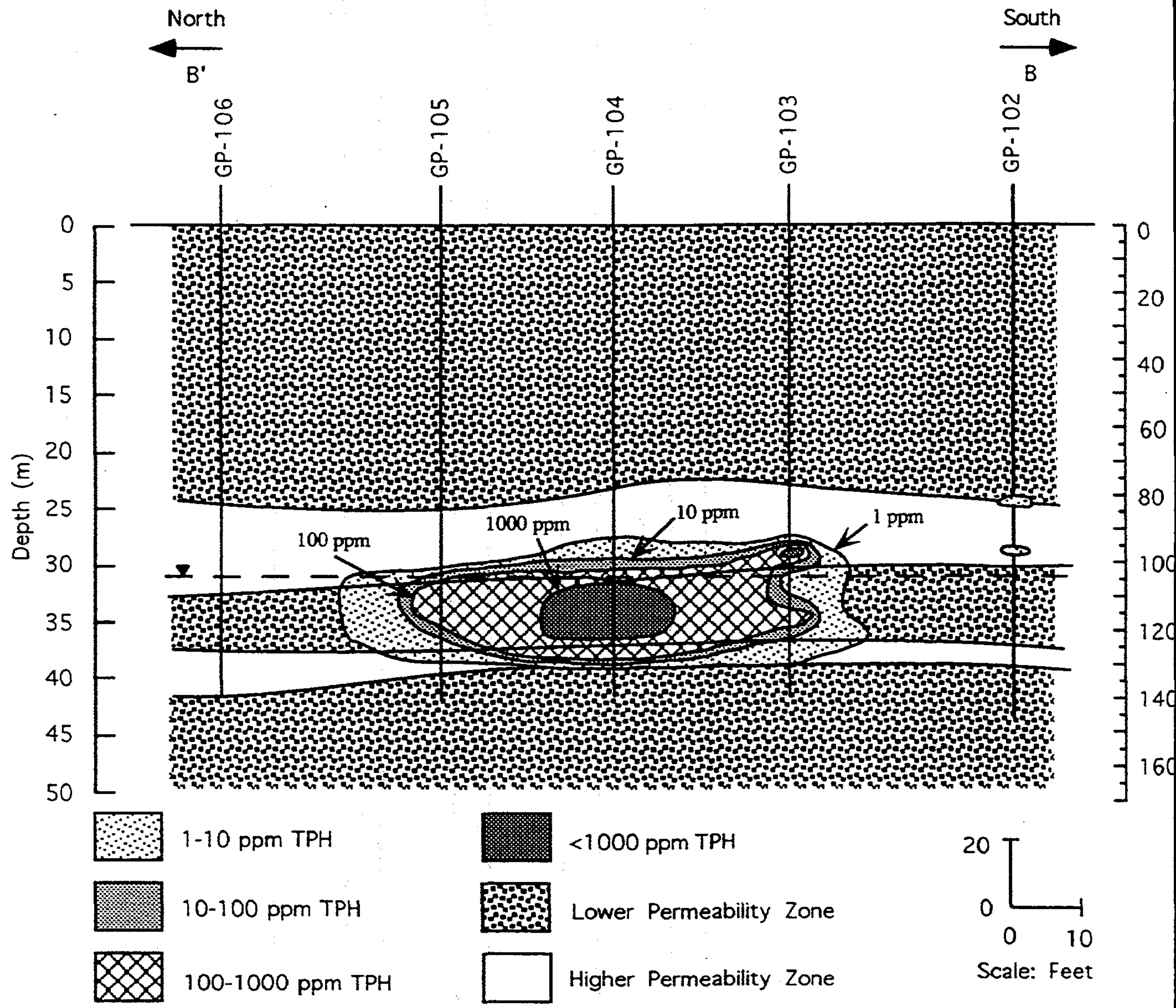

Figure 8. Geologic section showing the distribution of gasoline after the second pass, but before the final extraction phase.

Mixed Region Reactors for In Situ Treatment of DNAPL Contaminated Low Permeability Media

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Prepared by
Oak Ridge National Laboratory
Environmental Sciences Division

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Remediation of DNAPL in Low Permeability Media Project

1.0 ABSTRACT

Fine-textured soils and sediments contaminated by dense non-aqueous phase liquids (DNAPLs) present a significant environmental restoration challenge. An emerging approach to rapid in situ treatment within low permeability media involves the use of soil mixing to create mixed region reactors wherein biological or physical/chemical treatment processes can be employed. In cohesive soils, mixing breaks up the original soil structure and produces soil aggregates or clods separated by interaggregate void spaces. These void spaces create preferential flow paths for more efficient extraction of contaminants from the soil matrix or more rapid diffusion of treatment agents into the soil aggregates. This enhancement technology has been most successfully used with vapor stripping. However, other technologies can also be coupled with soil mixing including chemical degradation, biodegradation and solidification. The application of this technology to DNAPL-contaminated low permeability media appears promising but requires further experiments and models that can simulate the movement of DNAPLs in mixed regions.

2.0 DESCRIPTION OF SOIL MIXING TECHNOLOGY

Despite the overall low permeability of a fine-textured deposit, migration of DNAPLs into and throughout subsurface regions can occur over years to decades along a variety of preferential flowpaths (e.g., fractures, macropores, micropores). Diffusion can occur from the fractures and macropores into the matrix of fine-textured media. The resulting distribution of the contaminants makes remediation of such sites very difficult since the low permeability of the contaminated matrix hinders both contaminant extraction and treatment agent delivery. Yet DNAPL compounds can migrate from these deposits (e.g., by leaching) and cause groundwater contamination for decades. Environmental restoration of these sites has normally consisted of either (1) excavation and on-site storage, or off-site land filling or thermal treatment, or (2) in-place containment by capping and slurry wall emplacement.

