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Petroleum Contaminated Low Permeability Soil:

Hydrocarbon Distribution Processes, Exposure Pathways and In Situ Remediation Technologies

Health and Environmental Sciences Department
Publication Number 4631
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STEP

Strategies for Today's
Environmental Partnership

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ABSTRACT

Remediation of hydrocarbon contaminated sites having silty or clayey soils poses special technical challenges to site managers because such low permeability soils typically resist remediation with conventional technologies. Recognizing the limited information available to field practitioners charged with evaluating remediation options for low permeability soil, API initiated a multi-year program to consolidate information on the topic and conduct research on technologies that show promise for removing, or enhancing the removal, of contaminants in this media. The goal is to increase our understanding of the need and ability to remediate such soils in-situ. This report presents a set of ten papers focusing on light non-aqueous phase liquids (LNAPLs) in low permeability soils. Collectively, the papers address four key topics: (1) processes affecting the migration and removal of LNAPLs; (2) exposure potential posed by clay soil hydrocarbons via a soil, groundwater or air pathway; (3) available models for predicting LNAPL removal and (4) techniques presently available to remediate or enhance remediation. Each of the techniques discussed are capable of facilitating removal of hydrocarbons from low permeability soil. However, it is important to evaluate the degree to which human exposure can be further reduced given the effort and cost associated with applying these remediation approaches.

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SUMMARY OF PROCESSES, HUMAN EXPOSURES AND TECHNOLOGIES APPLICABLE TO LOW PERMEABILITY SOILS

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ABSTRACT

This paper summarizes a series of ten focus papers on the topic of light non-aqueous phase liquids (LNAPLs) in low permeability soils. Collectively, the papers address four key issues: (1) physical and chemical processes affecting the migration and removal of LNAPLs; (2) available models for predicting this behavior; (3) exposure potential posed by clay soil hydrocarbons via a soil, groundwater or air pathway; and (4) techniques presently available to remediate or enhance remediation. The goal is to provide guidance and understanding on the need and ability to remediate such soils in-situ. The focus is primarily on the vadose zone of petroleum-contaminated sites.

Section 1

INTRODUCTION

Recognizing the limited options available to field practitioners charged with remediating sites with silty or clayey soils, the API initiated a three-year program beginning in 1992 to consolidate information on the topic and conduct research on technologies that show promise for removing, or enhancing the removal, of contaminants in this media. A multi-discipline group was assembled under the umbrella of the API to address the four phases of the problem referenced above. These individuals agreed to work as a team and write *focus papers* on their areas of expertise, which included topics in the process, modeling, exposure and technology areas. The team included the following:

Topic	Author	Affiliation
• Process Issues	David McWhorter	Colorado State Univ.
• Modeling Issues	Marian Kemblowski	Utah State Univ.
• Exposure Issues	Terry Walden	BP Oil
• Soil Vapor Extraction	Fred Payne	ETG, Inc.
• Bioventing	Robert Hinchee	Battelle Memorial Inst.
• Thermal Processes	Kent Udell	Univ. of Cal. at Berkeley
• In-Situ Soil Mixing	Robert Siegrist	Oak Ridge National Lab
• Hydraulic Fracturing	Larry Murdoch	Univ. of Cincinnati
• Pneumatic Fracturing	John Schuring	NJIT
• Surfactant Flushing	Philip Gschwend	MIT

Section 2

PROCESS ISSUES

Low permeability soil refers to silts or clays whose saturated hydraulic conductivity is generally below 10^{-5} cm/s. These soils can be encountered in three distinct types of geologic settings. The first is a massive clay formation where the permeability is very limited and in fact dominated by secondary fractures normally the result of a desiccation or weathering process. The second is a layered or stratified formation where silt or clay layers are interspersed within sandy or higher permeability layers. The third can be considered a subset of the second and consists of silt or clay 'lenses' that tend to be discontinuous and of a limited lateral and vertical extent within a sandy matrix. Fluid (including contaminant) migration is distinct in each setting and the remediation strategies differ accordingly for each media.

In massive clay formations containing natural fractures in non-arid regions, the fractures a short distance above the water table are generally air-filled while the adjoining 'solid' matrix blocks between fractures are water-saturated due to capillary pressure forces. What this means is that should a hydrocarbon spill occur, the LNAPLs will fill the fractures in the soil and bypass the matrix blocks, traveling downward until they encounter the capillary fringe (the area just above the water table), at which point they will spread laterally in cross-cutting fractures. The large entry pressures required to 'push' the LNAPL into the matrix will tend to keep these separate phase hydrocarbons in the fractures.

Although separate phase product (i.e. LNAPL) invasion into the water-saturated matrix will not occur to any great extent, its constituents will eventually appear in the matrix as a result of the process of diffusion, i.e. movement resulting from the existence of concentration gradients. This is an aqueous phase - not a separate phase - process. The soluble constituents in the LNAPL will dissolve and a concentration gradient will be established between the dissolved hydrocarbon components in the fracture and the uncontaminated pore water in the matrix. The more soluble components will partition out of the LNAPL phase first, and over a period of weeks to months, part or all of the LNAPL mass in the fractures will diffuse into the matrix, with equilibrium established when the matrix storage capacity (including both dissolved and adsorbed phases) is reached.

The process of diffusion has a rather significant impact on remediation strategy. Diffusion is a slow process, and a phrase that is commonly heard is that 'if it takes x amount of years to diffuse into the soil, it will take x amount of years to get out'. In fact, this is extremely optimistic. Simple diffusion calculations indicate that the time to achieve 85% mass recovery is nearly 10 times as long as the time the contaminant is in the ground before remediation begins. So if a spill were to occur 2 years before remediation (defined as an air or liquid flushing system which sweeps the fractures free of contamination), it may take 20 years to get 85% of the mass out, and 200 years to achieve 95% removal, under the conceptual assumptions that were made (see McWhorter, this volume). These long remediation periods are the result of disparate concentration gradients. High gradients drive the contaminants quickly out of the fractures, whereas only low gradients exist when the fractures are cleared, establishing a slow process of reverse diffusion out of the matrix. It is apparent that technologies that rely strictly on diffusion-controlled fluid movement will take a long time to achieve success (if ever) and could therefore have high life cycle costs.

An important example of this concept is in the application of soil vapor extraction. The remediation literature has numerous examples where high vacuum systems (some approaching 25 inches of mercury or 0.8 atm) have been used for clay soils, presumably to improve the zone of influence of the induced air flow around the extraction wells. Air will likely, however, flow through the fractures in a massive clay formation, or the sandy layers in a stratified formation, and use of the term 'radius' - in implying uniform flow through the subsurface - is misleading in this regard. If the mass transfer of contaminants is diffusion-limited, the air flow rate through the fractures or high permeability layers is immaterial, and the vacuum system should be sized to the smallest unit that will simply keep the fractures swept clear, thereby minimizing operating costs.

Section 3

MODELING ISSUES

To define the exposure potential as well as the need for remediating hydrocarbons in low permeability media, a good understanding of the chemical composition of the LNAPL (e.g. crude oil or refined petroleum products), the geology and the subsurface processes affecting LNAPL behavior is needed. Regarding the first element, each key compound's vapor pressure, solubility and mole fraction in the LNAPL mixture are the critical parameters. The geologic factors that control exposure are subsurface permeability, the degree of stratification or fracturing, soil moisture content and distance of the source from the water table (for a groundwater pathway) or the receptor (for a vapor inhalation route of exposure). In order to assess exposure and the need or ability to remediate the site, the following geologic parameters should be measured in each of the three discussed settings:

Massive Clay	• Permeability and air-filled porosity of the fractures • Average fracture spacing and connectivity
Stratified Soil	• Permeability over discrete intervals • Air-filled porosity in low permeability layers • Average fracture spacing and connectivity, if any
Clay 'Lenses'	• Diffusion coefficient of contaminants in clay • Thickness and length scale of lenses

Tracer data may be used to estimate some of these parameters, such as air-filled porosity or average fracture spacing (which could be calculated from the tracer flow data after assuming or measuring an average aperture dimension). To determine the need for - or efficacy of - remediation, this data could be modeled to determine fate and transport of the contaminants, both with and without remediation. This is where the third element of the evaluation comes into focus - the subsurface process data. Partitioning, biodegradation and retardation effects need to be considered. Biodegradation in low permeability soils is particularly relevant because of the generally long residence times of dissolved or vapor phase product in the subsurface as it moves between a source and a receptor.

Given the varied subsurface conditions and contaminant compositions one might encounter and the data requirements for modeling heterogeneity, the use of analytical models for screening purposes rather than numerical models for detailed prediction is considered the most practical approach at the present time. This approach would provide answers to questions such as whether a particular remedial action can be effective and what gross exposure threats are posed by leaving the soil untreated.

Section 4

EXPOSURE ISSUES

Human exposure to contaminated media can be the result of either direct or indirect contact with soil, groundwater or their vapor emissions. What distinguishes the potential for exposure in clay soils from other more permeable media is the unique soil structure. The small pores comprising the matrix blocks increase the capacity of the soil (relative to a more permeable media), to store and 'sequester' contaminants over time and to retain water in the matrix. The secondary or 'dual porosity-dual permeability' nature of the material, due to the presence of natural fractures, results in non-uniform distribution and transport of LNAPL, water and vapor phases throughout the subsurface. The low permeability of the bulk media affects the migration of contaminants in the vadose and groundwater zones.

4.1 SOIL CONTACT

The direct soil contact pathway is strongly influenced in clays by bioavailability of the compounds. Bioavailability is a concept which refers to the fact that contaminants which may be present in the matrix (in the sense they are extractable with a solvent) may no longer pose a toxicity risk because of the way they are retained or sequestered in the soil matrix. In simplest terms, the contaminants diffuse into the interior pores of the soil or into the humic fraction, and are increasingly slow in reappearing at the surface of the soil (where their toxicity can manifest itself) due to desorption rate limiting mechanisms. While this phenomenon applies to all soils, it is particularly relevant for clay because of its small pore structure. From an exposure standpoint, reduced bioavailability lessens the absorbed dose (and hence risk) of direct soil contact, either by ingestion or dermal contact. Identifying the suite of tests to demonstrate and quantify bioavailability is the subject of recent research led by the Gas Research Institute and the oil industry.

4.2 GROUNDWATER EXPOSURE

Exposure via the groundwater pathway is strongly a function of the type of fine-grained geologic setting. In massive clay soils, with no underlying sandy aquifer, there is little exposure threat because the low permeability limits contact in the source zone (because wells would be unproductive and therefore, not used), and downgradient of the source (because of limited plume migration potential). However, for the case where a contaminated clay stratum containing fractures lies above or below an aquifer, mass transfer under two scenarios must be considered:

- If LNAPL is present in the fractures, rainfall or a fluctuating water table flowing through the fractures will release dissolved phase components at their effective solubility limit (defined by Raoult's Law as the pure phase solubility multiplied by the mole fraction of the constituent in the mixture) into the aquifer. Dissolved phase concentrations of the BTEX compounds in excess of their drinking water standards (their MCLs) could occur in the aquifer directly beneath the source.

- If the LNAPL has been depleted from the fractures (by some combination of the processes of volatilization, dissolution, biological degradation or diffusion into the matrix blocks), reverse diffusion of the dissolved phase contaminants from the matrix back into the fractures will occur. Unless the distance between fractures is on the order of meters, the resulting concentration in the fractures will essentially be equal to that of the water held in the matrix. For high matrix concentrations and limited mixing of the fracture leachate in the aquifer, dissolved phase concentrations of BTEX could also exceed their MCLs in the aquifer.

Both scenarios indicate that an exposure risk in the aquifer beneath the source area is possible. However, if the receptor well is downgradient of the source, exposure will be mitigated by natural attenuation processes affecting the BTEX plume.

4.3 AIR EMISSIONS

Air emissions from low permeability soils are generally unlikely to pose an inhalation exposure threat from outdoor or indoor vapors. This is true even when the hydrocarbon source is directly adjacent to a basement, an excavated trench, or the soil surface. Diffusional transport is limited by the normally high moisture content of the clay soils, which limits the number and size of the air-filled passages through which the volatile organic vapors can migrate. The vapor plume is further attenuated by the processes of dissolved phase partitioning into the vadose zone pore water, adsorption onto the organic fraction, and biodecay.

Section 5
TECHNOLOGY ISSUES

Seven technologies were judged to have some potential for the remediation of low permeability soils in the vadose zone. These technologies can be broadly segregated by the type of process they induce:

Contaminant Removal	• Soil vapor extraction (SVE) • Bioventing
Mobility Enhancement	• Thermal processes • Surfactant flushing • In-situ soil mixing
Permeability Enhancement	• Hydraulic fracturing • Pneumatic fracturing

To comparably evaluate each technology, an identical set of questions was posed to each of the seven technology paper authors. Generic questions included the effects on contaminant removal posed by high moisture content, the ability to access under buildings, the maximum depth to which the technology is appropriate, and the capability to remediate petroleum products other than gasoline. The two major geologic settings of a naturally-fractured massive clay formation and a stratified formation were described, and in each case, the author was questioned on the technology's ability to remove free product, dissolved product, adsorbed product, and residual product trapped within pore throats. The papers conclude with a breakdown of the costs to close a hypothetical site, commercial availability, case histories, and a summary of the strengths, weaknesses and complementary technologies which could enhance remedial effectiveness.

The most salient points for each technology follow, concluding with a table summarizing these above items. A common set of cost data (e.g. well costs) has been used to derive comparable data for each technology as applied to the hypothetical site.

5.1 REMOVAL TECHNOLOGIES

In-situ technologies that actually remove, not simply enhance the removal, of contaminants from the ground are limited to two air flushing techniques, which are very closely related.

5.1.1 Soil Vapor Extraction/Bioventing

Soil vapor extraction and bioventing refers to either the injection or extraction of air through a non-saturated medium. Both rely on the same principle for achieving success, i.e. the ability to sweep air through regions of contamination within the formation. In soil vapor extraction, the air induces volatilization of the contaminants; in bioventing, the oxygen encourages biodegradation. The distinguishing feature between the two processes is the air flow rate, with bioventing requiring less flow because the biodegradation rate (and thus the oxygen demand) is relatively low.

In fine-grained soils, the air will preferentially flow through the fractures in a massive clay and the higher permeability layers in a stratified soil. Remediation of the matrix blocks or the clay layers/lenses will then be diffusion-limited, although for vapor extraction, diffusion refers to the contaminants migrating into the swept fractures, while in bioventing, it refers to oxygen diffusing into the lower permeability regions. The success of both technologies depends on the diffusion path length, i.e. the distance between fractures or thickness of the clay layer.

The overall evaluation of these technologies is that they are reasonably effective, both from a technical and cost perspective. Stratified formations are somewhat problematic for soil vapor extraction because it is difficult to move the air anywhere other than the high permeability layers. In bioventing demonstrations, this was partially overcome by injecting air over narrow-screened intervals at close spacing in the clay layers. Both technologies may potentially be enhanced by dewatering and induced (pneumatic or hydraulic) fracturing, as long as the geometry and spacing of the fractures is well controlled. Soil warming could also enhance performance, although temperatures that would significantly improve vapor extraction (through pore water evaporation) would be at the expense of biological activity. Optimum temperatures for bioventing would be in the range of 20 to 30°C.

5.2 MOBILITY ENHANCEMENT TECHNOLOGIES

Mobility enhancement is broadly defined as a process which accelerates the movement of contaminant vapors or liquids to a subsurface collection system. Surfactant flushing is the typical example of this type of technology, but this definition also includes thermal techniques and soil mixing.

5.2.1 Thermal Processes

Soil can be heated through one of two ways: hot fluid injection (hot water, air or steam) or direct heating (electrical resistance (ER) or radio frequency (RF) heating). In the former, the fluids are introduced through wells or trenches. In the latter, the heat is introduced through electrodes or antenna placed in the ground. In both cases, the key design goal is to spread the heat away from the source and maintain roughly uniform temperatures throughout the remedial area. These higher soil temperature must be maintained near the extraction wells to avoid re-condensation or immobilization of the contaminants.

Thermal applications of water, air and steam are different. Hot water would be used to improve mobile LNAPL recovery in water extraction wells by lowering the interfacial tension and contaminant viscosity. Hot air would primarily function to dewater the formation by vaporizing the pore water near the flow channels, thereby improving the performance of vapor extraction. The target for steam is removal of both residual and free phase hydrocarbons which are volatilized and recovered in the gaseous phase or as condensate. Like vapor extraction, hot fluid injection is compromised by the tendency of the fluid to flow through higher permeability layers in a stratified formation or the fractures in a massive clay formation. These preferential pathways make it difficult to uniformly heat the formation, limiting the remedial effectiveness of hot fluid injection as a stand-alone technology.

ER and RF heating systems attempt to raise the vapor pressure of the contaminants to improve hydrocarbon recovery through vapor extraction wells. ER can heat the soil to close to the boiling point of water while RF can heat significantly above the boiling point, providing the added benefit of drying the soil (but at higher cost). These technologies actually perform better in low permeability media since they depend on the water content of the soil to conduct energy (and capillary forces retain higher moisture levels in silts and clays as compared to sands and gravels). Still, sufficient permeability must exist to remove the vapors.

Undoubtedly, thermal technologies improve hydrocarbon recovery (especially of middle distillates) but the costs are high and field experience limited. In low permeability soils, a complementary technology such as fracturing may be needed to ensure more uniform heat distribution and a hydrocarbon removal pathway.

5.2.2 Surfactant Flushing

Injection of surfactants through wells can aid in hydrocarbon recovery in one of four ways. The surfactant can promote dissolution of an LNAPL by increasing its solubility in the flushing solution, or it can increase its mobility in the subsurface by lowering the water-LNAPL interfacial tension. Surfactants can also reduce sorption onto soil particles and, finally, may accelerate the release of soil colloids which may be carrying sorbed contaminants.

There are two principal drawbacks to the general use of surfactants. The first is their cost and the other is their tendency to form emulsions which are difficult to break. Unfortunately, in an attempt to overcome the first problem through recycling, the second problem of emulsions manifests itself. There are relatively few examples of surfactant usage in the literature, and the ones that do exist apply mostly to DNAPLs (dense non-aqueous phase liquids which are typically solvents) rather than petroleum hydrocarbons.