An emerging approach to rapid in situ treatment within low permeability media involves the use of soil mixing coupled with treatment processes (dePercin, 1990; Siegrist et al., 1994). Equipment for soil mixing has been in existence for years and has primarily been used for mixing grout with soft soil to improve its geotechnical and foundation characteristics. More recently, soil mixing has evolved into a technology for enabling remediation of contaminated sites by various in situ treatment processes. Existing systems for delivering grout into the soil through the mixer blades can be modified to deliver and effectively distribute treatment agents that facilitate extraction (such as air in vapor stripping processes) or in-place destruction (such as hydrogen peroxide in chemical oxidation processes). In concept, continuously mixed subsurface soil reactors can be created in fine-textured soils and sediments. Within the mixed region, various treatment processes can then be implemented (Figure 1).

Soil mixing represents an aggressive approach to in situ treatment and is therefore most appropriate to source areas characterized by either high contaminant concentrations, biorefractory compounds, and/or sites with lower permeability media. Application to DNAPL contaminated low permeability media is attractive since it offers perhaps the only way to rapidly and extensively disperse treatment agents and concomitantly remove and degrade contaminants in such settings. Various auger and jetting techniques can be employed to achieve subsurface soil mixing. Ready implementation of current technology requires that a site be relatively level and free of overhead obstructions and large buried objects.

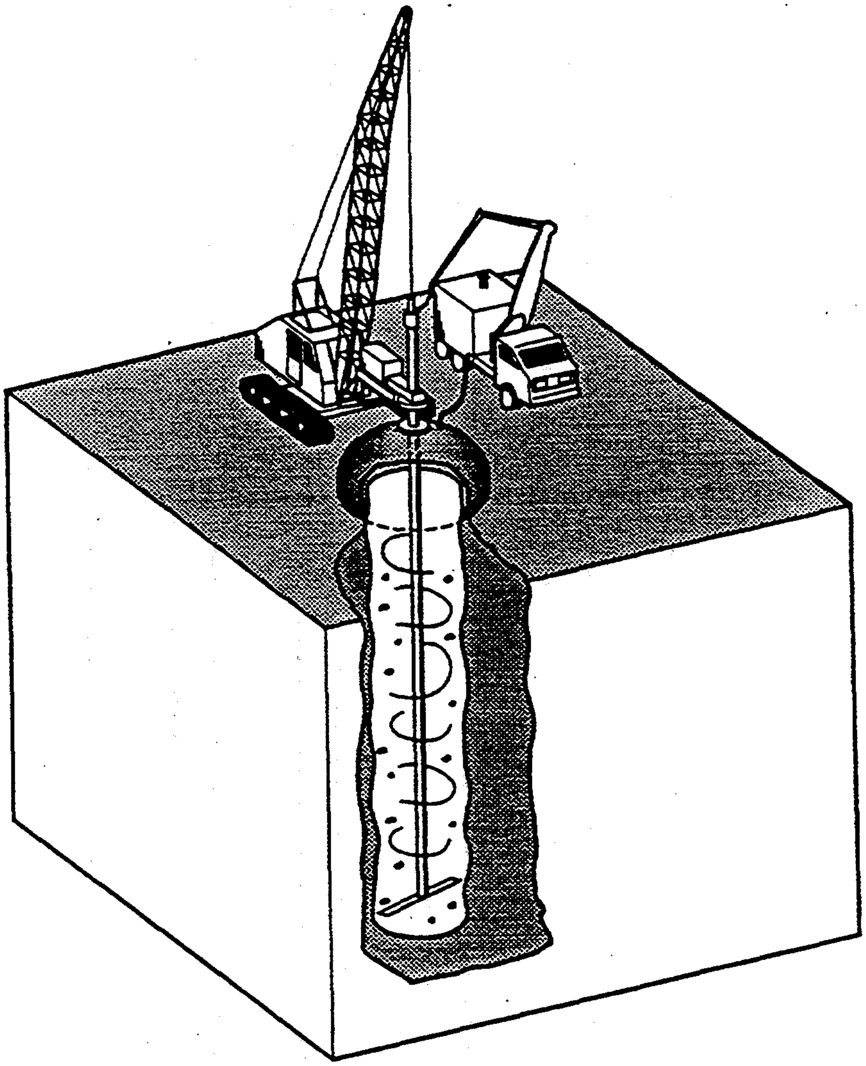

Figure 1. Illustration of soil mixing of low permeability media to facilitate in situ treatment in a subsurface reactor concept. (Note: Treatment agents are delivered through the missing blade(s) with any emissions captured in the hood covering the mixed region.)

3.0 GENERAL TECHNOLOGY CONSIDERATIONS

3.1 ***Is the technology primarily geared to soil or groundwater contamination?*** This enhancement technology is primarily geared towards the removal and/or destruction of contaminants in soil. However, the technology may also be effective in removing or enabling access to DNAPL pools within the saturated soil zone. Removal of these pools can facilitate groundwater treatment.

3.2 ***To what extent is the technology suited for remediating petroleum as well as chlorinated hydrocarbons?*** Since this is an enhancement technology that primarily affects the physical structure of the contaminated deposit, its applicability is not dependent on whether the primary contaminants are petroleum or chlorinated hydrocarbons. The selection of the treatment process to be combined with soil mixing is more a function of the nature of the contaminants. However, it is possible that the disturbance created by soil mixing may induce downward movement of chlorinated solvents or DNAPLs. Mobilization of DNAPLs in mixed regions needs further study.

3.3 ***How well is the technology able to access under buildings or pavements?*** Soil mixing may be feasible under obstructed sites, but data supporting its implementation in these situations are lacking. Remediation under concrete pavements and buildings should be possible as long as soil does not adversely affect the stability of the structures (e.g., by disturbing building foundations). However, current mixing technologies employ near-vertical penetration so that soil mixing treatment under surface obstructions could entail considerable disruption of surface features. To overcome this, implementation of soil mixing enabled by directional drilling or auguring equipment is needed. Any treatment process implemented in this manner would require further developments in off-gas capture and treatment techniques. In addition to potential surface physical disruption, the effects of soil mixing on foundation stability of surface structures need to be considered.

3.4 ***What is the maximum depth of remediation?*** Soil mixing equipment has been adapted from the construction industry where caisson drilling has occurred to depths well over 100 ft. Soil mixing of silt/clay soils to 22 ft depth has been demonstrated at a land treatment site located on a dense fluvio-lacustrine deposit in southern Ohio (Siegrist et al., 1992; Siegrist et al., 1993). Greater depths may be possible, although limits exist due to both geotechnical and treatment considerations. The maximum depth to which this technology can be applied is dependent on the mixed region diameter, the media properties (e.g., soil strength, density, water content, air permeability), and the power and geometry of the mixing equipment (e.g., maximum torque, mixing blade features). The type of treatment process to be combined with soil mixing also needs to be considered. For example, when soil mixing is combined with vapor stripping, higher air injection pressures may be necessary to induce reasonable air flow rates during treatment of deeper columns.

Mixing of deeper soil regions (e.g., >20 ft) may increase absolute volume expansion (e.g., more soil will be lifted above the original ground surface). The volume expansion observed during soil mixing to a depth of 15 ft in a dense silt/clay deposit was observed to be approximately 15% (i.e., 1.5 yd^3 within an above-ground berm per 10 yd^3 of media treated in situ) (Siegrist et al., 1993). During treatment of a mixed region, the best mixing strategy may be to move the auger up and down during treatment in order to maintain "high mixed-porosity" throughout the depth of column. This type of operation may be difficult to implement in very deep columns.

3.5 ***What are the utility, operation and maintenance requirements?*** The utility, operation and maintenance requirements of the soil mixing equipment are typical of construction and earth moving machinery. The soil mixer employed during the pilot-scale test at the land treatment site in southern Ohio (Siegrist et al., 1992; Siegrist et al., 1993) was driven by high torque (300,000 ft-lbs) earth drilling equipment. This equipment was capable of mixing soil that consisted of firm to stiff silty clays and clayey silts (i.e., clays with relatively high shear strength). Mixing speeds up to 5 revolutions per minute (rpm) and a penetration rate of 1 ft per minute were achieved within the 15 to 22 ft treatment depth using 10-ft diameter mixing blades. During this pilot-scale test, high-pressure air injection greatly facilitated soil mixing most likely through the air jets cutting through the dense soil. Mixing blade geometry significantly affects the effectiveness of the vapor stripping process. During full-scale remediation of the land treatment site in southern Ohio, an auger-like mixer was used instead of the two-blade mixer used during the pilot scale test. The former geometry was thought to have caused more difficulty in achieving the same rotational speed and mixer penetration rates as in the pilot test. In addition, air flow through the soil column was believed to have been obstructed by the auger blades, resulting in lateral air movement away from the vacuum shroud. The latter may have also been due to saturated conditions at the site brought about by heavy precipitation during full-scale treatment (see Section 4.1).

3.6 ***Are secondary waste streams produced?*** Secondary waste streams can potentially be produced by the treatment process that is combined with soil mixing. If air injection is used to facilitate the mixing, the generated off-gas must be collected and volatilized organics must be removed from the air stream before being released into the atmosphere.

3.7 ***Are there potential environmental impacts or safety risks associated with use of the technology?*** A potential environmental impact of soil mixing is the uncontrolled downward mobilization of DNAPLs during mixing. However, this may not occur in most physical settings. Safety risks are similar to those associated with any construction equipment.

3.8 ***Are models available to predict performance in porous media and to what extent are they developed?*** In cohesive soils with relatively low moisture content, mixing breaks up the original soil structure and produces soil aggregates or clods separated by interaggregate void spaces. Transport in the mixed system can therefore be simulated to some degree by existing dual-porosity flow models that consider contaminant movement through intra-aggregate and interaggregate voids (Wu and Gschwend, 1988). These models need to be modified to incorporate the dynamic effects of soil mixing as well as DNAPL transport. Such models can be used to simulate the movement of DNAPLs from aggregated soils into the void spaces that are created by the mixing process. Dispersion of treatment reagents into the soil aggregates can also be investigated. In general, a transport model in a mixed region will be useful for simulating remediation processes that are combined with soil mixing.