Low permeability media further complicates the effective use of surfactants. As with other fluid flushing approaches (air or liquid), the surfactant will bypass the lower permeability regions, relying on a diffusional process to reach the contaminants in the clay layers or matrix blocks. Induced fracturing of the soil could alleviate this problem to some extent, but when combined with the cost and emulsion issue, the feasibility of cost-effectively treating a silt or clay media with surfactants is doubtful and the technology appears to have limited potential at the present time.

5.2.3 In-Situ Soil Mixing

In-situ soil mixing refers to the process of physically disturbing the soil with the use of large diameter (up to 14 ft) augers mounted on a drill rig. Overlapping columns of soil are augured down to depths as great as 25 ft. The technology requires that the site be relatively level and free of overhead obstructions; the subsurface must likewise be free of boulders or other large buried objects.

In the process of mixing the soil, treatment of the contaminants can take one of three forms. Grout can be injected down the hollow auger stem to solidify the soil; air can be injected to volatilize the contaminants (which are then collected under a shroud placed on the surface); or a chemical oxidant (e.g. peroxide) can be introduced for promoting contaminant removal through chemical transformation. All three treatments have been demonstrated in the field, although the long term stability (leachability) of the grout has yet to be determined.

Soil mixing is an aggressive technology which causes significant site disturbance (the mixed soil has a volume at least 15% greater than the original volume). It is also very costly (relative to other technologies described in this summary), averaging as much as $150/cu yd. It has the advantage that it is not very sensitive to the geologic conditions and treatment is extremely fast, taking only on the order of hours for each soil column. The size of the equipment however makes it impractical for service station-type settings. In summary, it is a 'niche' technology that may be uniquely suited to some applications but is not expected to see widespread usage.

5.3 PERMEABILITY ENHANCEMENT TECHNOLOGIES

Enhancing the permeability of low permeability media is possible with two techniques that involve artificially fracturing the soil: hydraulic and pneumatic fracturing.

The permeability of silts and clays can be significantly increased by induced fracturing of the soil. It is important however that the fracturing process be controlled, since random fracturing can create unwanted short circuits for a remedial fluid flushing solution, making it difficult to treat the bypassed area. The goal is to create a pattern of fractures that decrease treatment time by minimizing the distance over which the diffusional process is required to remediate the contaminated zone.

Controlled fractures can be created either hydraulically or pneumatically. Hydraulically, a fracture is nucleated through injection of a fluid, followed by a slurry of granular material and gel to 'prop open' the fracture, thus maintaining a permanent channel in the matrix. In pneumatic fracturing, high pressure air creates the channel, which is 'self-propped' and will tend to close over time. In stiff clays, the time to closure may be on the order of a year or more; it could however be much less in soft saturated clays.

The key to successful fracturing is the ability to propagate the fractures in a horizontal plane. This will occur where the soil is 'overconsolidated', meaning that the horizontal compressive stresses exceed the vertical stresses. Under these conditions, both techniques are capable of initiating fractures to a radius of around 20-25 ft before they begin to rise toward the surface. Fractures can be created with a vertical spacing of 1 to 2 ft, thus providing a reasonably short diffusion path length for remediation. Creating fractures near building foundations must be carefully considered since surface displacements of up to 2 inches have been recorded.

Induced fracturing offers significant potential for remediating low permeability media by incorporating the technology with air flushing technologies or with thermal treatment. With air flushing, it may allow the amount of vacuum (and thus size of the equipment) to be reduced for moving comparable amounts of air through the subsurface. Both hydraulic and pneumatic fracturing have similar costs and installation requirements, but hydraulic fracturing has one distinct advantage. Sand-propped fractures are permanent and will not close over time - a characteristic making it less sensitive to moisture levels and the degree of stiffness in the clay.

Section 6

CONCLUSIONS

Distribution and migration of chemical compounds in low permeability soils is controlled primarily by fracture pathways and diffusional processes. If the clay contains natural desiccation fractures, transport of compounds will initially take place through the fractures, but diffusion into the matrix will quickly occur, until the storage capacity of the matrix is reached.

Human exposure can occur by contact with contaminated soil, groundwater or vapor emissions. The low air-filled porosity in typical clay soils severely limits the threat of vapor exposure. Direct soil contact exposure posed by dissolved or adsorbed contaminants that reside solely in the matrix blocks may be mitigated by reduced bioavailability of the compound(s). For groundwater however, where a clay stratum is in contact with a sandy aquifer, mass transfer into the aquifer may readily occur, even if no separate phase product resides in the fractures. Treatment of the clay layer above or below this aquifer may therefore be needed, if a receptor well or compliance point is located in this source area.

Remedial technologies that perform mostly by clearing the fractures of contaminants will be slow in reducing concentrations because reverse diffusion from the matrix into the fractures is much slower than diffusion in the other direction, due to a marked difference in concentration gradients. Because most remedial technologies rely on moving a fluid (air, steam, water or a surfactant) through the media, flow through the fractures, or a sandy layer adjacent to a clay stratum, is inevitable. Acknowledging this constraint, the best approach to remediating silty or clayey soils may be to ensure that the diffusional path length between adjacent fluid channels is minimized. Combining fluid flushing technologies with artificial fracturing (either hydraulically or pneumatically) at minimal vertical intervals may potentially offer the best approach for reducing contaminant concentrations at a reasonable rate. However, the degree to which this mass removal (which will likely be limited) reduces the potential for human exposure should be considered before applying these technologies.

TECHNOLOGY COMPARISON MATRIX

	Soil Vapor Extraction	Bioventing	Thermal Techniques	Surfactant Flushing	Soil Mixing	Hydraulic Fracturing	Pneumatic Fracturing
Applicability	Volatile fractions	Middle distillates	Gasoline, diesel and crude oil	Diesel and crude oil	Volatiles & semi-volat.	Massive clay formations	Massive clay formations
Strengths	Proven technology	Low cost(f)	- Improved HC recovery	Residuals reduction	- Fast(f) - Enhanced mass trans.	Reduce diffusion path length	Reduce diffusion path length
Limitations	Low K layers in strat. soils	- Slow(f) - Low K layers	- Non-uniform heating - High cost(f)	- Emulsions - High cost(f) - Limited experience	- Large equipment - Boulders - High cost(f)	- Overconsolidated geology only - Surface heave	- Geology - Surface heave - Fractures close w/time
Costs ($/yd^3)(a)	$24 (b)	$23 (b)	$62 (c)	$65 (d)	$125	$6 (e)	$7 (e)
Time to Closure(a)	9 months	2 yrs	50 days	64 days	50 days	3 weeks (fracturing only)	3 weeks (fracturing only)
Availability	Widespread	Widespread	Sparse	Very limited	Sparse	Very limited	Very limited
Complementary Technologies	- Fracturing - Dewater	- Fracturing - Warming	- Fracturing - SVE	Fracturing	Heating	All fluid flush technologies	All fluid flush technologies

Notes:

(a): Costs were calculated from information provided in the papers included in this report; closure refers to gasoline cleanup from 1000 to 200 ppm in stratified site, with 100 ft x 100 ft x 15 ft source dimension.

(b): Includes $15k for design, $20k for a pilot study and $20k for pre and post-soil sampling.

(c): Assumes steam stripping.

(d): Assumes 80% recycling of the surfactant.

(e): Costs are for fracturing only, not subsequent remediation.

(f): Relative to other technologies described in this report.

RELEVANT PROCESSES CONCERNING HYDROCARBON CONTAMINATION IN LOW PERMEABILITY SOILS

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ABSTRACT

This paper describes the processes associated with predicting the distribution and removal of LNAPL's in low permeability media after a release occurs. It assumes the clay soil contains natural dessication fractures and describes LNAPL behavior in these fractures as well as the matrix blocks between fractures. This behavior is strongly influenced by the presence of water in the fractures and matrix, and equations for predicting the capillary rise of water in both the fractures and matrix are also developed. The paper also shows the dramatic effect that the time between release and remediation plays in affecting the efficient removal of LNAPL's from the subsurface.

Section 1

INTRODUCTION

Contamination of groundwater by organic liquids such as petroleum hydrocarbons and chlorinated solvents creates especially challenging problems for those charged with site investigation and remediation. This paper describes several of the important processes that occur when petroleum hydrocarbons are released into low permeability soils. Particular emphasis is placed on clay and clay-rich till soils characterized by vertical fractures superimposed on a fine-grained matrix. Comments are also directed toward stratified, low permeability soils. The soils considered in this paper are widespread in North America and are particularly difficult to remediate.

Petroleum hydrocarbons are immiscible with respect to both water and air. Also, hydrocarbons are nonwetting with respect to water and wetting with respect to air. For these reasons, the pre-release distribution of water and air in the geologic medium is an important factor in the determination of the hydrocarbon distribution, both during and subsequent to the release. The pre-release distribution of water and air is the first technical issue undertaken for each of the two soil types that are discussed. Emphasis is placed on the way fractures and variable strata influence the water and air distribution. This sets the stage for a description of hydrocarbon infiltration.

Processes that occur during infiltration of LNAPL are considered next. Important questions concerning the potential for LNAPL invasion of the fine-grained matrix and low permeability strata are addressed. This is followed by a description of the way water, air and LNAPL are likely to distribute themselves once the release is terminated and significant fluid motion ceases (i.e., mechanical equilibrium prevails). These distributions are especially relevant to site investigation and the potential for LNAPL removal during remediation efforts.

Diffusion of dissolved chemicals into the fine-grained matrix and low permeability strata is the final process described. This process occurs because of chemical disequilibrium that exists, even after the bulk fluids are no longer in motion. An analysis for a simple, idealized case is presented to illustrate how difficult it is to remove dissolved chemical from fine-grained matrix and low permeability strata once they have become contaminated.

Section 2

MASSIVE CLAY/TILL SOILS

2.1 DESCRIPTION

These soils consist of a network of interconnected fractures of variable aperture and spacing superimposed on a porous matrix. Typically, the characteristic fracture aperture is orders of magnitude greater than the size of interstitial openings in the porous matrix. The fraction of total porosity contributed by the open fractures usually is very small. Fracture porosities are often less than 1 percent while matrix porosities may be 40 percent or greater (Freeze and Cherry, 1979). On the other hand, it is the fractures that are primarily responsible for the overall fluid transmissive capacity of the bulk medium. While having only a modest effect on total porosity, the frequency and aperture of fractures are the controlling factors in respect to the bulk medium permeability.

Fracture apertures typically are within the range of 1 to 200 microns. Within an individual fracture, the aperture is thought by the author to be log-normally distributed. The void volume represented by the fractures is directly dependent upon both the fracture aperture and fracture spacing in three dimensions. Fracture spacing is not uniform, of course, and neither do the matrix blocks bounded by fractures form regular rectangular or cubic boxes. Nevertheless, it is this view of fractured porous media usually invoked to estimate the void volume contributed by fractures. Freeze and Cherry (1976) and Parker (1992) mention fracture porosities as low as 10^{-5}.

Fracture aperture and volume are not often constants in clays. Rather these features are dependent upon the water content of the clay. The fractures in a swelling/shrinking clay are more open when the clay tends toward dryness and vice-versa. Within the context of this paper, the more important effect of desiccation is to permit the spontaneous imbibition (entry) of pure phase hydrocarbons into the matrix blocks. This process will be significant in desiccated clays, even though the matrix permeability is very small. As will be shown in subsequent discussion, pure phase hydrocarbons are generally excluded from water-saturated matrix blocks under the typical conditions taken as the basis for discussion in this work.

Classical analyses of the behavior of subsurface fluids rests on the concept of a representative element of volume, or REV (Bear, 1972). The REV is a volume element that is small relative to the overall scale of the flow process, but is large relative to pore scale. Variables of interest (e.g. pressure, concentration) that are included in the analysis are thought of as average values within the REV. Measurement devices used to sense the variables of interest automatically yield the average values for porous media because the measurements are made at scales much larger than the pore scale. Thus, there is a direct correspondence between the predicted and measured variables.

The same concepts can be applied to a fractured porous medium but often the direct correspondence between the variables in the analysis and those that are measured is lost. This is because the scale of the measurement is smaller than the characteristic dimension of the REV and, thus, the measurement does not yield the mean value that is required by the analysis. Several measurements within a block of the medium may be required to obtain an average value in conceptual correspondence to that predicted by the 'equivalent porous medium' approach.

This and other shortcomings of the equivalent porous medium approach have spawned other conceptualizations that give explicit attention to interactions between the fractures and the matrix. One such approach views the fractured porous medium as being comprised of two completely overlapping continua that interact via mass transfer between them. That is, one calculates the fluid behavior in the fractures as if they occupied all the space. The same is done for the matrix. Interactions between fractures and matrix are accounted for by calculating mass transfer between the two solution spaces. Other approaches view the porous matrix as a continuum but treat individual, discrete fractures imbedded in the matrix.

There appears to be no single conceptualization of fluid behavior in fractured porous media that works best for all purposes. The brief foregoing discussion is presented only to provide context for subsequent descriptions of LNAPL behavior in massive clay and clay-rich till soils. In particular, there exists no generally accepted conceptual or mathematical model that can be applied to the task at hand. Instead the process description that emerges in the following paragraphs does so through a discussion of a collection of individual phenomena without the benefit of a cohesive model capable of quantitatively tying them all together. Quantitative descriptions of processes in homogeneous porous media are much more advanced than for fractured and highly stratified porous media.

The following discussion makes use of a 'typical' fractured clay or till. The first step is to analyze the pre-spill distribution of water and air in the fractures and the matrix. This is necessary because the way LNAPL moves through the medium following a release is highly dependent upon this distribution. The infiltration of LNAPL, with an emphasis on the potential for entry into the matrix, is discussed next. Once the source is terminated, the fluids redistribute themselves and eventually approach static equilibrium. This equilibrium distribution has important implications for site investigation and the potential for removal of the non-aqueous phase. Finally, the processes of matrix contamination and decontamination by diffusion are described.

2.2 PRE-SPILL MOISTURE DISTRIBUTION

The medium into which LNAPL infiltrates is conceptualized as a fractured porous medium extending only a very few meters above the water table (Figure A-1). When the system is at hydrostatic equilibrium, the air-water capillary pressure at a distance **z** above the water table is (Corey, 1976)

$$P_c \equiv P_a - P_w = \rho_w g\, z \tag{1}$$

where: P_c = capillary pressure (F/L^2)
P_a = air pressure (F/L^2)
P_w = water pressure (F/L^2)
ρ_w = water density (M/L^3)
g = gravitational constant (F/M)
z = vertical coordinate (L)

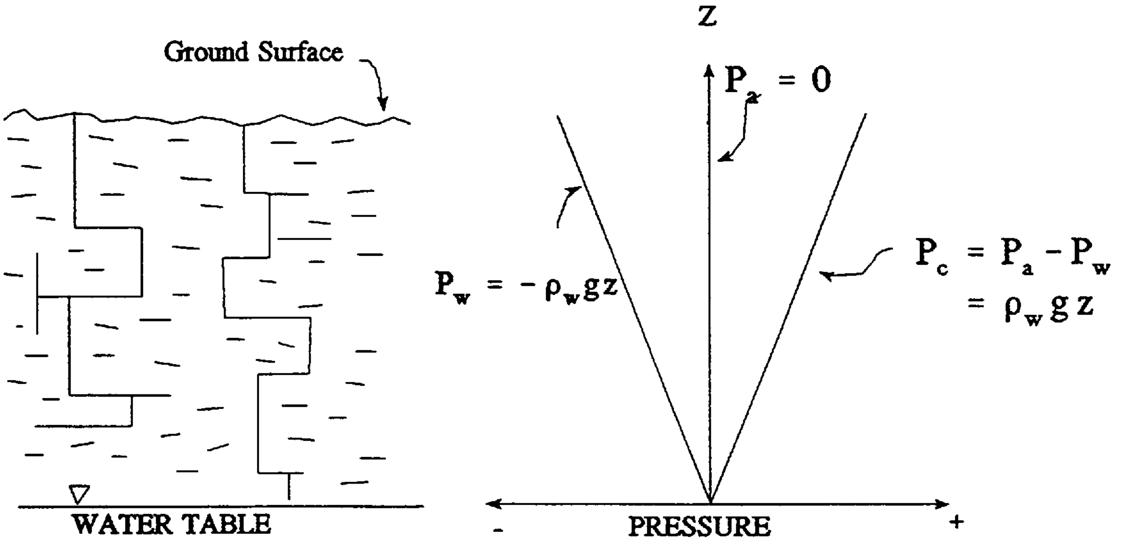


Figure A-1. Distributions of Air, Water and Capillary Pressures at Static Equilibrium. Note above the water table, the fluid pressure is under tension, so the hydrostatic pressure line is negative. Since the atmospheric gauge pressure is zero, the capillary pressure is positive and is equal to the hydrostatic pressure measured relative to the water table, positive towards the surface.

The capillary pressure at any **z** is the same in the fracture or in the matrix. However, because the characteristic size of a fracture opening is larger than the matrix or interstitial opening, the water content in the fractures can be expected to be much less than in the matrix at the same capillary pressure.

The capillary pressure at which the opening between two parallel smooth solid planes will desaturate is given by (Corey, 1986)

$$P_e = \frac{2\,\sigma \cos \alpha}{b} \tag{2}$$

where: $\mathbf{P_e}$ = entry pressure (F/L^2)
σ = air-water interfacial tension (F/L)
α = contact angle
b = fracture aperture (L)

The opening remains filled with water until the air pressure exceeds the water pressure by an amount equal to $\mathbf{P_e}$. By equating the capillary pressure from Eqn. 1 with the entry pressure of Eqn. 2, one obtains an estimate of the height above the water table at which fractures will remain saturated (i.e., contain no continuous air):

$$Z_e = \frac{2\,\sigma \cos \alpha}{\rho_w\, g\, b} \tag{3}$$

Table A-1 contains estimated values of $\mathbf{Z_e}$ as a function of aperture. Note that $\mathbf{Z_e}$ can be thought of as the height of the capillary fringe in fractures. At heights greater than $\mathbf{Z_e}$ the fracture will contain some continuous air. Of course Eqn. 2 is based on a highly idealized fracture and the values of $\mathbf{Z_e}$ in Table A-1 can be regarded as no more than rough estimates.

Z_e, meters	b , microns
1.22	10
0.82	15
0.61	20
0.49	25
0.41	30
0.35	35
0.31	40
0.24	50
0.20	60
0.12	100
$\sigma \cos \alpha = 60$ dynes/cm , $\rho_w g = 980$ dynes/cm^3	

TABLE A-1. Estimated Heights Above a Water Table At Which Fractures Remain Saturated

Based on Table A-1, a fractured porous medium with fracture apertures in the range of 10 to 40 microns can be expected to consist largely of air-filled fractures at heights of about 1 meter or greater above the water table. The matrix, however, is much less likely to contain any significant air-filled pores because interstitial openings are very much smaller.

Thomas et al. (1968) provide a means of estimating the entry pressure of fine-grained matrix material. The empirical relationship determined by these authors is:

$$P_e = 7.37\, k^{-0.43} \tag{4}$$

where: **P_e** = the entry pressure in psi
k = intrinsic permeability in millidarcys

Unlike all other equations in this paper, Eqn. 4 is not dimensionally consistent; only the units specified can be used. Of course the results calculated from Eqn. 4 can be subsequently converted to any set of desired units. Table A-2 contains estimates of the height above a water table at which Eqn. 4 predicts the matrix would begin to desaturate. The data in Table A-2 are expressed in units usually employed by hydrogeologists. The hydraulic conductivity, **K(L/T)**, is directly proportional to intrinsic permeability and is the quantity most often measured by hydrologists, either in the laboratory or the field. The height $\mathbf{Z_e}$ in Table A-2 is simply the pressure, $\mathbf{P_e}$, expressed as the height of water required to generate pressure, $\mathbf{P_e}$.

It is expected that the matrix blocks in a massive clay/till would exhibit a hydraulic conductivity on the order of 10^{-6}cm/s or less. Therefore, the data in Table A-2 indicate that matrix blocks located 5 m or less above the water table will be water-saturated.

Z_e meters	Hydraulic Conductivity cm/s
37	1×10^{-8}
18.6	5×10^{-8}
13.8	1×10^{-7}
6.9	5×10^{-7}
5.1	1×10^{-6}
2.6	5×10^{-6}
1.9	1×10^{-5}

Table A-2. Estimated Heights Above a Water Table At Which Matrix Blocks Will Be Partially Desaturated

The above discussion suggests that for water tables about 3 m deep, fractures in the upper two-thirds of the vadose zone will be largely air-filled. Matrix blocks throughout the 3-meter zone above the water table will be saturated with water. Of course, any deviation from static equilibrium as would result from, for example, infiltration or evaporation will affect the moisture distribution in way not accounted for in the above analysis. Downward water flow due to infiltration will cause the fractures to be wetter than predicted here and upward flow due to evaporation will cause the vadose zone very near the ground surface (i.e., within a few centimeters) to be dryer. Evaporation creates a thin zone of dry soil near the surface toward which water flows from below by capillary action.

2.3 LNAPL INFILTRATION

The infiltration of LNAPL into the geologic medium preferentially occurs along paths already containing a continuous air phase. Because the LNAPL is a wetting phase in respect to air, it spontaneously imbibes into air-filled openings. As indicated above, fractures are likely to be the only air-filled openings in massive clay/till materials, except near the water table where they too will be water saturated.

On the other hand, spontaneous imbibition of LNAPL into the water-saturated matrix does not occur. The LNAPL is a nonwetting fluid with respect to water and spontaneous displacement of water does not occur. In fact, the pressure of the LNAPL must exceed the water pressure by a threshold value, the entry pressure, in order to initiate penetration.

Entry pressures required for an LNAPL to displace water from the matrix are shown for several LNAPLs in Figure A-2 as a function of the hydraulic conductivity of the porous medium. As before, the entry pressures, $\mathbf{P_e}$, are expressed as the height of a water column required to generate the pressure $\mathbf{P_e}$. Expressing pressure in this manner is highly convenient and not unusual (e.g., 14.7 psi = 10.4 m of water = 761 mm of mercury). These curves were calculated from Eqn. 4 after adjustment to account for the different interfacial tensions of the various LNAPL-water fluid pairs. The interfacial tensions given in Appendix A-I were employed. Clearly the entry pressure depends strongly on both the type of LNAPL (i.e., the interfacial tension) and type of porous medium as indicated by the hydraulic conductivity. Recall that hydraulic conductivity **K(L/T)** is directly proportional to intrinsic permeability, **k**.

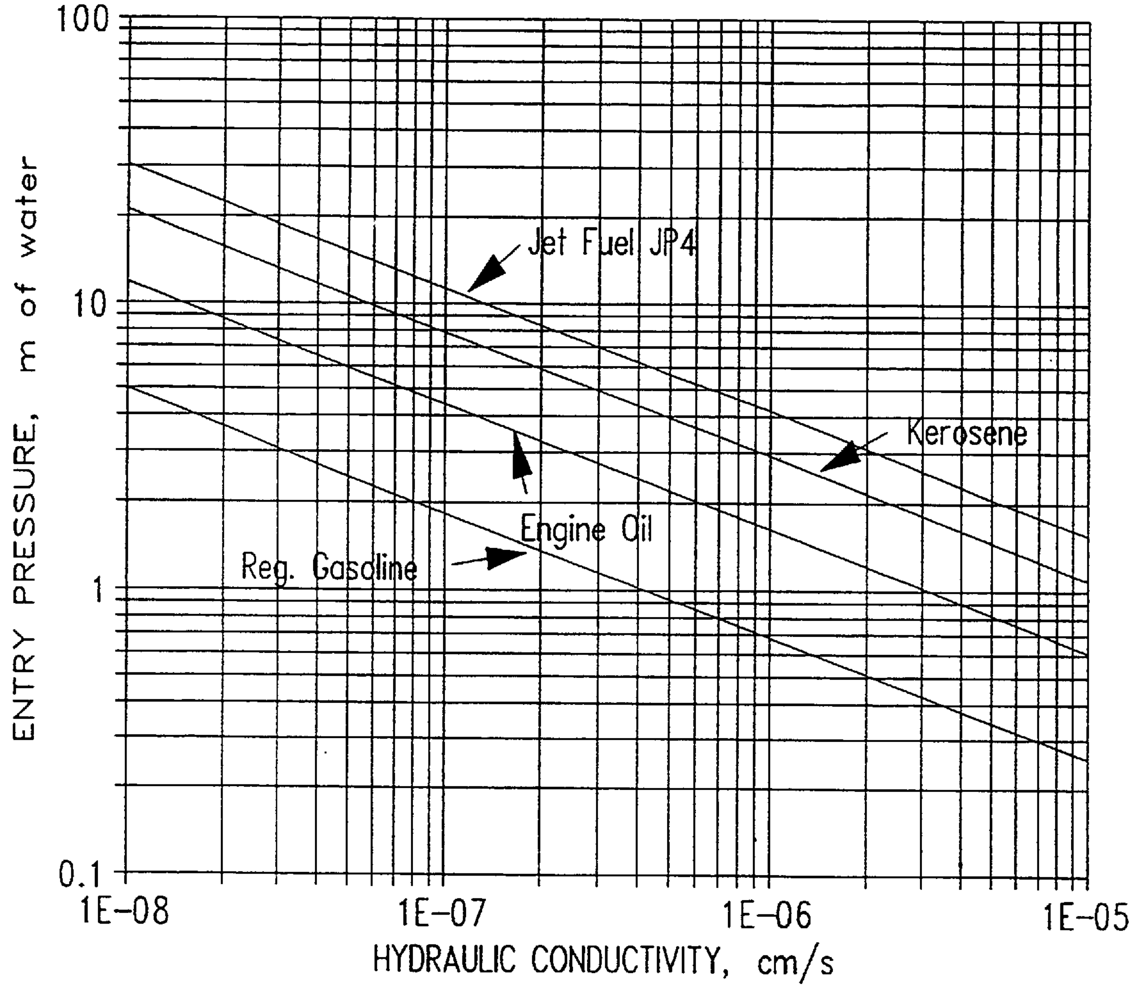
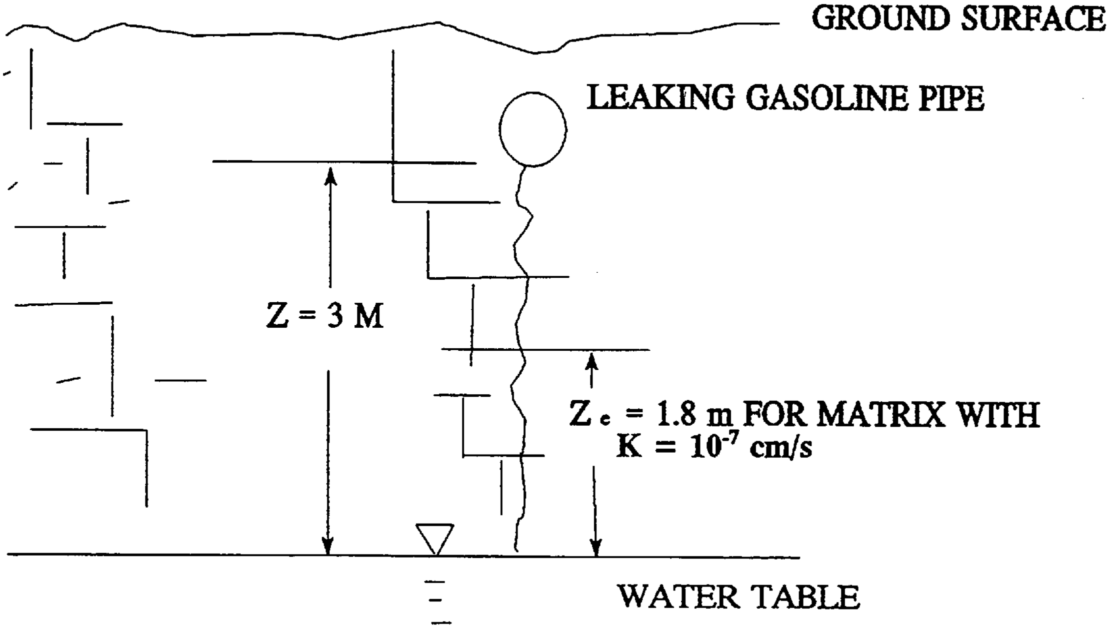


Figure A-2. Entry Pressures for Various LNAPL's as a Function of Hydraulic Conductivity. Note that the entry pressure is a direct function of the oil-water interfacial tension. Jet fuel has an interfacial tension almost 2.5 times that of engine oil (hence its higher entry pressure).

How can one determine if the matrix entry pressure is exceeded during infiltration along the fractures? Typically, in the case of a slow leak, the LNAPL enters the soil at or near atmospheric pressure. Thus, the greatest LNAPL pressure during infiltration is likely to be zero gage and occur in the immediate vicinity of the source. Furthermore, the process of LNAPL infiltration is not expected to influence the water pressure in the matrix in any significant way. That is, the distribution of water pressure in the matrix can be taken as hydrostatic.

Suppose the point of entry of LNAPL is Z meters above the water table as shown in Figure A-3. Then the water pressure there is $-\rho_w g Z$. With zero pressure in the LNAPL at the source, the LNAPL-water capillary pressure is $\rho_w g Z$. Again, it is convenient to express this pressure as equivalent height of water, in which case it becomes simply Z. The conclusion is that the matrix entry pressure will likely be exceeded if the LNAPL source at Z is located more that Z_e meters above the water table, (i.e., if $Z > Z_e$) where Z_e is determined by the ordinate in Figure A-2.

As an example, consider a zero-pressure release of gasoline into a fractured till at a point 3 meters above the water table. Note that the gasoline is assumed to reside in a continuous NAPL column and not be in a residual state (with snapped-off NAPL globules). Suppose that the hydraulic conductivity of the matrix is 10^{-7} cm/s, corresponding to an entry pressure of 1.8 m of water, according to Figure A-2.



LNAPL-water capillary pressure at z = 3 m is 3 m of water. This exceeds the LNAPL-water entry pressure of 1.8 m of water. Therefore, invasion of the matrix by LNAPL is to be expected.

Figure A-3. Example of a Situation in which LNAPL Invasion of the Matrix is Expected

Because the LNAPL-water capillary pressure of 3 m of water in the vicinity of the source exceeds the estimated entry pressure, some invasion of the matrix is to be expected for this hypothetical case. Had the LNAPL been engine oil, no invasion of the matrix would be anticipated because the entry pressure for engine oil is much greater than for gasoline.

The question now is how rapidly the LNAPL will make its way downward through a fracture to the saturated zone (i.e., the top of the capillary fringe in that fracture). The time required for the LNAPL in a individual fracture to reach a depth L_f below the ground surface can be estimated from the generalized Green-Ampt formula (Green and Ampt, 1911, Bouwer, 1978):

$$t = \frac{f}{K}\left[L_f - h_{cf}\ln\left(\frac{L_f + h_{cf}}{h_{cf}}\right)\right] \qquad (5)$$

where: t = time (T)
L_f = depth of infiltration "front" (L)
h_{cf} = capillary drive (L)
K = conductivity of the fracture to LNAPL (L/T)
f = fraction of fracture cross-section that is air filled (dimensionless)

Equation 5 is dimensionally consistent and any set of consistent units may be used. The capillary drive, h_{cf}, represents the capillary action that results in the spontaneous imbibition of the wetting fluid. Recall that the LNAPL is the wetting fluid with respect to the displacement air. To a close approximation, the capillary drive can be taken to be equal to the air-LNAPL entry pressure, expressed as an equivalent height of LNAPL (i.e., the height of a column of LNAPL that will generate the pressure equal to the air-LNAPL entry pressure).

Insight into how rapidly LNAPL will reach the top of the tension-saturated zone (i.e., the top of the capillary fringe) can be gained by putting $f = 1$ and h_{cf} equal to the air-LNAPL entry pressure expressed as an equivalent height of LNAPL. Further, the hydraulic conductivity of the fracture can be estimated from (Corey, 1986):

$$K = \frac{b^2 \rho_o g}{12 \mu_o} \qquad (6)$$

where: b = fracture aperture (L)
$\rho_o g$ = unit weight of LNAPL (F/L^3)
μ_o = dynamic viscosity of LNAPL (FT/L^2)

Each of the above parameter estimates is exact for a smooth-walled fracture of constant aperture, but are only rough approximations for a real fracture.

Figure A-4 shows the time estimated from Eqns. 5 and 6 for LNAPL to reach a depth of $L_f = 2$ m as a function of fracture aperture. Viscosity, density, and interfacial tension data appearing in Appendix I were used.

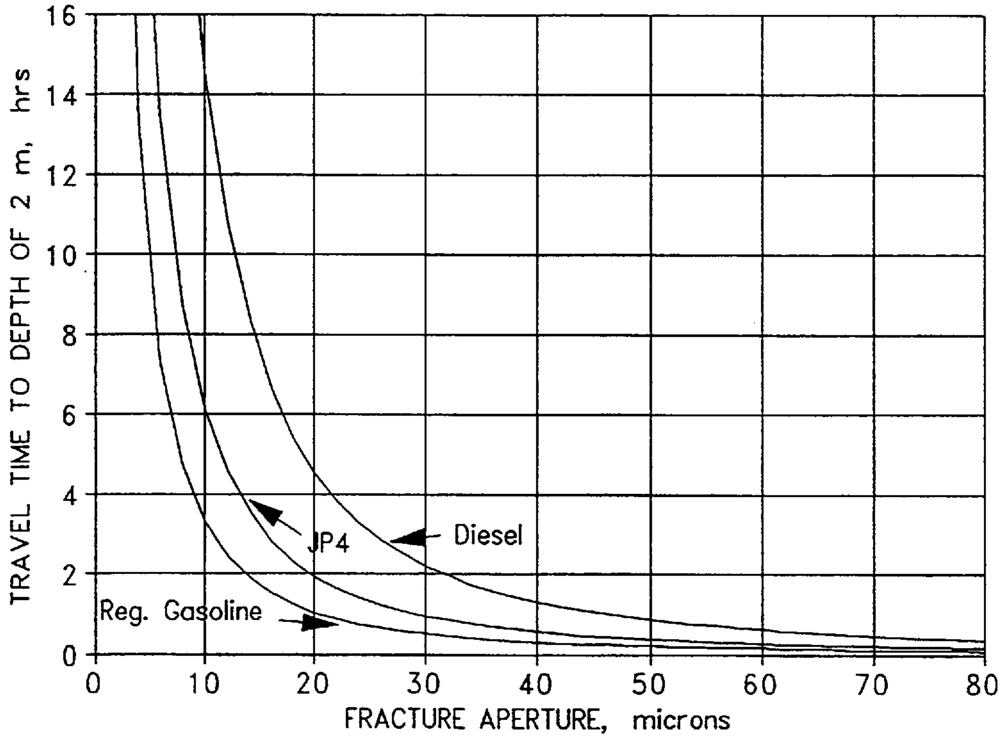


Figure A-4. Time for LNAPL to Infiltrate to a Depth of 2 m

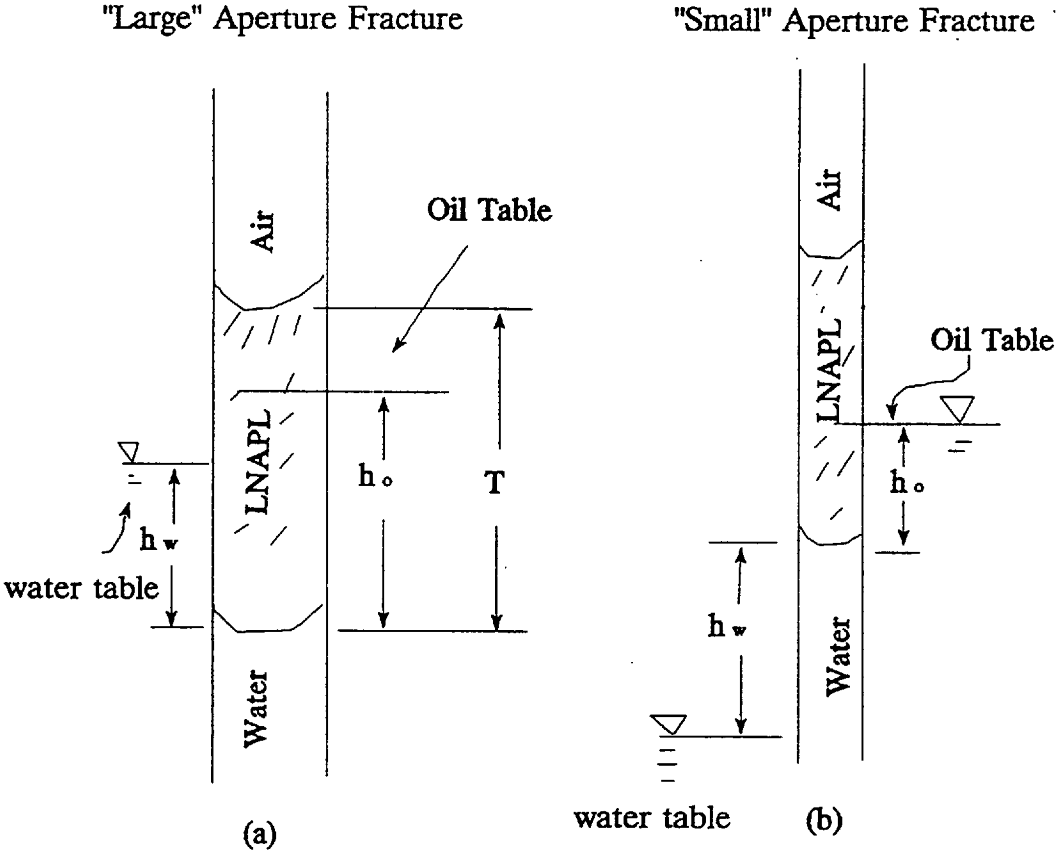
The conclusion supported by Figure A-4 is that LNAPL will travel a distance of 2 m in vertical fractures in a matter of hours or less, even in fractures with apertures as small as 10 microns. Diffusion of LNAPL components into the water-saturated matrix during infiltration will be insignificant due to the small travel time. However, residual LNAPL, formed during redistribution of LNAPL following the cessation of the release, may remain in the fracture for long periods and significant diffusion into the matrix is to be expected after infiltration is complete. Any invasion of the matrix by LNAPL however will increase its travel time to the tension-saturated zone.