4.0 LOW PERMEABILITY MEDIA CONSIDERATIONS

4.1 ***What is the effect of soil water content on contaminant removal?*** The water content of the soil affects the effectiveness of the mixing process by influencing the resulting consistency of the mixed soil. At normal moisture contents, mixing produces soil aggregates with interaggregate air-filled void spaces. These void spaces create preferential flow paths for the injected treatment agents which can more rapidly diffuse into the soil aggregates. At very high moisture content or in liquefying soils, the resulting mixed soil may turn into a slurry, and preferential gaseous flowpaths are not created by the mixing. Slurrification may not be entirely undesirable, however, since a more homogeneous distribution of treatment agents may be achieved in slurries. More studies need to assess the extent to which soil mixing can increase subsurface permeability and improve the dispersion of treatment agents in saturated soils with various geotechnical characteristics. Saturated conditions can also cause injected air to flow laterally instead of up through the soil column into the vacuum shroud. This was observed during the full-scale treatment of the land treatment facility described in Section 3.5.

Soil mixing has been employed in conjunction with vapor stripping on at least one occasion for treatment of saturated soils below the water table (Siegrist et al., 1993). Removal of trichloroethylene (TCE) from the saturated zone of a silt/clay deposit was high (>85%) but was somewhat lower than in the overlying unsaturated zone (>95%). However, the relative effect of water content could not be elucidated as the TCE concentrations varied with depth, and the treatment time per unit volume of media also varied.

4.2 ***Is hydraulic control of the water table critical to success?*** Since effects of water content on soil mixing effectiveness are currently unknown, it is difficult to determine whether or not hydraulic control of the water table is critical to success. Most likely, hydraulic control will depend on treatment process features, rather than on mixing.

4.3 ***How effective is soil mixing in the following scenario?*** *• Stratified soil with layers ranging from a medium sand (permeability of* 10^{-3} *cm/s) to a clay (permeability ranging from* 10^{-6} *to* 10^{-8} *cm/s), clay layers contain natural desiccation fractures, effective soil porosity of the clay is <1%. • An underground storage tank of PCE and TCE has leaked slowly over many years and contaminated a sand layer and the underlying clay aquitard. The clay layer, which is 3 m thick, overlies a sand aquifer. The water table is at the top of the clay layer. • Describe the ability of the technology to remove free product pooled on top of the clay, separate phase product trapped in the continuous and "dead-end" clay fractures, and dissolved phase product diffused into the matrix blocks.* Since the original structure of the deposit would be substantially disrupted during soil mixing, the original distribution of contaminants within the fractures/blocks of the clay deposit is not expected to significantly influence treatment effectiveness. Separate phase products trapped in fractures within the original deposit can potentially be released when the mixer breaks up the soil structure. These DNAPLs would be more accessible to an extraction medium (such as air in vapor stripping) or a treatment agent (such as oxidants in chemical oxidation). Dissolved phase contaminants will also be more easily treated since diffusion path lengths for contaminants to move out of the aggregates or for treatment reagents to move into the contaminated aggregates are shortened by soil mixing.

A potential problem when applying soil mixing to this scenario is the downward migration of DNAPLs that may be induced by disturbing the original soil structure. This is of particular concern since the clay layer is underlain by a sandy aquifer. As mentioned previously, additional studies must be conducted to determine DNAPL movement in mixed regions.

Another consideration in this scenario is the accessibility of the contaminated zones. If current mixing technology is to be used, the leaky underground storage tank must be removed if contamination occurs primarily beneath this structure.

5.0 COST AND RELIABILITY

For the scenario described under section 4, assume that the contamination covers a plan area of 40 x 40 m, and the clay layer is 3 m thick. The TCE concentration in the clay is 2000 mg/kg, and the target cleanup level is 200 mg/kg (90% removal). Soil mixing is a technology for the enhancement of remediation in low-permeability media. Therefore, remediation costs as well as required treatment times are primarily a function of the treatment process to be combined with soil mixing. Based on a limited amount of full-scale data with chlorinated solvents like TCE, the estimated cost for soil mixing combined with vapor stripping to achieve a 90% removal efficiency is approximately \$200/yd^3 (Siegrist et al., 1993). This assumes that off-gas treatment constraints are nominal. The total volume of soil to be treated in the scenario described above is 6315 yd^3; the estimated cost for remediating this site to the target level is ~\$1.3M.

6.0 COMMERCIAL AVAILABILITY

Soil mixing is a commercially available technology, although its application for in situ treatment of DNAPLs in low permeability media is limited. One of the first commercial vendors of in situ soil mixing combined with hot air and steam extraction was NovaTerra, Inc., Torrance, CA (formerly Toxics Treatments) (Treweek and Wogec, 1988; U.S. EPA, 1989; dePercin, 1990; Guenther, 1990; Roy, 1990). The NovaTerra system, referred to as the Detoxifier, consists of three main components: (1) a process tower, (2) a control system and (3) a chemical treatment train. The process tower is essentially a drilling rig composed of dual, overlapping, counter-rotating, 5-ft diameter, hollow augers designed to penetrate to approximately 30 ft while simultaneously injecting steam and hot air into the subsurface. The steam and hot air are added to and mixed with the soil at increasing depths as the drilling proceeds. Steam is injected at 450-475°F and 380 psi, and the soil temperature reaches 160-175°F. Treatment is achieved in overlapping blocks with an effective ground surface area of 27 ft^2. The ground surface is covered by a shroud that is under vacuum to contain the stripped contaminants and direct them to the chemical process train. The control system includes process monitoring and control through the use of on-line analytical instrumentation such as a flame ionization detector (FID) for total hydrocarbon analysis, a gas chromatograph (GC) for specific organic analysis, and temperature and depth probes. The chemical process train includes a condenser for liquid contaminant recovery, a carbon adsorption system for removal of contaminant vapors, a reheat system for heating and recycling of injected air, and a feed system to supply agents (steam, etc.) to the drill head assembly.