Cross-cutting fractures provide the opportunity for LNAPL to spread laterally during the infiltration process. Forces responsible for lateral spreading are, again, capillary drive and gravity. However, the component of gravity acting along cross-cutting fractures is proportional to the sine of the fracture dip angle. Therefore, gravity is most important in steeply-dipping or vertical fractures and has no influence on LNAPL movement in horizontal fractures. Lateral spread of LNAPL during infiltration is expected to be minimal in media with predominantly vertical fractures.

The most significant lateral spread of LNAPL occurs when the infiltrating LNAPL encounters the tension-saturated region just above the water table. At this point the driving force due to gravity is reversed. During air displacement, gravity acts downward on the LNAPL and is proportional to the LNAPL density minus the density of air. Upon encountering the saturated zone, the buoyant force acts upward with a magnitude proportional to the water density minus the LNAPL density. Also, the displacement process shifts from a spontaneous one (LNAPL displacing air) to a nonspontaneous one (LNAPL displacing water). These changes cause the downward movement of LNAPL to cease. Continued infiltration of LNAPL is accommodated by lateral spreading with the pressure gradient as the dominant driving force.

2.4 STATIC DISTRIBUTION OF FLUIDS

This analysis again utilizes the idealization of a fracture as the constant-aperture space between two parallel, solid planes. Figure A-5 shows two of the possible configurations that might exist in such a fracture. Consideration of this simple and highly idealized system provides insight to how LNAPLs are distributed at mechanical equilibrium in real fractures.



h_w = Location of water table relative to the LNAPL/water interface in the fracture. Negative if the interface is below the water table and positive if interface is above the water table.

h_o = Location of the "oil table" relative to the LNAPL/water interface in the fracture

T = Thickness of the LNAPL in the fracture.

Figure A-5. Two Possible Distributions of LNAPL in an Idealized Fracture: (a) h_w is negative and (b) h_w is positive

The principles of fluid statics, together with Eqn. 4, lead to the following equations for the location h_w of the water table and h_o of the 'oil table' relative to the LNAPL-water interface in the fracture:

$$h_w = \frac{2}{b}\left(\sigma_{ao}\cos\alpha_{ao} + \sigma_{ow}\cos\alpha_{ow}\right) - \frac{\rho_o}{\rho_w}T \qquad (7)$$

and

$$h_o = T - \frac{2\,\sigma_{ao}\cos\alpha_{ao}}{\rho_o g b} \qquad (8)$$

where: h_w = water table location relative to the LNAPL-water interface (L)
h_o = oil table location relative to the LNAPL-water interface (L)
ρ_o = LNAPL mass density (M/L^3)
T = thickness of LNAPL layer (L)
b = fracture aperture (L)
σ = interfacial tension (F/L)
α = contact angle

and subscripts **ao** and **ow** denote air-LNAPL and LNAPL-water, respectively. The oil table is defined as the surface on which the LNAPL pressure is zero gage.

Putting $h_o = 0$ in Eqn. 8 yields the combination of parameters for which all of the LNAPL in the fracture exists at negative gage pressure, i.e. held in the fracture by capillarity. LNAPL at negative pressure will not enter a piezometer or monitoring well and will not be detected by these devices. Figure A-6 shows the maximum thickness T_m that can exist in a fracture at negative pressure. Fluid properties used to prepare Figure A-6 are those in Appendix A-I. The curves for all other fluids tabulated in Appendix A-I fall between the two extremes shown in Figure A-6.

While these calculations are based on a highly idealized model of a fracture, it may, nevertheless, be concluded that large thicknesses of LNAPL can reside in fractures at negative pressure and would be incapable of flowing into a monitoring or extraction well. Even if the volume of LNAPL is such that T exceeds T_m, a highly significant fraction of the LNAPL will be at negative pressure and inaccessible by wells or drains. For example, only 50 percent of a 30 cm thickness of regular gasoline in a 20 micron fracture is potentially recoverable by direct pumping.

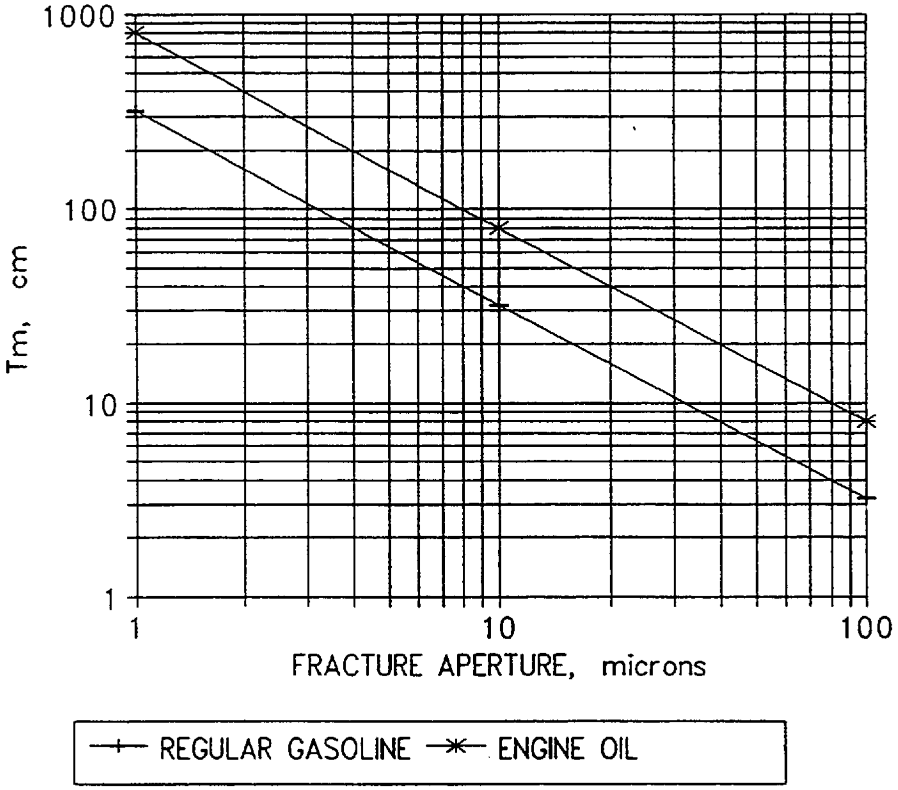


Figure A-6. Maximum Thickness of LNAPL that can Exist in a Fracture at Negative Pressure

Equation 7 indicates where the LNAPL is likely to be located in the fracture relative to the water table. Large thicknesses **T** in fractures with large apertures will be located so that a part of the LNAPL is below the water table (i.e., h_w is negative). Thin layers of LNAPL in fractures with small apertures reside above the water table. Furthermore, Eqns. 7 and 8 show that it is possible for LNAPL at positive pressure to be located entirely above the water table where the water pressure is negative.

Because real soils contain fractures with a variety of apertures, little or no uniformity of LNAPL thicknesses and locations is to be expected. While cross-cutting fractures that interconnect the LNAPL in many vertical fractures cause the LNAPL pressure to be uniform in horizontal planes, the variety of apertures still produces a nonuniform upper surface of the LNAPL body as a whole. And there exists a distribution of apertures in a single fracture that causes an individual fracture to exhibit properties of a porous medium at some scale (Kueper and McWhorter, 1991, 1992).

Finally it should be mentioned that the LNAPL at mechanical equilibrium in the fractures is not likely to coexist in the matrix. That is, LNAPL that readily enters the fracture is not likely to also enter the matrix. Very large thicknesses of LNAPL would be required to develop LNAPL-water capillary pressures sufficient to exceed the entry pressures calculated in Figure A-2. Note that LNAPL-water capillary pressures increase with elevation at a rate proportional to the difference $\rho_w - \rho_o$. This rate of increase is typically a factor of 5 less than in an air-water system. Therefore, if the air-water capillary pressure prior to the LNAPL release was insufficient to effect air entry into the matrix, the LNAPL-water capillary pressure will likewise be insufficient to initiate LNAPL invasion of the matrix. The exception occurs when the LNAPL-water interfacial tension is more than a factor of 5 less than air-water interfacial tension. This is rarely the case, and if the matrix was water-saturated prior to the release, it is highly likely that LNAPL will not enter the matrix during or after the release. However, as discussed in the next section, dissolved constituents will enter the matrix via aqueous diffusion.

2.5 MATRIX CONTAMINATION BY DISSOLVED COMPONENTS

While the high entry pressure of water-saturated matrix blocks is expected to prevent LNAPL invasion, matrix waters may, nevertheless, become contaminated. Constituents of the LNAPL in the fractures dissolve into the contiguous aqueous phase and diffuse through the water into the matrix. The rate of diffusion is enhanced by the tendency for dissolved chemicals to partition to the solid by adsorption.

The maximum mass of a particular chemical species that can be stored in dissolved and adsorbed form in a saturated matrix block per unit volume of soil can be deduced from the work of Feenstra et al. (1991):

$$M_m = \phi_m R C_o \tag{9}$$

where: M_m = maximum mass of an individual species that can be stored in the dissolved and adsorbed form in the matrix per unit bulk volume (M/L^3)
ϕ_m = porosity of the matrix (dimensionless)
R = retardation factor (dimensionless)
C_o = effective solubility (M/L^3)

The retardation factor is defined by (Freeze and Cherry, 1979):

$$R = 1 + \frac{K_d \rho_b}{\phi_m} \tag{10}$$

where: K_d = distribution coefficient (L^3/M)
ρ_b = dry bulk density (M/L^3)

The distribution coefficient, K_d, characterizes the tendency for dissolved constituents to partition to the solid. Adsorption of organic species is a strong function of the amount of organic matter in the soil (Karickhoff et al., 1979) and K_d is usually estimated from:

$$K_d = f_{oc} K_{oc} \tag{11}$$

where f_{oc} is the fractional organic content of the soil and K_{oc} is the organic carbon partition coefficient. Mercer and Cohen (1990) list values of K_{oc} for several compounds important in many LNAPL's.

The potential for mass storage of chemicals in the dissolved and adsorbed state in the matrix is often significant relative to the mass that can be stored in fractures in the liquid state. Consider benzene as an example and suppose that f_{oc} = **0.005.** Then $\mathbf{K_d}$ is estimated to be about 0.4 cm^3/g, and **R** is 1.9 for a matrix material with ρ_b = **1.7 g/cm**^{3} and ϕ_m = **0.36.** The pure-phase solubility of benzene is 1750 mg/ℓ (Mercer and Cohen, 1990) and Eqn. 9 predicts $\mathbf{M_m}$ = **1.2 kg** of dissolved and adsorbed benzene per cubic meter of matrix material.

Assume the fracture porosity to be 0.001. Then the volume of liquid benzene in the fractures can be no greater than 1 ℓ/m^3, corresponding to a mass of about 0.87 kg/m^3. In this example, the capacity for storage as dissolved and adsorbed chemical in the matrix exceeds the capacity for storage in the fractures. Of course, it is not expected that benzene would occur as a pure phase, as assumed in this example. The effective solubility of benzene in water, when the benzene is only one component of a hydrocarbon liquid, is far less than the pure phase solubility. The calculation is presented here only to illustrate that quite significant mass of chemical can be stored in the matrix.

Parker (1992) has calculated diffusion from fractures into matrix blocks for several DNAPL's under a variety of circumstances. A salient conclusion of this work is that the liquid phase contaminant in a fracture is eliminated by the diffusion process in time intervals ranging from weeks to several months, depending on the chemical in question, the fracture aperture, and the organic carbon content of the soil. Parker's calculations have not yet been extended to the complex chemical mixture comprising the typical LNAPL (e.g., gasoline). Nevertheless, Parker's analysis leaves little doubt that significant mass loss from the liquid in the fracture occurs in time periods on the order of weeks to months. Also, the mass loss due to diffusion is generally most rapid for the most soluble species. For this reason, the chemical composition of any remaining liquid in the fracture is significantly modified.

Attempts to remove dissolved and adsorbed chemical from the matrix are severely limited by the rate at which diffusion in the reverse direction can be effected. The concentration of dissolved chemical in the fractures can be reduced by flushing with air or water, thus establishing a reverse gradient in the vicinity of the fracture faces. However, the reverse gradient is not as great, on the average, as is the gradient during the contamination period. Also, diffusion in the interior of the matrix blocks proceeds inward concurrently with outward diffusion on the boundaries. These factors combine to cause the process of contaminant removal from the matrix to be much slower than the process of becoming contaminated in the first place.

A simple analysis for diffusion in a semi-infinite matrix block demonstrates the difficulty. Let M_R be the dissolved and adsorbed mass remaining after a period t_R of 'remediation'. Remediation in this case refers to the act of reducing the chemical concentration in the fractures to zero. The mass diffused into the matrix during a time interval t_D prior to remediation is M_D. Then the fraction of M_D that remains in the matrix at remediation time t_R is (see Appendix A-II for derivation):

$$\frac{M_R}{M_D} = \left(1 + \frac{t_R}{t_D}\right)^{1/2} - \left(\frac{t_R}{t_D}\right)^{1/2} \tag{12}$$

Only as t_R approaches infinity will remediation be complete. Perhaps more revealing from a practical point of view is the fact that only 85 percent of the mass is removed (i.e., $M_R/M_D = 0.15$) when remediation has proceeded for an interval 10 times as long as the contamination interval. If the LNAPL had been present in the fractures for 2 years prior to the initiation of remediation, 85 percent removal would require 20 years. Ninety-five percent removal requires a remediation interval 100 times as long as the contamination interval.

Section 3

STRATIFIED LOW PERMEABILITY SOILS

Many of the principles employed in the discussion of massive clay/till soils are relevant to stratified, low permeability soils as well. The soils of concern in this section are fine-grained and exhibit an overall low permeability. But the profile is not homogeneous. Rather the soil is regarded as being comprised of randomly distributed layers of variable thickness, each with a different permeability (hydraulic conductivity). The outline of subjects undertaken in the present case is the same as in the previous discussion.

3.1 PRE-SPILL MOISTURE DISTRIBUTION

At mechanical equilibrium, the distributions of fluid pressures are independent of the geologic medium in which the fluids reside. Thus, Eqn. 1 calculates the air-water capillary pressure in the stratified porous media of concern in this section. As in the previous case, there exists a capillary fringe (or tension-saturated zone) immediately above the water table in which the porous medium contains no continuous air phase. The capillary pressure at points above the top of the capillary fringe exceeds the air-water entry pressure, at least for some strata, and continuous air co-exists with water in the pores.

However, the entry pressure of a stratified soil is not uniform. The layers with low hydraulic conductivity have higher entry pressures and vice-versa (see Table A-2). Given a random distribution of strata with different textures, the zones high above the water table exhibit higher overall air contents than those near the water table. However, a particular stratum with low hydraulic conductivity may remain water-saturated, regardless of where it is located in the profile.

The relationship between water saturation and capillary pressure is called the capillary pressure-saturation curve or, sometimes, the water retention curve. In general, this relationship must be measured and it is different for each soil type in the profile. Even for a particular stratum the capillary pressure-saturation curve is not unique; it depends upon the saturation history (i.e., on the history of wetting and drying).

Insight to the variability of water saturation that is to be expected in a stratified soil is gained by examining a popular algebraic expression for the capillary pressure-saturation curve (Brooks and Corey, 1966):

$$S_w = (1 - S_r)\left(\frac{P_c}{P_e}\right)^{-\lambda} + S_r \quad , \quad P_c \geq P_e \qquad (13)$$

$$S_w = 1.0 \quad , \quad P_c \leq P_e$$

where: S_w = water saturation; i.e. the fraction of pore space occupied by water (dimensionless)
S_r = residual saturation (dimensionless)
P_c = capillary pressure (F/L^2)
P_e = air-water entry pressure (F/L^2)
λ = pore-size distribution index (dimensionless)

At static equilibrium the value of P_c (expressed as an equivalent height of water) is numerically equal to the elevation of the point in question relative to the water table elevation. Hence, $S_w(z)$ can be computed if the parameters P_e, λ, and S_r are known for each stratum. By far, the biggest influence on S_w is imparted by P_e. Clearly, a jagged, highly irregular water-saturation distribution is to be expected, owing to abrupt changes of P_e from stratum to stratum. Because the soil under consideration is of overall low permeability, all entry pressures are rather large, and the overall water content is high.

3.2 LNAPL INFILTRATION

As in the previous discussion, LNAPL spontaneously imbibes into pore space occupied by continuous air. Infiltration proceeds, therefore, along paths in which there existed continuous air prior to the release of LNAPL. However, in contrast with the vertically fractured soil, the infiltrating LNAPL is likely to encounter a water-saturated stratum that it is unable to readily penetrate. Recall that the LNAPL-water entry pressure must be exceeded for the initiation of LNAPL invasion.

Upon encountering a water-saturated layer (and the layer can be quite thin), the LNAPL begins to spread laterally. At the same time, the LNAPL pressure increases as more LNAPL accumulates from above. If the pressure becomes sufficiently great, the LNAPL-water entry pressure of the water-saturated layer is exceeded and LNAPL once again moves downward. Prediction of the degree of lateral spreading and the eventual breakthrough of LNAPL is severely constrained because of the lack of knowledge of the media properties at the very small scale required.

Consider the following situation in which a stratum of known hydraulic conductivity is located at elevation **Z** above the water table and **(D - Z)** below ground surface. If LNAPL should accumulate on this stratum to the maximum possible depth of **(D - Z)**, then the maximum LNAPL-water capillary pressure that can develop is:

$$P_{cm} = (\rho_w - \rho_o) g z + \rho_o g D \qquad (14)$$

Penetration of the stratum will not occur if the capillary pressure calculated from Eqn. 14 is less than the entry pressure estimated from Figure A-2. Clearly, a water-saturated stratum is more likely to form a barrier to further downward migration if it is located near the water table (i.e., small **Z**). Also, it is apparent that the likelihood of a water-saturated layer above the water table preventing any further downward migration of LNAPL becomes less as the depth **D** to the water table increases.

3.3 STATIC DISTRIBUTION OF FLUIDS

Owing to the essentially unknowable distribution of capillary properties in a stratified soil, the calculation of fluid distributions is not practical, although possible in principle. However, there is value in the examination of fluid distributions in homogeneous soils. In particular, the way that overall soil texture influences the fluid distribution is important.

Air, water and LNAPL distribute themselves at mechanical equilibrium as shown in Figure A-7 (Farr et al., 1990, Lenhard and Parker, 1990). It is observed that there exists a zone in which all three fluids coexist. Below that zone is one in which only LNAPL and water fill the pores. The bottom of the LNAPL zone may be located somewhat below the water table or above it, depending upon the volume of LNAPL and the capillary properties of the fluid-porous medium system.

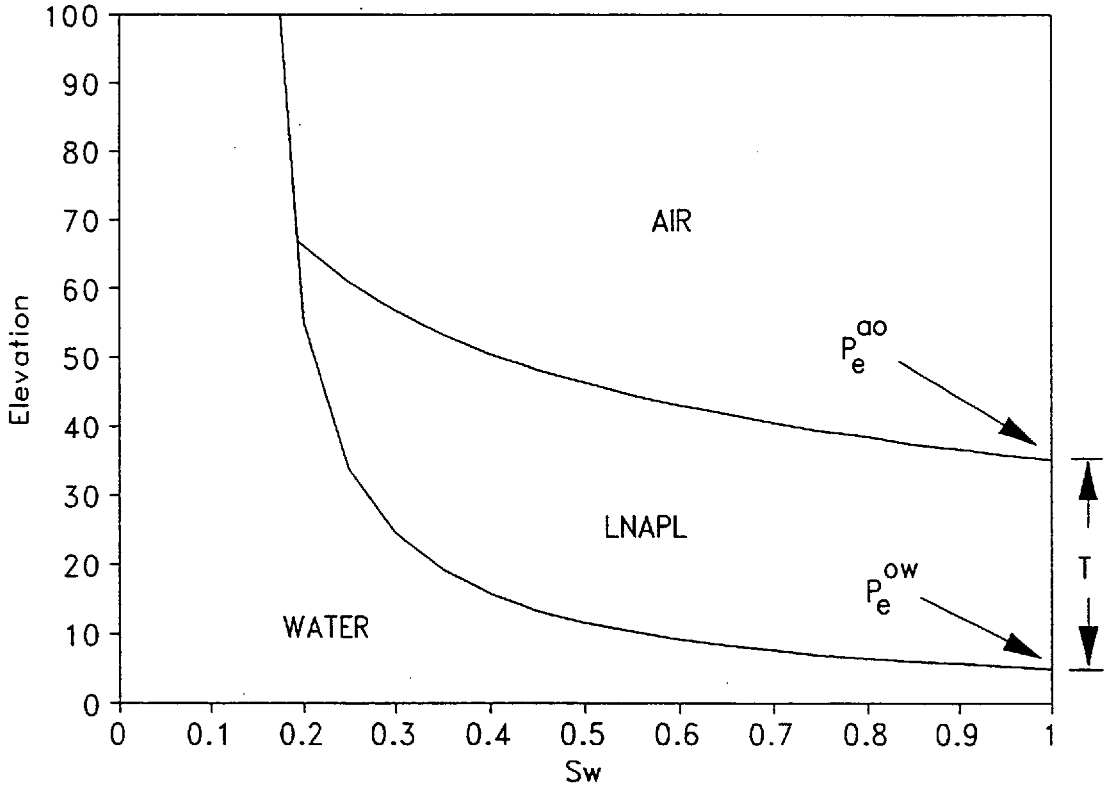


Figure A-7. Fluid Distributions in a Homogeneous Porous Media at Static Equilibrium

The capillary pressure at the bottom of the LNAPL body is the LNAPL-water entry pressure. At the bottom of the zone in which air exists, the capillary pressure is the air-LNAPL entry pressure. All of the LNAPL in the soil resides at negative gage pressure if:

$$T \leq P_e^{ao} / \rho_o g \qquad (15)$$

Low permeability soils with no cracks, root holes or other macro-features have large entry pressures. For this reason, low permeability soils are capable of storing significant quantities of LNAPL at negative pressure. Such LNAPL has no potential to be detected or removed by wells.

It is possible to relate **T** in Eqn. 15 to the volume of LNAPL present for homogeneous soils. However, stratification of the soil and fluctuation of the water table largely invalidate the numerical results of such a computation. A rising water table entraps some LNAPL in the form of occluded bubbles and globules. Such LNAPL is known as residual. A large rise in the water table can deplete the entire mobile LNAPL body into residual. When the water table falls, the residual LNAPL again becomes continuous and potentially mobile. Most of the LNAPL is found to reside in the more permeable strata.

3.4 CONTAMINATION BY DISSOLVED COMPONENTS

During infiltration of LNAPL into a stratified soil, it is to be expected that significant lateral spreading will occur in the more permeable layers. At any particular location, low permeability layers may remain water-saturated, yet be bounded above and below by strata containing LNAPL. Components of the LNAPL dissolve in the contiguous water and diffuse into the water-saturated strata. As with the matrix blocks in a fractured porous medium, removal of the dissolved contaminants from such strata is diffusion-controlled.

Section 4

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APPENDIX A-I

LNAPL Physical Data*

LNAPL	Dynamic Viscosity cp	Density g/cm^3	$\Delta\rho_w$ H_2O g/cm^3	Interfacial Tension dynes/cm	Surface Tension dynes/cm	Contact Angle
Toluene	.55	.865	.135	34	28	2
Benzene	.60	.874	.126	33	28	2
Styrene	.75	.907	.093	34	27	2
Reg Gasoline	.65	.728	.272	8	23	1
Jet Fuel JP4	1.3	.763	.237	49	26	2
Kerosene	2.3	.795	.205	34	26	3
Contaminated Kerosene**	2.3	.810	.190	2	28	3
Diesel	3.3	.852	.148	52	26	4.5
Soltrol	4.2	.789	.211	44	27	9.5
Mineral Oil	29	.861	.139	61	34	16.5
Automatic Trans Oil	46	.864	.136	18	33	15.0
10W30 Engine Oil	83	.869	.131	20	35	15.5
10W40 Engine Oil	108	.866	.134	20	35	15.5

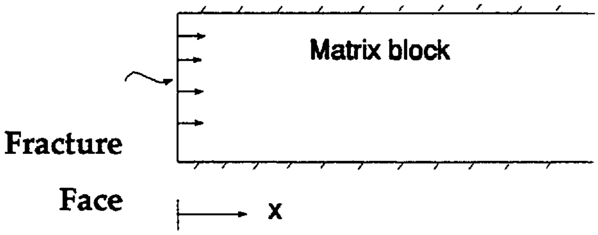
*Provided by N. Fischer, Colorado State Univ., Fort Collins, CO. Properties vary with source and aging. Direct measurement on the fluids of interest is recommended.

**Any immiscible liquid which has been premixed with a dye, surfactant, or solvent will have a reduced interfacial and surface tension.

APPENDIX A-II

DERIVATION OF EQUATION 12

Equation 12 is derived for the situation in which diffusion occurs in one dimension in a semi-infinite matrix block bounded at x = 0 by a planar fracture.



The matrix block is taken to be fully saturated with water. Diffusion occurs in response to concentration gradients created by differences in solute concentration on the boundary and the interior of the block.

Prior to a hydrocarbon release the contaminant concentration in the matrix block is zero. Following the release of the hydrocarbon, the fracture will contain organic liquid. Constituents of the liquid dissolve into the contiguous water on the fracture face. It is assumed that a particular constituent of interest instantaneously reaches a concentration C_o in the water on the fracture face. This creates a steep concentration gradient that promotes diffusion of that constituent into the matrix block. Diffusion into the matrix will occur indefinitely so long as a source persists in the fracture.

If at some time, say $t = t_D$, the hydrocarbon in the fracture is removed by soil vapor extraction or other means, the concentration on the fracture face is reduced. This process is approximated by the condition that the concentration on the fracture face drops instantaneously to zero at time $t = t_D$.

Translated into a mathematical statement, the above process becomes the following boundary value problem:

$$\frac{D_e}{R}\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \qquad \text{II-1}$$

$$C(x, 0) = 0$$

$$C(\infty, t) = 0$$

$$C(0, t) = \begin{cases} C_o & 0 \le t \le t_D \\ 0 & t > t_D \end{cases}$$

where:

where:	D_e	=	effective diffusion coefficient (L^2/T)
	R	=	retardation factor (dimensionless)
	C	=	mass concentration (M/L^3)
	x	=	space coordinate (L)

The solution to this boundary value problem is well known and available from numerous sources.

When the solution is manipulated to provide expressions for the mass flux of contaminant on the plane x = 0, one obtains:

$$J(0, t) = \phi_m C_o \left\{\frac{D_e R}{\pi}\right\}^{1/2} t^{-1/2} \quad , \quad t \le t_D \qquad \text{II-2}$$

and

$$J(0, t) = \phi_m C_o \left\{\frac{D_e R}{\pi}\right\}^{1/2} \left\{t^{-1/2} - (t - t_D)^{-1/2}\right\} \qquad \text{II-3}$$

where: J = mass flux ($M/L^2 \cdot T$)
ϕ_m = porosity of matrix

and other symbols are as previously defined. Examination of Eqns. II-2 and II-3 show that the mass flux is directed into the matrix block (Eqn. II-2) until "remediation" starts at $t = t_D$, after which the mass flux is directed out of the matrix block (Eqn. II-3).

The cumulative mass that has diffused into the matrix following the release is obtained by integrating Eqn. II-2 up to $t = t_D$:

$$M_d = \int_0^{t_D} J(0,t)\,dt = 2\,\phi_m C_o \left\{\frac{D_e R}{\pi}\right\}^{1/2} t_D^{1/2} \qquad \text{II-4}$$

where: M_D = mass of contaminant that has diffused into the matrix block per unit area (M/L^2)

'Remediation' begins at $t = t_D$ and induces a reversal in the mass flux at $x = 0$. The mass per unit area that has diffused out of the matrix block up to time t is obtained by integrating Eqn. II-2 from t_D to t:

$$M_o = 2\,\phi_m \left\{\frac{D_e R}{\pi}\right\}^{1/2} \left\{(t - t_D)^{1/2} + t_D^{1/2} - t^{1/2}\right\} \qquad \text{II-5}$$

where: M_o = mass of contaminant that has diffused out of the matrix block per unit area after 'remediation' is initiated

It is now a simple matter to calculate the mass of contaminant remaining in the matrix at any time:

$$M_R = M_D - M_O \qquad \text{II-6}$$

where: M_R = mass of contaminant remaining in the matrix per unit area at time $t > t_D$.

Expressed as a fraction of the contaminant mass that had diffused into the matrix:

$$\frac{M_R}{M_D} = 1 - \frac{M_O}{M_D} \qquad \text{II-7}$$

It is convenient to define $t - t_D$ as the 'remediation' time t_R. Then Eqn. II-7 takes the especially simple form:

$$\frac{M_R}{M_D} = \left(1 + \frac{t_R}{t_D}\right)^{1/2} - \left(\frac{t_R}{t_D}\right)^{1/2} \qquad \text{II-8}$$

which is Eqn. 12 of the text.

It is not proposed that the above result is an accurate simulator of reality. Rather it is a result for an idealized situation that illustrates how slow removal by diffusion is relative to the time for contamination to occur in the first place. The author has made similar calculations for rectangular parallelepipeds. The calculations are significantly more complicated for the three-dimensional case and simple formulae analogous to Eqn. II-8 are not available.

ASSESSMENT OF HUMAN EXPOSURE POSED BY LNAPLs IN LOW PERMEABILITY SOILS

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ABSTRACT

This paper describes the human exposure pathways to LNAPL hydrocarbons present in clay-rich soils (which may have undergone partial or no remediation), and how low permeability soils typically present a reduced exposure threat, as compared to more porous media. The exposure pathways include direct soil ingestion or dermal contact, groundwater exposure and subsurface vapor transport. For the direct contact pathways, there is discussion on bioavailability, especially the concept that contaminants become 'sequestered' in the clay matrix over time and pose progressively less of a toxicity risk. For the groundwater pathway, a theoretical derivation is presented to calculate the concentrations that would occur in a sandy aquifer adjacent to a clay stratum once the product is no longer present as a NAPL in the clay fractures. Finally, the potential exposure to vapors migrating either into a basement or to the surface from a clay soil source is presented.

The results indicate that the exposure threat due to vapors in high water content, low permeability soils is small. Furthermore, studies which demonstrate reduced bioavailability may lessen the calculated risk due to direct soil exposure. For the groundwater pathway, there is little potential exposure in massive clay formations due to low migration potential. However, for contaminated clay layers in contact with sandy aquifers, mass transfer of the contaminants from the clay to the aquifer may readily occur, unless the average spacing between the natural clay fractures is on the order of meters.

Section 1
INTRODUCTION

Removal of non-aqueous phase liquids (NAPLs) from source zones of contaminated soil is generally the primary objective of any in-situ remediation effort. In sandy porous media, some reasonable degree of success has been achieved with certain technologies, such as soil vapor extraction and bioventing. There are also documented demonstrations with air, steam and surfactant injection. However, there is little experience and limited success with these, or any other remedial technologies, in silty or clayey soils, which are commonly referred to as low permeability media.

The ability of these technologies to remove NAPL relies principally on the ability of the flushing medium (air, steam or the surfactant) to contact - preferably uniformly - the contaminated soil particles. The permeability of the soil and the heterogeneities in the subsurface are the major conditions affecting this process. Since silt and clay soils have a low permeability, and typically exhibit dual porosity flow behavior (due to the existence of natural fractures in the soil structure), they pose the greatest challenge to achieving remedial success.

Evaluating the risk posed by this media leads to an interesting question. If the ability to remove NAPLs in low permeability soils by both conventional and unconventional means is low, does it also imply that the potential exposure to humans who may come into contact with this media is correspondingly low? This is the topic explored in this paper.

Section 2
LOW PERMEABILITY SOIL DESCRIPTION

For purposes of this paper, low permeability soils are classified into two geologic settings. In Scenario A, the soil consists of massive silt or clay deposits that may or may not contain natural desiccation fractures that create a secondary permeability structure through the formation (usually referred to as a dual porosity - dual permeability system). A fracture-matrix block schematic depicting this setting is illustrated in Figure 1a. In Scenario B (see Figure 1b), the soil is stratified, consisting of interbedded low and higher permeability layers, usually oriented horizontally. There is a third geologic scenario consisting of low permeability isolated lenses - rather than continuous layers - in a permeable media, but in a practical sense, this is simply a variation of Scenario B.

In both scenarios, the presence of the fractures is the key element for all the risk pathways other than direct soil ingestion or dermal contact. Therefore, in the remainder of this paper, the label 'low permeability soils' will be assumed to refer to clay soils containing natural fractures with some degree of interconnectivity.