Another commercial system was developed by Millgard Environmental Corporation, Livonia, MI (Siegrist et al., 1992). Their crane-mounted vertical mixing system is designed to mix the subsurface using 6- to 14-ft diameter horizontal mixing blades. During the in situ mixing process, treatment agents are injected through a vertical, hollow shaft and out into the soil through orifices in the horizontal soil mixing blades. The system also includes a dome-like shroud that sits on top of the treatment columns to collect off-gases generated during mixing. Treatment is achieved in butted or overlapping columns. Monitoring and process control can be accomplished with on-line sensors and instruments similar to those described for the NovaTerra technology.

Other mixing technologies have been developed and are commercially available. These include systems by GeoCon, Inc., Halliburton Environmental Technologies, and In Situ Fixation Company. These soil mixing technologies include various configurations of hydraulically driven mixing paddles and augers. Air, steam, or other agents reportedly can be fed to the subsurface through a hollow shaft or jets on the mixing blades. GeoCon, Inc. is currently involved in the full-scale remediation of the DOE land treatment unit where soil mixing was proven to be an effective enhancement technology during laboratory experimentation and a full-scale field demonstration (Siegrist et al., 1992).

7.0 CASE HISTORIES

In its earliest adaptations soil mixing was used to deliver solidification agents into the subsurface to immobilize contaminants. In 1988 an EPA demonstration was completed at a PCB contaminated site in Florida where two 10 ft by 20 ft areas were treated in 3-ft diameter columns to depths of 14 and 18 ft (Stinson and Sawyer, 1989).

There have been at least four independent tests of the NovaTerra Detoxifier system (Treweek and Wogec, 1988; U.S. EPA, 1989; dePercin, 1990; Guenther, 1990; Roy, 1990). Three tests were conducted at a site in San Pedro, CA, (two conducted as part of the EPA SITE program and one under the direction of the California Department of Health Services Toxic Substances Control Division) and the fourth was conducted at a petroleum hydrocarbon contaminated site in Carson, CA (evaluated by Tetra Tech, Inc.). This fourth test was done by the original manufacturers of the technology, Alternative Technologies for Waste, Inc. (ATW) and Calweld, Inc.

At the San Pedro site over 8,000 yd^3 of soil was contaminated with up to 12,000 ppm of chlorinated hydrocarbons plus other volatiles and semi-volatiles from a few ppm to 50,000 ppm. Up to 99% removal of volatiles from the soil was achieved (efficiencies of removal ranged from 54% to 99+%). Semi-volatile organics (SVOCs) were removed with efficiencies ranging from 7% to 98%. Post treatment concentrations of VOCs averaged 57, 53, and 71 ppm, respectively, in the three tests. For the SVOCs, 920 and 490 ppm remained after completion of two of the tests. At the Carson site, when the total petroleum hydrocarbon (TPH) concentration was less than or equal to about 1,000 ppm, removal efficiencies were 75 to 90% for a 15-ft deep soil column with an average treatment time of 47 min per column. When TPH was greater than 10,000 ppm, removal efficiencies were 90 to 95% in a 20-ft deep column at 78 min./column.

Treatment time with the Detoxifier system is reportedly a function of four factors: type of contaminant, depth of contamination, the soil matrix, and the cleanup standard. Treatment is reportedly not limited by soil particle size, initial porosity, chemical concentration, or viscosity. Waste streams produced by the Detoxifier system include off-gas that is contained by the shroud and routed through a scrubber for particulate removal and through activated carbon for organic removal. The off-gas is reheated after clean up and reinjected through the hollow drill rods to provide a closed loop. The saturated steam is condensed and is recycled for solvent recovery or stored for disposal. Air emissions as measured by EPA during the SITE program test were only 0.073 lb/d for four blocks treated. For successful operation the site must be graded to 1% and must be greater than 0.5 acres. The area must be capable of supporting the equipment's weight and all underground obstructions greater than 12 in diameter must be removed. Treatment costs, typically ca. \$300/yd^3, are strongly dependent on soil type and contaminant volatility.

Research and demonstration of soil mixing as a technology for treatment enhancement of organics in low permeability media has been performed by Oak Ridge National Laboratory (ORNL) over the past few years (e.g., Gierke et al., 1992; West et al., 1993a; West et al., 1993b; Siegrist et al., 1992; Siegrist et al., 1993). Research efforts have been directed at treatment of a silt/clay deposit beneath the X-231B Solid Waste Management Unit at the DOE Portsmouth Gaseous Diffusion Plant located in southern Ohio. The X-231B Unit was used from 1976 to 1983 as a land disposal site for waste oils and solvents. Dense silt and clay deposits (K_{sat} $<10^{-6}$ cm/s) beneath the unit were contaminated with trichloroethylene, 1,1,1-trichloroethane, and other volatile organic compounds (VOCs) (~1-100 ppm range) and very low levels of uranium and technetium. The shallow ground water (water table at ~12-14 ft depth) was also contaminated, with some contaminants at levels well above drinking water standards. ORNL research has included a comparative evaluation of vapor stripping, chemical oxidation, and solidification processes in continuously mixed subsurface soil reactors (Figure 1).