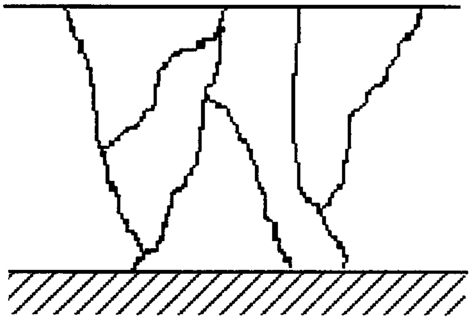

Figure 1a: Massive fractured clay

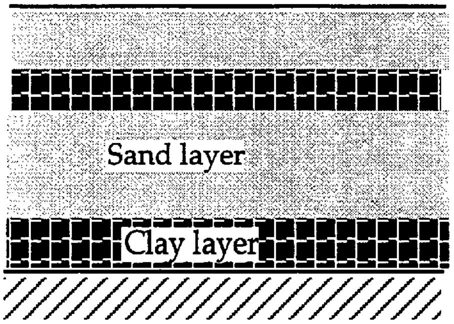

Figure 1b: Stratified scenario

Contaminant transformation and migration are very different in these two main geologic settings. In Scenario A, any mobile NAPL in the soil will initially distribute itself and migrate through the fracture network (assuming the fractures have some inter-connectivity). If the soil matrix block is water-saturated, no NAPL would be expected to enter the pore space of the matrix block because there will be insufficient 'head' or driving force to overcome the capillary forces retaining water in these small spaces. However, as the NAPL moves through the fractures (the NAPL can more easily displace water in these larger openings), part of it will dissolve into the water at the fracture-matrix boundary and then adsorb to the walls of the fracture. A concentration gradient will be established between the dissolved product on the fracture walls and the initially clean pore water of the matrix. With such a gradient, the process of diffusion will be initiated, transporting dissolved phase contaminants into the matrix. This process will continue, with contaminants diffusing toward the center of the matrix, until the gradient disappears or is reversed (by the process of either active or passive remediation). Advection through the fractures and diffusion through the matrix are thus the primary mechanisms for distributing NAPL and its dissolved phase constituents in the Scenario A-type setting.

The situation is somewhat different in Scenario B. Assuming that a sandy surface layer overlies a clay lens, mobile NAPL released into the sand will initially move vertically downward until it intersects the clay layer. At this point it will 'pool' and begin to move laterally. If the clay has little or no fracturing and the capillary entry pressure is not exceeded (i.e. 'breakthrough' does not occur), the NAPL will continue to move laterally until the head or driving force disappears. If the clay contains inter-connected fractures, the NAPL will move through the fractures and the processes described under Scenario A will begin to manifest themselves.

Note that these processes affecting NAPL distribution are identical to the movement of a remedial flushing fluid (air, water, steam or surfactants) through the formation. In concept then, one would expect the flushing fluid to follow the same path as the contaminant, and would achieve the necessary 'contact' to allow remediation, as described above. However the time element now becomes of importance. For while liquid phase diffusion is a significant process with regard to NAPL distribution, it is an even slower process with regard to remediation (McWhorter, 1995), and technologies that rely on such a process are generally inefficient. This could also imply however that the release of contaminants to a potentially exposed individual would be correspondingly slow. The rationale for how this slow contaminant release can be translated to a correspondingly low human exposure will be developed in the remainder of this paper.

Section 3
THE HUMAN HEALTH RISK PARADIGM

The U.S. EPA has developed a paradigm to quantify the health risks posed to humans in contact with contaminated soil or groundwater (U.S. EPA, 1989). In its simplest expression, risk is described as the product of two effects: contaminant exposure (in the form of a dose or intake) and toxicity. The analysis in this paper will be limited to a discussion of the exposure effects only.

Exposure to a contaminant can occur via a number of *pathways,* through either the air, surface water, groundwater or by the soil itself. The *routes* by which the contaminant can enter the human body are by ingestion, dermal (skin) contact or by inhalation.

Some of these routes are considered *direct*, meaning there is intimate contact with the soil or groundwater at the source, such as ingestion of soil by a child or dermal contact to the skin of a construction worker. Other routes are *indirect*. Examples of indirect contact are migration of groundwater through an aquifer to a drinking water well (where it can be ingested or its vapors inhaled in a shower) or subsurface transport of volatile contaminants either into a basement or an excavated trench. Food chain pathways (e.g. ingestion of milk or meat from a cow which has grazed in surface-contaminated soil) are other indirect routes of exposure that are sometimes considered.

The ways in which humans can be exposed to contaminants in the ground (excluding the food chain) can be divided into three pathways and their corresponding routes:

Pathway	Route of Exposure
1. Soil Contact	This is a direct exposure pathway involving the ingestion or dermal contact of surface-contaminated soil or subsurface soil exposed during excavations.
2. Groundwater Contact	This is usually indirect exposure in which the leachate from a contaminated soil can enter an aquifer and contact a receptor through well water usage or drainage into a trench.
3. Air Emissions	This is usually considered indirect exposure by the inhalation route. Vapors migrate from contaminated soil or groundwater either to the outdoor air (e.g. impacting construction workers in an excavated trench) or to the subsurface, where it can enter a basement.

The unique considerations these exposure routes pose in regard to the two low permeability geologic scenarios is as follows:

Pathway	Low Permeability Soil Considerations
1. Soil Contact	The U.S. EPA algorithms quantifying ingestion or dermal contact exposure contain a bioavailability factor, which may be different for clay soils as compared to sandy porous media. The application would be the same for both geologic scenarios.
2. Groundwater Contact	In both Scenarios A and B, the relevant issue regarding groundwater is the existence of an aquifer. Both scenarios can be treated identically if a sandy aquifer is assumed to underlie the massive clay deposits in Scenario A or comprise the sandy stratified layer in Scenario B.
3. Air Emissions	Vapors can only migrate in clayey soils if the clay contains pores which are at least partially air-filled. In Scenario A, the relevant consideration is migration through the air-filled pores to the surface, an excavated trench or into a basement. Scenario B can be treated identically if the relevant pathway is vapor migration through air-filled pores to the sandy stratified layer (at which point vapor migration mechanisms in porous media would apply).

Section 4

DIRECT SOIL INGESTION OR DERMAL CONTACT

The U.S. EPA (1989) has published simple algorithms for calculating the absorbed dose associated with human ingestion or dermal contact with contaminated soil. The standard absorption expression is the following:

$$\text{Absorbed dose (mg/kg-day)} = \frac{C \times IR \times EF \times ED \times CF \times Bio}{BW \times AT} \qquad (1)$$

where:
C = chemical concentration in soil (mg/kg)
IR = ingestion rate (mg/day)
EF = exposure frequency (days/yr)
ED = exposure duration (yrs)

CF = conversion factor = 10^{-6} kg/mg
Bio = bioavailability or absorption factor (dimensionless)
BW = body weight (kg)
AT = averaging time (days)

In this expression, the key term that is particularly relevant for clay soils is the 'Bio' factor. This considers the fact that not all soil that is ingested or which dermally contacts an individual may be 'available' for contributing to toxicity.

AVAILABILITY

A number of organizations, including the Gas Research Institute (GRI), the Petroleum Environmental Research Forum (PERF) and API are conducting research on the idea that contaminants may have reduced 'bioavailability' over time, thus reducing their toxic risk. Bioavailability, as described by Menzie (1995), can have both ecological as well as human health implications. Ecologically, bioavailability can refer to: (1) the aqueous phase leachability of the contaminant from the soil matrix; (2) the availability of the contaminant to microbes for biodegradation; or (3) the uptake efficiency of the contaminant in plants or by soil invertebrates (e.g. earthworms). From a human health perspective, bioavailability can refer to the efficiency of: (1) absorption through the skin; (2) absorption within the digestive system; or (3) absorption within the respiratory system.

In the GRI program, Alexander (1995) has extensively reviewed the soil agricultural literature to show evidence that a variety of factors support the idea that soils containing contaminants that have 'aged' exhibit declining bioavailability over time. These factors include:

- Persistence patterns of compounds in a soil matrix
- Reduced biodegradation rates with time, interpreted as reduced availability to microorganisms
- Increased resistance with time to extractability of compounds by a solvent
- Non-linear sorption-desorption behavior with decreasing contaminant release rates (desorption) with time

Alexander attributes this behavior to 'sequestration' of the contaminants into the interior pores of the matrix - a process that increases with time. Beck et al. (1995) provides further evidence of reduced biodegradation and bioavailability with time, especially in clay soils. In his literature review, Beck indicates that fundamental sorption/desorption mechanisms are the rate-limiting factors responsible for reduced availability. These mechanisms include:

- Transport-related or physical non-equilibrium reflecting mass transfer kinetic limitations as the desorption reactions do not 'keep up' with advection, i.e. 'new' advective fluids displace incompletely equilibrated 'old' fluids (Wu and Gschwend, 1986).
- Intraparticle diffusion as the contaminant molecules are retarded by partitioning between the aqueous and solid phases while diffusing through the pore fluids of the matrix
- Intraorganic matter diffusion of contaminants into the interior small pores of the humic fraction or the clay minerals (which bacteria can no longer penetrate)
- Chemical non-equilibrium where a contaminant forms strong chemical bonds with the soil particles or humic materials

Although little work has been conducted to date, there is some limited bioassay data showing a link to decreased toxicity. The evidence indicates that the reduced availability of the clay-bound contaminants to organisms yields a toxicity that is less than the same dosage of contaminants delivered in a more permeable media. It is not the toxicity, per se, of the contaminant to the organism that is altered; rather, it is the effective dose of the contaminant to the organism that is reduced. Bioassay data from some animal and plant studies lend credence to the argument that bioavailability and reduced toxic impact (via a lower absorbed dose) are parallel phenomena (Alexander, 1995).

The nature of the sequestration mechanisms identified by Alexander and the sorption/desorption limitations identified by Beck suggest that clay soils offer the highest potential for reduced bioavailability over time. The next step needed to be able to defend a 'Bio' factor of less than one in clay is to develop the test protocols and data for demonstrating that reduced bioavailability is equivalent to reduced toxicity in humans. The GRI and PERF programs are attempting to provide this link by developing a matrix of short and long term tests to demonstrate the environmental acceptability of residually-contaminated soils, which will be a function of the soil matrix. When this data is validated, a 'Bio' factor less than one may be applied to more accurately quantify the human health risk for the direct exposure pathways in clay.

As an example of how Equation (1) and bioavailability can be used, assume a situation where a child ingests surface-contaminated soil containing benzene, with an assumed total (100% bioavailable) concentration of 300 mg/kg. Assume the following exposure parameters apply:

- Ingestion rate (IR) = 200 mg/day
- Exposure frequency (EF) = 350 days/yr
- Exposure duration (ED) = 5 yrs (life as a 'child')
- Body weight (BW) = 15 kg
- Averaging time for carcinogens such as benzene (AT) = 70 yrs (25,550 days)

Substituting into Equation (1) yields an absorbed dose (assuming 100% bioavailability) of 2.7×10^{-4} mg/kg-day. The individual excess lifetime cancer risk is the dose multiplied by the oral toxicity (or ingestion slope factor) for benzene, which is 0.029 $(mg/kg\text{-}day)^{-1}$. This results in a health risk of 7.9×10^{-6}. Some regulatory agencies base their cleanup levels on achieving a risk level of 10^{-4} to 10^{-6} (depending on site use), in which case further action may be needed in this example. However, if it were demonstrated that only 10% of the benzene were bioavailable, the risk would be reduced below the 1×10^{-6} threshold (to 7.9×10^{-7}), potentially resulting in an early site closure.

Section 5
GROUNDWATER LEACHABILITY

When a release occurs into a fractured clay media, the NAPL will initially move through the interconnected fractures, which constitute the effective porosity of the media. Because these fractures occupy a relatively small volume (the effective porosity in clays is typically less than 1%), the release will spread out in the subsurface over a distance greater than would occur in a sandy media. This was documented in a set of API experiments (Johnson and Grady, 1994) in which 50 liters of NAPL was released inside a sheet pile cell near Sarnia, Ontario in 1992. In this report, these authors demonstrated how to calculate the contaminated soil volume:

- The average fracture aperture at Sarnia is 20 to 40 microns
- The distance between near-surface fractures at Sarnia is 1 to 2 cm
- Assuming these fractures contain no water, the calculated effective porosity for NAPL flow is therefore $20 \times 10^{-6}/0.02$ to $40\times10^{-6}/0.01$ or 0.1% to 0.4%
- The residual NAPL saturation of the soil is therefore 0.001 to 0.004 m^3/m^3, which is equivalent to 1 to 4 liters/m^3
- The volume of soil affected by a 50-liter release is therefore 12.5 to 50 m^3

The contaminant will initially reside as phase-separated product, or NAPL, in the fractures. However, as described earlier, the more soluble components of the NAPL will partition into the aqueous phase, allowing them to diffuse into the matrix blocks. This process will continue until the storage capacity of the matrix is reached. This capacity is based on the amount of constituents that can be stored in both the dissolved phase and adsorbed phases, assuming no liquid or vapor phase hydrocarbon can enter the water-saturated matrix. As such, the capacity is a function of the effective solubility of the mixture as well as the fraction of organic carbon in the soil (ignoring any storage capacity due to adsorption to the non-organic clay minerals in the matrix). As described by McWhorter (1995), this 'mass storage capacity of the matrix' can be expressed as:

$$M_m = \phi_m \left[1 + \frac{\rho_b f_{oc} K_{oc}}{\phi_m} \right] C_{sol} \tag{2}$$

where: M_m = mass storage capacity of the matrix (M/L^3)

ρ_b = dry bulk density of the soil (M/L^3)

f_{oc} = fraction of organic carbon (dimensionless)

K_{oc} = organic carbon partition coefficient (L^3/M)

ϕ_m = matrix porosity (dimensionless)

C_{sol} = effective solubility of the component or mixture (M/L^3)

Consider benzene as an example (K_{oc} = 80 cm^3/g, C_{sol} = 35 mg/l, assuming it to represent 2% mole fraction of a mixture such as gasoline). For a soil with a ρ_b of 1.7 g/cm^3, a ϕ_m of 0.36, and an f_{oc} of 0.005, the benzene storage capacity of the matrix is approximately 36 g/m^3, which equates to a benzene soil concentration of 21 mg/kg.

The gasoline mixture itself will have a higher matrix capacity. Assuming an effective mixture solubility of 100 mg/l and an effective mixture K_{oc} of 1000 cm^3/g (Johnson and Johnson, 1994), the storage capacity equates to 0.9 kg/m^3. The corresponding soil concentration is therefore approximately 500 mg/kg. Assuming the adsorption capacity of the non-organic clay minerals is negligible, any hydrocarbon concentration (as represented by a TPH or Gasoline Range Organic [GRO] analysis) in excess of this amount will be retained as phase-separated product or NAPL in the fractures.

In the Sarnia soils described above, Johnson and Grady (1994) calculate that approximately half of the NAPL that was originally released remained in the fractures once equilibrium was reached. It should be re-emphasized that this is an equilibrium condition and is not a time-dependent phenomenon. The NAPL in the fractures will remain as NAPL and can act as a source of groundwater contamination (assuming an aquifer exists below the clay layer) until the source is depleted by the processes of volatilization, dissolution and biodegradation. Assuming biodegradation only manifests itself on low concentration dissolved components in the fractures or matrix however, this process may not however be a major contributor to source decay.

Any rainfall or a fluctuating water table that brings clean water into contact with the NAPL in the fractures will release dissolved compounds at their effective solubility concentration (defined by Raoult's Law as the pure phase solubility multiplied by the mole fraction of the constituent in the mixture) into the Scenario A or B sandy aquifer. The effective solubility of each of the BTEX compounds in gasoline, for example, is typically in the range of 15 to 50 mg/l, which is anywhere from 1 to 3+ orders of magnitude higher than their current MCLs for drinking water.

If NAPL is present in the fractures, a drinking water aquifer exists beneath the fractured clay layer through which rainfall can percolate, and the receptor well or compliance point is in the aquifer directly beneath the source, an exposure scenario could readily be postulated that would indicate a human health risk outside of the 'acceptable' range of an incremental lifetime cancer risk to an exposed individual of 10^{-4} to 10^{-6}. In this case a remedial scheme which removes the NAPL from the fractures may be needed to reduce the risk. However, there are situations that may obviate the need for active intervention, including:

- If the aquifer is some distance below the source area, or if the withdrawal point is downgradient of the leachate-water table interface, natural attenuation processes in the vadose zone leachate or groundwater plume, or some combination of both, may reduce the concentration to an acceptable risk level by the time it reaches the receptor.

- The NAPL is naturally depleted from the fractures by physical processes including volatilization and dissolution, biological degradation, as well as mass redistribution by diffusion into the matrix. (Note that the degree to which this phenomenon lowers exposure is discussed in more detail below.)

In this latter scenario, once the source zone NAPL in the fractures is depleted, contamination is due only to diffused aqueous and adsorbed contaminants in the matrix blocks. The groundwater impact posed under these circumstances is the result of reverse diffusion, i.e. dissolved phase components diffusing from the matrix into the fractures, and potentially carried into an underlying aquifer by infiltration or a fluctuating water table.

Consider as an example the risk due to benzene that is no longer in the fractures but is diffused at its maximum concentration in the matrix blocks. As derived in the Appendix, the maximum concentration in the leachate as a result of reverse diffusion is given by:

$$C_{l(m)} = \frac{C_{m(o)}}{1 + Q_l/K} \qquad (3)$$

where:
$C_{l(m)}$ = maximum concentration of compound in leachate (M/L^3)
$C_{m(o)}$ = mean concentration in matrix pore water at the moment the NAPL has disappeared from the fractures (M/L^3)
Q_l = volume of leachate passing through the source zone per unit of time (L^3/T)
K = mass transfer coefficient of compound out of matrix (L^3/T)
= $3\pi^2 \phi_m D_e V_s/L^2$ (see Appendix)
ϕ_m = total porosity of matrix (dimensionless)
D_e = diffusion coefficient (L^2/T)
V_s = volume of the source zone (L^3)
L = average distance between fractures, assuming that the matrix blocks are cubes (L)

The term, $1 + Q_l/K$, can be considered as a dilution factor in the fractures, i.e. the ratio indicating how much the leachate concentration is reduced relative to the matrix concentration as a result of mass transfer limitations.

As illustrated in Figure 2, assume that rainfall infiltrating through the fractures in a clay layer can carry any reversely-diffused benzene into an underlying sandy aquifer where this permeable source area is considered the point of compliance. Further assume (conservatively) that the leachate from the source will not biodegrade before reaching the water table. The leachate mixes with the water in the underlying aquifer over a discrete mixing zone, represented by 'd' in Figure 2. Using the standard mixing algorithm, the concentration of a compound in the aquifer mixing zone, C_{aq}, can then be described by:

$$C_{aq} = \frac{C_{l(m)}\, Q_l}{Q_a} = \frac{C_{m(o)}\, Q_l}{Q_a\,(1 + Q_l/K)} \tag{4}$$

where Q_a is the volume flow rate through the mixing zone in the aquifer (which is assumed to be clean upstream of the leachate source).