Initial evaluation of soil mixing combined with vapor stripping and peroxidation was first conducted in the laboratory using undisturbed soil cores from the site as well as on cores prepared from packed soil spiked with TCE (West et al., 1993a; West et al., 1993b). The cores were mixed using a simulated mixing system built from a reconfigured drill motor equipped with a swivel joint through which treatment agents were delivered to the cores (see Fig. 2). Mixing of the cores broke up the cohesive soil into smaller aggregates, thereby improving treatment efficiency by increasing the soil's bulk permeability and surface area for mass transfer (see Fig. 3). Air injection at 5 cfm would have been impossible if the core had not been mixed prior to treatment. Removal efficiencies for vapor stripping coupled with soil mixing were variable, but ranged up to 95% for the clay soils with initial VOC concentrations in the ppm range. Similar efficiencies with peroxidation were achieved.

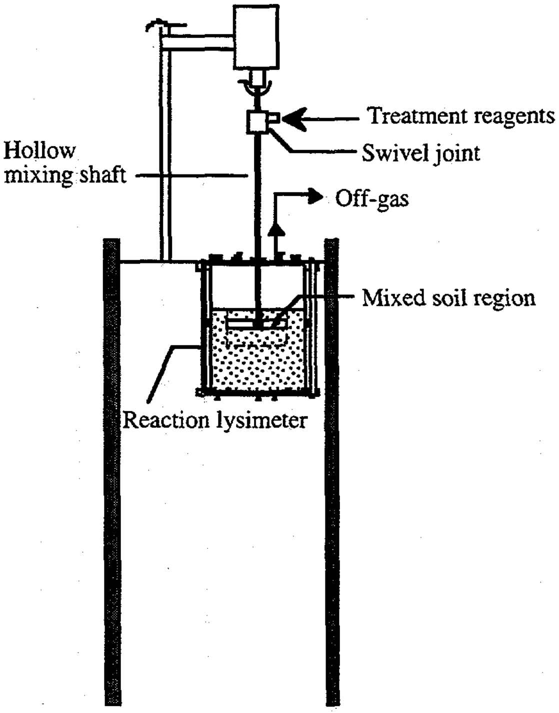

Figure 2. Mixing apparatus for laboratory-scale evaluation of soil mixing (West et al., 1993)

A full-scale field demonstration was conducted at the X-231B site during late Spring 1992 (Siegrist et al., 1992; Siegrist et al., 1993). Tests were conducted using mixed region vapor stripping (MRVS), peroxidation (MRP) and solidification/stabilization (MRSS). MRP is discussed in more detail in a companion paper in this volume (Gates and Siegrist, 1994) while details on MRSS may be found elsewhere (Siegrist et al., 1995). Three, 10-ft diameter soil columns were treated using hot air (i.e., ~130°C) to a depth of 15 ft while one column was treated to a depth of 22 ft. Three, 10-ft diameter soil columns were treated using ambient air (i.e., ~35°C). In all columns treated, the operating conditions were largely the same with the 10-ft diameter mixing blades moving continuously up and down during a total treatment time of ~225 min. Air injection flow rates ranged from 1300 to 1500 scfm. Due to mixing of the soil system, a berm was created above the original ground surface with the soil volume representing ~15-18% of the original volume within a treated column.

Soil and contaminant translocation during mixing were investigated through a bromide tracer test. A bromide slug was implanted at a depth 4.5 ft within one of the 10-ft diameter treatment columns (Fig. 4a). Bromide was not detected in any of the premixing samples collected. Post mixing samples were collected from the column at three borehole locations along a transect that runs through the bromide implant (see Fig. 4a). Locations TG-A and

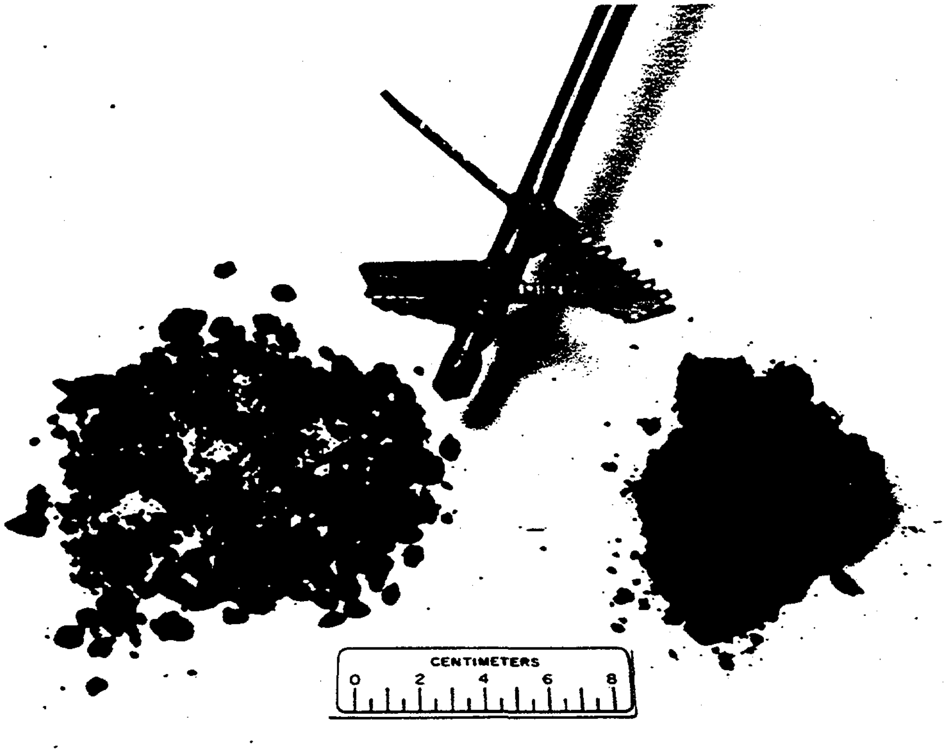

Figure 3. Physical structure of X-231B silty clay soil before (right) and after (left) mixing in the laboratory-scale tests. Mixing blade used is shown at the center of the photograph.

TG-C are the boreholes that are, respectively, farthest and closest to the slug location. Analysis results indicated a radially inward and upward bromide movement without substantial downward movement caused by mixing. This result is significant since there was an initial concern that mixing may cause contaminants to migrate downward towards the water table. It should be noted however that the bromide tracer study only simulates the behavior of VOCs that are sorbed onto the soil or dissolved in the porewater, and may not be applicable to DNAPL movement in mixed regions. The latter was beyond the scope of the project since DNAPL presence at the site was thought to be unlikely based on soil contaminant levels that were predominantly below 100 ppm.

Mass removal curves deduced from off-gas hydrocarbon concentrations suggested that removal of VOCs from the hot air soil columns continued throughout the entire treatment interval (see Figs. 5 and 6). In the columns treated to 15-ft depth, VOC removal efficiencies were roughly 50% after the initial 90 min of operation and 85% after approximately 120-150 min of operation. Statistical analysis of the pre- and post-treatment soil VOC field data indicated that the removal efficiency for a 15-ft deep treated column was between 95 and 98%. VOC removal efficiency during hot air treatment to 22-ft depth was ~88%, somewhat lower than that achieved during treatment of the 15-ft depth zone. This lower efficiency could have been due to several factors including higher concentrations of pre-treatment soil VOCs, reduced treatment time per volume of soil treated, and treatment below the ground water table. The treatment performance achieved with ambient air MRVS was similar but slightly lower than that achieved with hot air. In the columns treated to 15-ft depth, VOC removal efficiencies of 50% were achieved during the initial 90 min of operation, while 85% was achieved after 140-180 min. of operation. Processing rates and costs estimated from demonstration were ~200 yd^3/d and ~\$200/yd^3 (Siegrist et al., 1993).

ORNL has also provided technical support for the full-scale remediation of this site through MRVS and conventional soil vapor extraction in the mixed regions. Work has been completed, and preliminary analysis of soil VOC data shows excellent removal efficiencies.

8.0 SUMMARY

Soil mixing is an effective technology for enabling remediation of contaminated low-permeability media. It has been most effectively combined with vapor stripping but has also been coupled with chemical oxidation and solidification/stabilization. Soil mixing technologies have been used to remediate DNAPL compound contamination in low-permeability media but not when DNAPL pools or residuals have been present. Prior to the application of this technology to such sites, it is necessary to conduct further studies on DNAPL movement in mixed soils. Experimental investigations in this direction should provide an understanding of contaminant movement in mixed regions. Based on these experiments, models for mixed-region DNAPL transport can be developed and used for designing and simulating treatment processes combined with soil mixing.