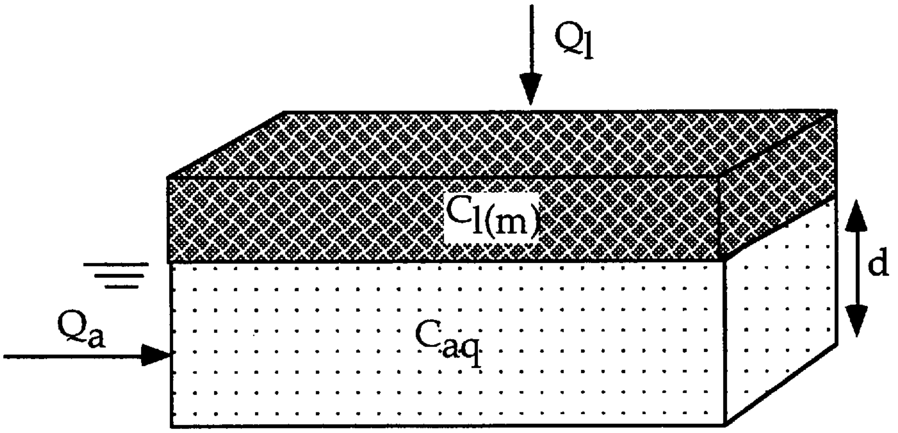

Figure 2: Infiltration through fractured clay and mixing in sandy aquifer

To illustrate the use of these equations, assume the following parameters apply:

- Benzene has a concentration, $C_{m(o)}$, in the matrix of 10 mg/l
- A source in the clay has a volume, V_s, of 20 m^3 (4 m long x 5 m wide x 1 m thick)
- The depth of the mixing zone, d, in the aquifer = 2 m (ASTM, 1994)
- The groundwater darcy velocity in the aquifer = 25 m/yr (ASTM, 1994)
- The infiltration rate = 10 cm/yr (0.1 m/yr)
- The total matrix porosity, ϕ_m, = 0.36
- The effective diffusion coefficient, D_e, for benzene = 3×10^{-6} cm^2/sec (0.01 m^2/yr)
- The matrix block cube dimension, L, = 2 cm (0.02 m)

With these assumptions, the following can be calculated:

- Q_l = 4m x 5m x 0.1m/yr = 2 m^3/yr
- Q_a = 25 m/yr x 5 m x 2 m = 250 m^3/yr
- K = $3\pi^2$ x 0.36 x 0.01 m^2/yr x 20 m^3/$(0.02\ m)^2$ = 5330 m^3/yr
- C_{aq} = 0.08 mg/l, or 80 ug/l

These calculations indicate that mass loading to the aquifer is fairly insensitive to the fracture spacing dimension, L. If the spacing were 1 m, the aquifer concentration, C_{aq}, would still be 41 ug/l. In order to not exceed the MCL for benzene of 5 ug/l, a 4 m spacing between fractures is needed for the conditions outlined above. Except when these very large fracture spacings exist, the concentration in the leachate is essentially equal to the concentration in the matrix. Unless large fracture spacings exist, the aquifer concentration is simply the matrix concentration diluted by the ratio between the infiltration flow rate through the source zone and the aquifer flow rate through the mixing zone.

Note that the above aquifer concentration is calculated directly below the clay source zone. For receptors located downgradient of the source, lower concentrations would likely be experienced as a result of natural attenuation mechanisms. Also note that the modeled groundwater setting assumes the contaminated clay layer is in direct contact with a sandy aquifer - a worst case scenario. If there is no aquifer in contact with the fractured clay, there is little potential exposure because the low permeability soils both limits contact in the source zone (because wells would be unproductive and therefore, not used), and downgradient (because of the limited plume migration potential).

Section 6

SUBSURFACE VAPOR TRANSPORT

Besides the previously analyzed pathways of direct soil exposure and groundwater contact, the inhalation route of exposure from vapor transport into outdoor air or through a basement wall or foundation should also be considered in a risk assessment evaluation.

In this scenario, contaminated soil or a groundwater plume would act as a source zone of vapors, which would be transported through the air-filled pores of the clay, primarily via the process of diffusion. However, transport rates are very sensitive to moisture content since vapors cannot move through a water-saturated medium. In low permeability soils such as fractured clays, the fractures will generally have a much lower moisture content than the clay matrix because of the larger capillary pressures in the matrix (McWhorter, 1995). McWhorter furthermore shows that, contrary to the fractures, the clay matrix will remain saturated on the scale of meters above the water table. If the source zone is concentrated near the water table, as is the case with many LNAPL spills, the air-filled porosity - through which the source zone vapors will migrate - will essentially represent that of the fractures.

To perform an exposure analysis, vapor concentrations in either the outdoor or indoor air must be derived. Jeng et al (1994) presents a subsurface vapor transport model following Jury et al (1983) for calculating emissions in buildings. The general case of this model includes the driving force mechanism of diffusion as well as attenuation of both the vapor plume (by water phase partitioning, soil phase adsorption and biodegradation) and the source itself. The simplest case is the Farmer's model (Farmer et al, 1980).

The Farmer's model will be used in the following example. Although this model ignores advective flow, which could occur in the immediate vicinity of a basement wall due to a pressure differential between the soil gas and the interior air, a number of conservative assumptions more than offset the omission of advection, including:

- The source is assumed to be infinite.
- No attenuation mechanisms act on the vapor plume.
- A 1-D model geometry is assumed. In reality, vapor flow is radial, which would result in lower concentrations near the basement.
- The presence of the concrete wall is ignored, so that all vapors outside the wall are assumed to enter the basement.

Using Farmer's model, which assumes vapor transport is strictly due to Fick's Law diffusion, the vapor flow of hydrocarbons into a building is calculated as:

$$F_g = \frac{A\,(C_{gs})\,D_g}{L} \qquad (5)$$

where:
F_g = vapor flux (M/T)
A = diffusion area = depth of basement in diffusion pathway x width of building perpendicular to flow direction (L^2)
C_{gs} = vapor concentration at source (M/L^3)
D_g = gaseous diffusion coefficient in soil (L^2/T)

L = distance between source and building (L) (Note that if the relevant route of exposure were outdoor air inhalation, this would represent the distance between the source and the ground surface or excavation surface.)

The gaseous diffusion coefficient, D_g, is derived using the Millington and Quirk (1961) expression:

$$D_g = \frac{D_{air}\ \phi_a^{10/3}}{\phi_t^2} \qquad (6)$$

where:
D_{air} = compound diffusion coefficient in air (L^2/T)
ϕ_a = effective air-filled porosity (dimensionless)
ϕ_t = total porosity (dimensionless)

In the Sarnia soils, the effective air porosity was measured with a helium tracer (Johnson and Grady, 1994) over a control volume approximately 1 m above the water table. A maximum value of 0.016 was obtained. Using these soils and the compound benzene as an example:

$D_{air(benz)}$ = 7520 cm^2/day
ϕ_a = 0.016
ϕ_t = 0.4
Therefore: D_g = 0.048 cm^2/day

If benzene were present at its effective solubility in gasoline (35 mg/l), the vapor phase concentration at the source, using a simple Henry's Law approximation (dimensionless H = 0.23), would be 8 mg/l, or 8 ug/cm^3. If a basement is 3 m below ground and has a width of 10 m, Equation (5) can be used to calculate a vapor flow rate or flux, F_g, at various distances between source and basement, as illustrated in Chart 1:

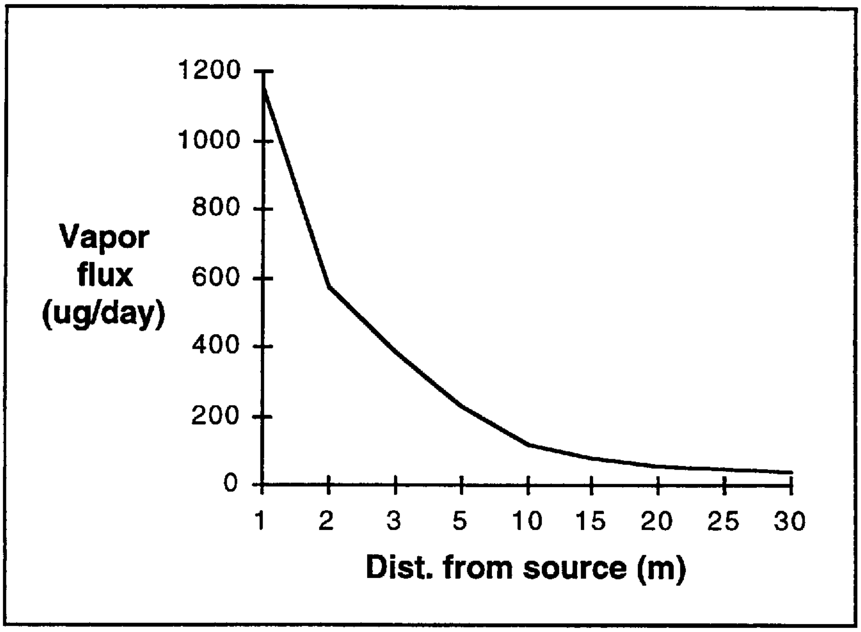

Chart 1: Maximum vapor flux vs. distance from source to a building

Vapor flux can be converted to a concentration in the building by the following expression:

$$C_{blg} = \frac{F_g}{N\,V_b} \tag{7}$$

where: N = number of air exchanges per day $(T)^{-1}$
V_b = volume of the building (L^3)

Assume a mean air exchange rate of 12 per day along with a building volume of 500 m^3 (Jeng et al, 1994). For the case where the source is 2 m from the basement (a distance where convection of the vapors is likely to be unimportant), the vapor flux, F_g, is calculated as 576 ug/day. Using Equation (7), this corresponds to a concentration in the air of 0.096 ug/m^3. To calculate the risk this poses to a resident, this concentration would be input into an intake expression like Equation (1). Typical reasonable maximum exposure (RME) values that are assumed for air intake by a resident are:

- Inhalation rate (IR) = 0.83 m^3/hr
- Exposure frequency (EF) = 350 days/yr (24 hrs/day)
- Exposure duration (ED) = 30 yrs
- Body weight (BW) = 70 kg
- Averaging time for carcinogens such as benzene (AT) = 70 yrs

Using these values, the intake from Equation (1) is 1.1 x 10^{-5} mg/kg-day. The individual excess lifetime cancer risk is simply the intake multiplied by the inhalation slope factor for benzene, which equals 0.029 $(mg/kg\text{-}day)^{-1}$. This translates to a risk of 3.3 x 10^{-7}, which is below the U.S. EPA-defined acceptable risk range of 10^{-4} to 10^{-6}. What this indicates is that high water content clay soils, where the effective air-filled porosity is low, are unlikely to pose a health risk due to vapor transport through the subsurface, even when the source is adjacent to the basement.

Section 7

CONCLUSIONS

This paper describes and assesses the exposure potential to humans due to LNAPLs in low permeability soils. Three pathways are explored including direct soil exposure (either through ingestion or dermal contact), groundwater exposure and subsurface vapor transport. The purpose is to show the particular factors that distinguish exposure in low permeability soils from other more permeable media.

Although decreased bioavailability due to contaminant sequestration applies to all soils, it manifests itself most prominently in clay soils because of the small pore structure of the matrix. Bioavailability however is only one factor to consider in mitigating the risk due to direct soil exposure. Other potential risk management strategies include land use restrictions, institutional controls and remediation.

For the groundwater pathway, there is little exposure potential in massive clay formations not in contact with underlying aquifers due to low plume migration potential. However, for the scenario where a contaminated clay layer is adjacent to a sandy aquifer, a theoretical derivation shows that mass transfer to the aquifer is primarily affected by the same factors controlling groundwater loading rates in more porous media, including the infiltration rate and the mixing zone depth in the aquifer. The fact that the mass loading originates from a clay layer makes little difference (vis a vis a more porous layer), unless the average fracture spacing in the clay is on the order of meters. However, once in the porous aquifer, the exposure to receptors located downgradient is mitigated by natural attenuation processes acting on the groundwater plume.

A simple model (Farmer's) was chosen to demonstrate that vapor migration is limited in low permeability soils having a high water content, even when the source is adjacent to a basement or an excavated trench. For soils which are drier (higher air-filled porosity), vapor exposure is also limited by other factors not modeled in the example, including source depletion with time and vapor plume attenuation due to dissolved phase partitioning, adsorption and biodecay. The vapor emission pathway is therefore not expected to pose a human exposure threat in most low permeability settings.

Section 8
ACKNOWLEDGMENTS

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Appendix

DERIVATION OF GROUNDWATER LEACHABILITY EXPRESSIONS

1. Calculation of Leachate Concentration in a Fractured Clay Source Area

The conceptual model for this problem is depicted in Figure 3:

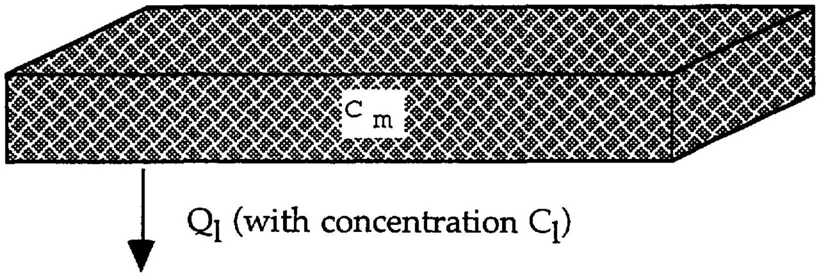

Figure 3. Conceptual model for leachate concentration in fractured clay.

a) Mass balance in the fractures:

$$Q_l C_l - K(C_m - C_l) = -V_s \phi_f \frac{dC_l}{dt} \qquad \text{(A-1)}$$

where:
Q_l = leachate flow rate through source area (L^3/T)
C_l = concentration in leachate (M/L^3)
K = mass transfer coefficient (L^3/T)
C_m = average concentration in matrix blocks (M/L^3)
V_s = volume of source area (L^3)
ϕ_f = fracture porosity (dimensionless)

b) Mass balance in the matrix:

$$K(C_m - C_l) = -\phi_m R_m V_s \frac{dC_m}{dt} \qquad \text{(A-2)}$$

where:
ϕ_m = matrix porosity
R_m = retardation coefficient accounting for matrix adsorption

c) Combined mass balance: (Put Eqn A-2 into Eqn A-1)

$$Q_l C_l + \phi_m R_m V_s \frac{dC_m}{dt} + V_s \phi_f \frac{dC_l}{dt} = 0 \qquad \text{(A-3)}$$

Remembering that this analysis assumes NAPL is no longer present in the fractures, and making the assumption that mass storage of dissolved phase product in the fractures is negligible relative to that in the matrix:

$$C_l = -\frac{\phi_m R_m V_s}{Q_l} \frac{dC_m}{dt} \qquad \text{(A-4)}$$

Substituting Eqn A-4 into Eqn A-2:

$$K C_m + \frac{K \phi_m R_m V_s}{Q_l} \frac{dC_m}{dt} = -\phi_m R_m V_s \frac{dC_m}{dt} \qquad \text{(A-5)}$$

or: $$\phi_m R_m V_s \frac{K + Q_l}{Q_l} \frac{dC_m}{dt} = -K C_m \qquad \text{(A-6)}$$

or: $$(C_m)^{-1} \frac{dC_m}{dt} = -\frac{Q_l}{\phi_m R_m V_s (1 + Q_l/K)} \qquad \text{(A-7)}$$

Integrating Eqn A-7:

$$C_m = C_m(o) \exp\left(\frac{-Q_l}{\phi_m R_m V_s (1 + Q_l/K)} t \right) \qquad \text{(A-8)}$$

where: $C_m(o)$ = average matrix concentration at the initiation of the leaching process (i.e. when the NAPL has just disappeared from the fractures)

Differentiating Eqn A-8:

$$\frac{dC_m}{dt} = -\frac{C_m(o)\, Q_l}{\phi_m R_m V_s (1 + Q_l/K)} \exp\left(\frac{-Q_l}{\phi_m R_m V_s (1 + Q_l/K)} t \right) \qquad \text{(A-9)}$$

Substituting Eqn A-9 into Eqn A-4:

$$C_l = \frac{C_m(o)}{(1 + Q_l/K)} \exp\left(\frac{-Q_l}{\phi_m R_m V_s (1 + Q_l/K)} t\right) \qquad \text{(A-10)}$$

The maximum concentration in the leachate occurs at time zero where the exponential term equals 1:

$$C_{l(m)} = \frac{C_m(o)}{1 + Q_l/K} \qquad \text{(A-11)}$$

which is Eqn 3. Note that although C_l is a function of time, for typical problems it varies very little over time frames normally associated with a residential exposure duration (30 years). For all practical purposes, it can be treated as a constant.

2. Estimation of Mass Transfer Coefficient

For purposes of estimating K, assume the matrix blocks are cubes and the initial concentration in them is uniform and equal to $C_{m(o)}$. On the boundary between the matrix and fracture, as well as in the fracture, the concentration is taken as zero. Then the mass remaining in the matrix after some time t of outward diffusion is:

$$M_r = C_m(o)\ \phi_m R_m V_s\ P^3 \qquad \text{(A-12)}$$

where: M_r = mass remaining in matrix after time t

ϕ_m = matrix porosity

R_m = retardation coefficient accounting for matrix adsorption

P = one-dimensional diffusion expression

$$= \frac{8}{\pi^2} \sum n^{-2} \exp\left(- n^2 \pi^2 \frac{D_e t}{R_m L^2}\right) \qquad \text{(A-13)}$$

(n = 1, 3, 5 ....)

D_e = diffusion coefficient

L = cube dimension

The factor, P, appearing in Eqns A-12 and A-13 is Glover's (1974) 'part remaining' term, as adapted to the diffusion problem by Parker and McWhorter (1994). It appears to the third power in Eqn A-12 as the result of applying the product rule (Carslaw and Jaeger, 1959) to this problem of three-dimensional diffusion.