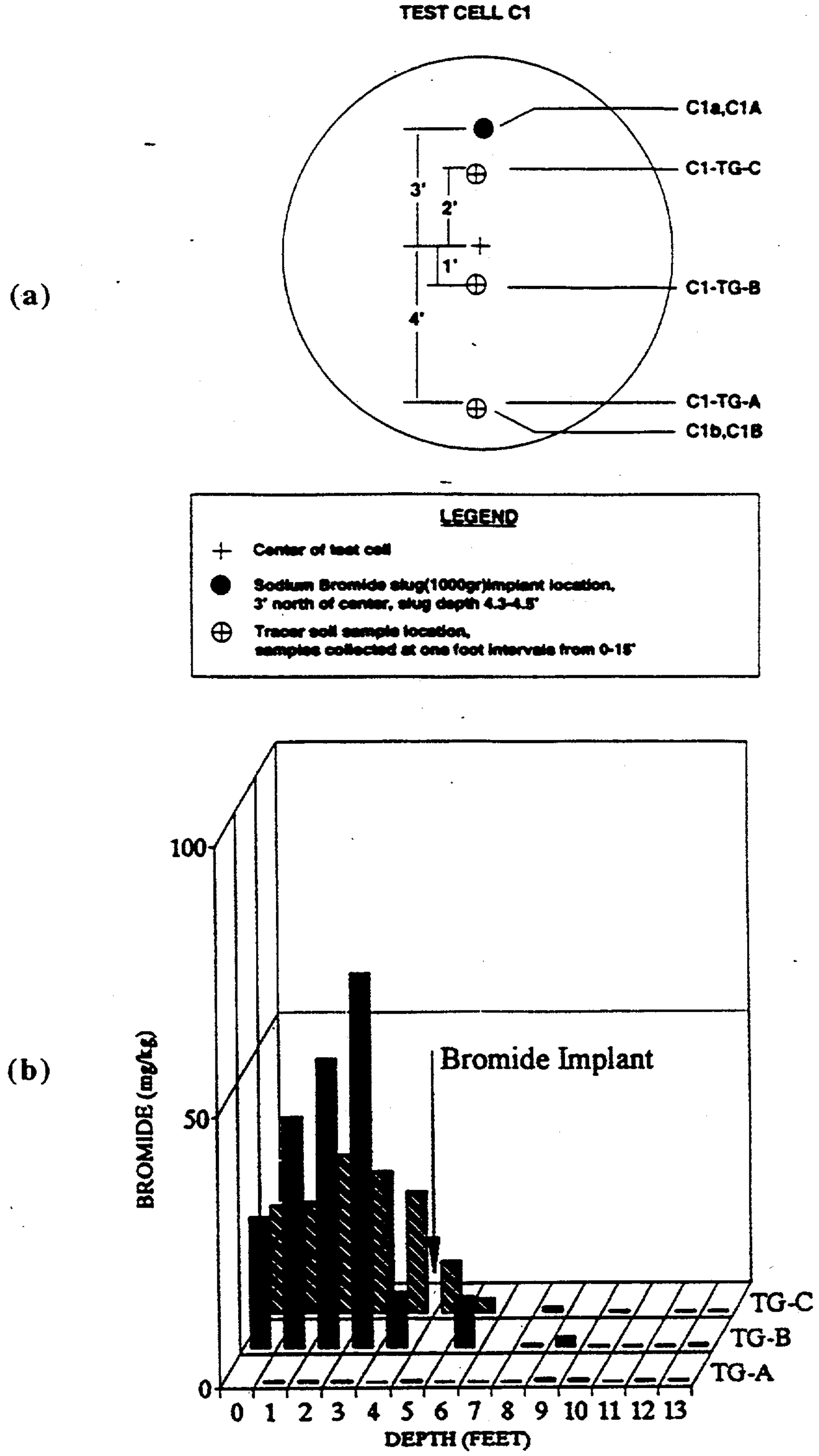

Figure 4. Bromide tracer test during soil mixing at the X-231B unit in the Portsmouth Gaseous Diffusion Plant. (a) Bromide implant and postmixing sampling locations. (b) Bromide content of postmixing samples. Note: Bromide was not detected in any of the premixing samples.

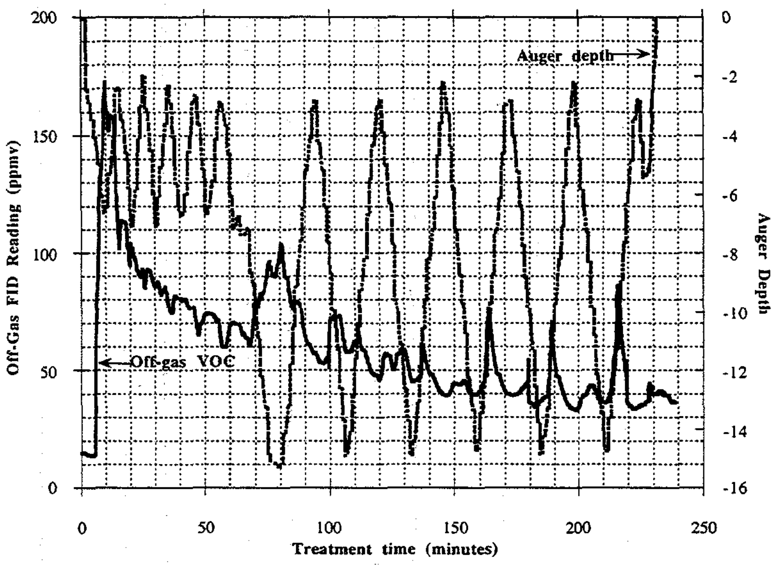

Figure 5. Off-gas VOC content monitored by an online flame ionization detector (FID) during hot air MRVS (Siegrist et al., 1994). Auger depth also shown in graph. VOCs in off-gas include trichloroethylene, 1,1,1-trichloroethane and 1,1-dichloroethene.

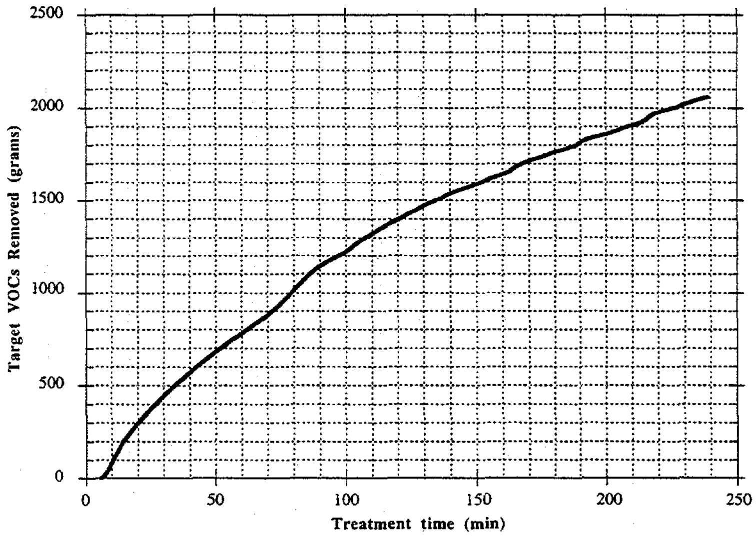

Figure 6. Cumulative mass removal curve calculated from off-gas VOC content and flow rate during MRVS (Siegrist et al., 1994).

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