For estimating K, ignore all but the first term in Eqn A-13.

Then:
$$P = \frac{8}{\pi^2} \exp\left(-\pi^2 \frac{D_e t}{R_m L^2}\right) \qquad \text{(A-14)}$$

Note that M_r is also equal to:

$$M_r = C_m \phi_m R_m V_s \qquad \text{(A-15)}$$

where: C_m = average concentration in the matrix blocks

Substituting Eqn A-15 into Eqn A-12:

$$C_m = C_{m(o)} P^3 \qquad \text{(A-16)}$$

and:
$$\frac{dC_m}{dt} = 3\, C_{m(o)}\, P^2\, dP/dt \qquad \text{(A-17)}$$

Substituting Eqns A-16 and A-17 into Eqn A-2, noting that $C_l = 0$ yields:

$$K = \frac{-\phi_m R_m V_s \ (3\, C_{m(o)}\, P^2\, dP/dt)}{C_{m(o)}\, P^3} \qquad \text{(A-18)}$$

or:
$$K = -3\, \phi_m R_m V_s \frac{dP/dt}{P} \qquad \text{(A-19)}$$

Differentiating Eqn A-14:

$$\frac{dP}{dt} = \frac{8}{\pi^2} \frac{-\pi^2 D_e}{R_m L^2} \exp\left(-\pi^2 \frac{D_e t}{R_m L^2}\right) \qquad \text{(A-20)}$$

$$= \frac{-\pi^2 D_e}{R_m L^2} P \qquad \text{(A-21)}$$

So:
$$K = \frac{3\, \pi^2\, \phi_m D_e V_s}{L^2} \qquad \text{(A-22)}$$

SOIL VAPOR EXTRACTION IN LOW PERMEABILITY SOILS

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ABSTRACT

This paper describes one of the seven in-situ technologies that may offer the potential to, at least partially, remediate LNAPL's in silty or clayey soils. The soil vapor extraction process is described and its capability to remove product in two types of low permeability settings evaluated. The paper also includes a summary of the commercial availability and typical costs of the technology as well as case histories where it has been applied in low permeability media.

Section 1
DESCRIPTION OF TECHNOLOGY

Soil vapor extraction (SVE) is a process to recover volatile and semi-volatile contaminants from soils above the water table (the vadose zone), and in specially designed systems, from the partially saturated transition zone between the vadose zone and the aquifer (the capillary fringe). SVE systems operate by inducing air flow in the target soils through creation of pressure gradients. The induced air flows trigger two primary removal mechanisms:

- Evaporative recovery - Contaminants are recovered as they evaporate into the soil atmosphere and are transported with the induced air flow.
- Biological degradation - Evaporative recovery is augmented by bacterial and possibly fungal breakdown of susceptible contaminants (e.g. the BTEX compounds) since most SVE systems supply oxygen to the subsurface.

As long as air flows through targeted soils, these recovery mechanisms will reduce contaminant concentrations. It is the induction of air flow in the soils which requires significant design attention.

Air movement is induced by creating a pressure gradient in the subsurface. High pressure can be provided by the atmosphere overlying an uncapped site, open (passive) wells or trenches which are constructed to release air into the soils below the ground surface, and through pressurized air injection wells or trenches. Low pressure zones are created by applying vacuum to wells or trenches constructed in the soils targeted for cleanup. Even in homogeneous soils, the air flows are not uniform over the entire treatment volume. This results in variable treatment rates of the target soil volume. Strategies such as site capping and well field rotation have been developed to overcome the unequal distribution of air in SVE treatments.

The rate of air flow through soils is determined by the rate of pressure drop, or gradient, and the resistance of the soil to air flow. High rates of air flow can be established in coarse soils with small pressure drops. These soils are relatively easy to treat using SVE. Fine-grained soils present a high resistance to air flow and require large pressure gradients to induce flow rates to remove contaminants. Sites with stratified soils of contrasting grain size develop air flow in the coarser-grained strata while air flows very poorly through the finer-grained material. SVE system designers must determine pressure drops that will induce sufficient air flows, and plan flow patterns which cover all soil zones requiring treatment.

Section 2
GENERAL TECHNOLOGY CONSIDERATIONS

2.1 SOIL WATER CONTENT

Soil water content is a common impediment to the soil vapor extraction process, and must be considered in any SVE system design. There are two mechanisms by which soil water decreases SVE removal efficiencies:

- Blockage of air flow pathways: Pore water within the vadose zone occludes a portion of the soil profile which would otherwise be available for air flow. This problem is particularly severe in fine-grained soils where the capillary fringe (100% water-saturated soils that are under tension relative to atmospheric pressure) has a significant thickness.

- Contaminant partitioning from LNAPL to pore water: Compounds which are highly soluble in water will dissolve into soil pore water and yield poorly to soil vapor extraction systems. High soil pore water content increases the likelihood that SVE contaminant production will fall below detectable levels while the soils fail post-treatment concentration targets for water-soluble compounds.

On the other hand, soil pore water may benefit SVE recovery for compounds which adsorb to soil particle surfaces. The thin film of water which coats soil particles blocks access to the particle surface, limiting adsorption of compounds such as chlorinated solvents. The potential of soil pore water to act as a protective mechanism requires that SVE system designers avoid creating conditions which overly dry the soils.

Soil vapor extraction system designers utilize one or more of the following methods to overcome limitations imposed by soil water content:

- Seal the site surface: Precipitation water can be excluded from an SVE treatment zone by installation of an impermeable surface cover. Most designers also utilize this cover to prevent pressure and vacuum losses through the ground surface.

- Limit water lift: Vacuum applied at withdrawal well locations lifts the water table, blocking some portion of the treatment area.

This problem is greatest in low-permeability soils, since the pressure drops required to drive air flow are high. Two approaches are commonly utilized to limit water lift: vacuum dewatering and injection-withdrawal airflow configurations. Vacuum dewatering is accomplished by adding small water recovery points beneath the withdrawal well, intercepting groundwater as it rises in response to applied vacuum. The injection-withdrawal approach splits the required pressure drop between pressure and vacuum points to halve the vacuum lift at the withdrawal well.

- Soil heating: Vadose zone soil pore water content can be dramatically reduced by certain soil heating methods, including hot air, radio frequency, or electrical resistance heating. The incremental cost of these heating methods generally limits their application to projects which require very fast treatment completion or require recovery of low volatility compounds.

Vadose zone soils which have a high pore water content will be treated slowly under any of the soil vapor extraction design strategies. The capillary fringe can be addressed through injection of air into the underlying aquifer (air sparging), although the efficacy of this technique is still under debate.

2.2 ACCESS BENEATH BUILDINGS AND PAVEMENT

Soil vapor extraction can access contaminants beneath buildings and pavement with limited disturbance, which was an important factor in acceptance of the technology when it was first introduced to the market. But buildings and pavement do present technical difficulties which must be considered in system design and operation:

- Limitation of make-up air availability: System designers who wish to utilize the vacuum-only pumping strategy face serious limitations due to lack of make-up air pathways beneath buildings.

- Flow blockages: Foundation footers block air flow, which requires segmentation of the treatment system.

- Site surface seal: Pavement and building floors are often poorly sealed, which allows leakage of air as well as entry of precipitation water.

- High permeability stratum losses: Building floors and pavement are normally installed on a porous bedding. In low permeability soils, this porous material diverts a high percentage of the available air flow away from the target zone soils.
- Pressure lifting potential: Pressurized air injected beneath buildings and pavement exerts a lifting force which may cause structural damage.

Costs for installation and operation beneath buildings and pavement are higher than comparable open-surface sites. Some savings are achieved due to the existence of a surface cover, but they are often offset by trenching costs, increased well densities and extended operation time.

2.3 OPERATIONAL DEPTH LIMITATIONS

- Maximum Depth: There is no theoretical limit for maximum depth in the soil vapor extraction process. Air flow efficiencies increase with depth as air leakage at the ground surface diminishes as a percentage of total air flow. Normally, the cost per treatment volume decreases as site depth increases, since the surface piping and trenching costs are distributed over increasing treatment volume. Total costs however obviously increase with depth.
- Minimum Depth: There are clear limitations for the minimum vadose zone thickness in vapor extraction. SVE vacuum wells exert lift on the water table surface, as described above. As the treatment zone thickness decreases, the impact of water surface lifting increases. The problem is most evident in low permeability soils which require large pressure drops to induce air flows sufficient to remove contaminants. Sites with limited soil thickness require decreased well spacing to reduce operating vacuum levels. This avoids blockage of the treatment zone soils by lifted groundwater. The practical minimum depth limit is reached when, even with minimal distance between wells, air flow cannot be induced through the soils without raising groundwater levels into the treatment zone. Trench-based systems are favored in sites less than 10 feet in thickness due to their minimal pressure drop requirements.

2.4 PETROLEUM PRODUCTS OTHER THAN GASOLINE

Gasoline recovery in soil vapor extraction is driven by a combination of evaporation and biological breakdown. The relative contribution of the two mechanisms is determined by air exchange rates and the balance of low boiling point and high boiling point compounds remaining to be treated. High air exchange rates tend to increase recovery by evaporation, while very low exchange rates accomplish recovery almost exclusively by biological breakdown (e.g. bioventing). As recovery proceeds, the residual contaminant load generally increases in average boiling point. Even at high air exchange rates, evaporative recovery for high boiling point compounds is sparingly small. Biological breakdown is likely the principal treatment mechanism in this case.

Evaporative recovery represents a much smaller portion of treatment in soils contaminated by petroleum products other than gasoline. The higher boiling petroleum products require biological breakdown to achieve closure concentrations in most jurisdictions. This means that the optimum air exchange rate decreases as the product boiling range increases. Biological treatment can be supported at much lower air flows than are used for evaporative treatment. The treatment therefore switches from SVE to bioventing.

Enhanced soil vapor extraction design, particularly soil heating systems, can be used to achieve treatment objectives in shorter time frames. This option appears to be cost-effective only when site closure must be achieved quickly.

2.5 OPERATIONAL MODES

2.5.1 Continuous Flow

Typical SVE systems operate continuously with a constant pressure drop through the soil treatment volume and a stable air flow pattern. Sectors within the soil which do not lie on an air flow pathway will be treated much more slowly since any movement of contaminant will be diffusive. Continuous flow SVE has been a successful operational strategy for high permeability homogeneous soils. In these cases the air flow pathways are well-distributed throughout the soil mass. Many sites however have poor air flow distribution. Thus, due to the presence of low permeability strata, continuous flow operations fail to produce acceptable treatment rates.

2.5.2 Pulsed Operation

There is some field evidence that contaminant yields may be increased at sites with poor air flow distribution by pulsing the pressure gradient at a frequency established through field trials (Boersma et al, 1993). Each time an SVE system is started the soils are at 1 atm pressure initially. The pressure gradients develop over some time period, usually short duration, during which the soil air pressures are "pumped down" to stable gradient levels. It is expected that most of the air movement during pump-down will be in the primary air flow pathways. But soil pore space adjacent to the air flow pathways is likely to release air into the pathway, reaching local pressure equilibrium with the air path. The soil gas released from the matrix block during pump-down should be near equilibrium contaminant partial pressures, and will generally result in a contaminant concentration spike observed at the system air discharge. Operations are pulsed to repeat the spiking at a regular interval, significantly increasing yield rates relative to stable, continuous gradient operations.

Figure C-1 shows a stylized cross section of a matrix block-fracture flow system during a pulse cycle. In this figure, the vacuum source lies to the right, and the passive makeup air source lies to the left. The pulsing process shown in Figure C-1 operates as follows:

- Pump-down - As the site is brought to operational vacuum levels, there is a net outflow of air from the matrix blocks, which is triggered by the pressure drop in the adjacent flow pathway. The air flowing from the matrix block carries contaminants into the air path, producing a short-term increase in off-gas concentration.

- Purge - When a stable system pressure gradient has been reached in the soil, there is no further air released from the matrix blocks. During this phase, the net flow in the matrix blocks is zero, and system contaminant yields should fall to low levels.

- Relaxation - The pumping system is turned off to allow the soil pore space to relax to 1 atm throughout. Air flow continues until the soils reach 1 atm. During pressure relaxation,

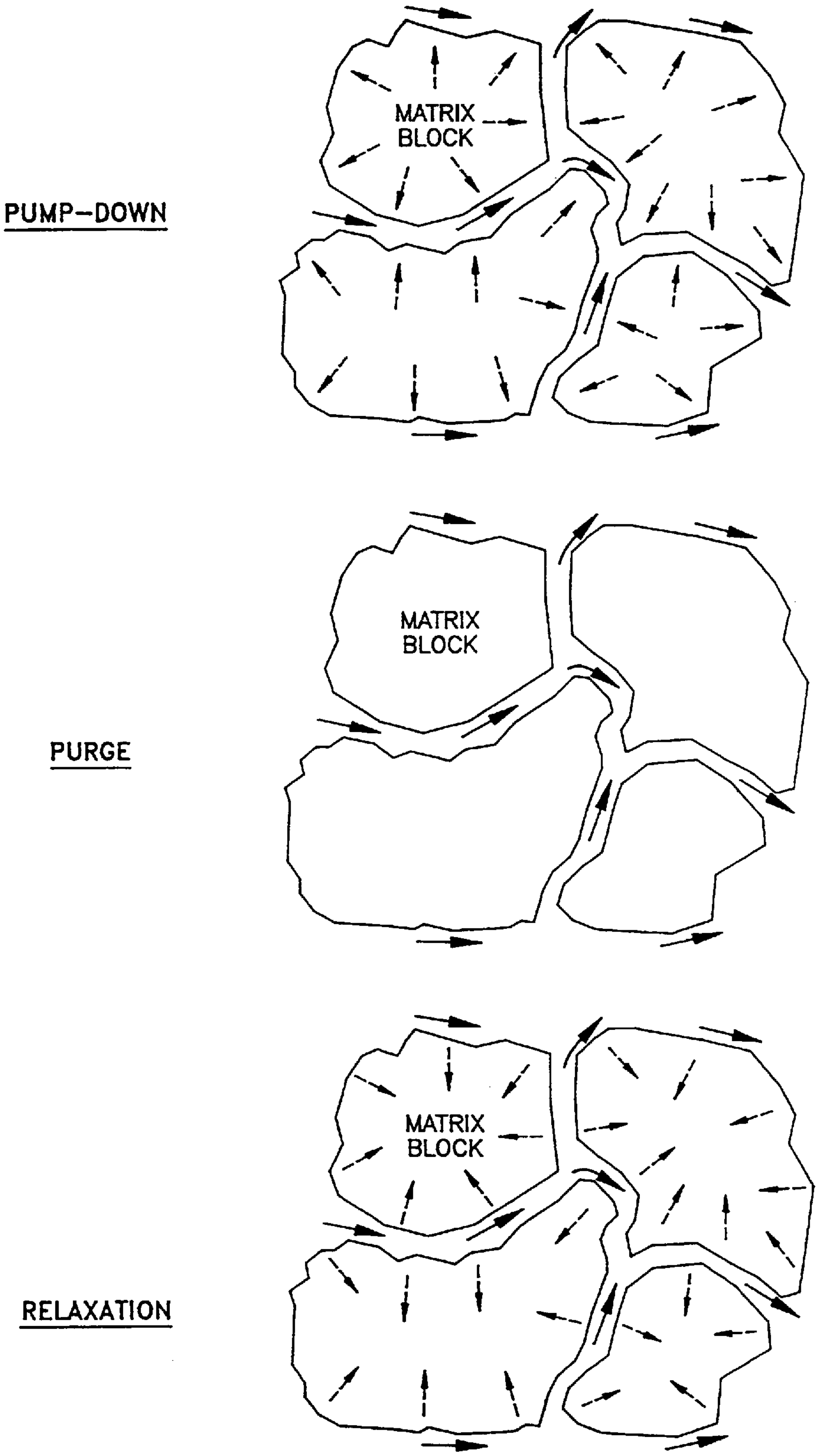


Figure C-1. Stylized representation of air flow in and out of matrix blocks during pulsed SVE operation

> relatively clean air from the swept air path enters the matrix blocks, as the net flow in the matrix blocks is inward. This influent air dilutes the matrix block soil gas, encouraging incremental evaporation. When the system is pumped in subsequent cycles, the net outflow of air and contaminants from the matrix block is repeated.

Pulsed operation would likely be most effective in systems with a tight surface seal, which will allow development of significant soil vacuum. As air path pressures fall, the pressure drop from the matrix block increases, improving yield gains. The most suitable air flow structure is the vacuum-passive injection pattern, with the injection shut off during pump-down phase. Relaxation is accomplished by slowly opening the passive injection wells, then slowly turning off vacuum withdrawal well flows.

Two soil structure characteristics will resist pulsed operation yield increases:

- The soil structural strength may produce a threshold effect in which the matrix blocks withstand pressure drops up to some level without releasing any air. In this case there may be a yield improvement with repeated cycles as the structure is eventually disrupted. But it may also not be possible to generate sufficient pressure drops to cause a release. (The stress applied by the pressure drop through the matrix blocks should be shear, against which soils are weak compared to their compressive strength).

- Pore space in the matrix block may be water-filled, adjacent to open air pathways. This may be common in low permeability fractured clays. Pulsed operation can improve system yield in this case only by encouraging water release from the matrix blocks, which requires very high in-situ vacuum levels.

Section 3

REMEDIAL CAPABILITY IN NATURALLY-FRACTURED MASSIVE TIGHT SOILS

Naturally-fractured, massive low permeability soils is the first of two geologic settings which are addressed in this paper. The basic scenario is as follows:

- The clay is areally extensive and 30-50 m thick
- The upper 2 m of the clay is highly weathered due to desiccation
- The fractures are on 1-100 cm spacing, primarily vertical
- The fractures have 10-40 mm apertures
- The clay blocks between fractures are saturated (i.e. there are no continuous air pathways)
- Depth to the water table is 1-3 m
- The effective air-filled porosity is <1%

3.1 AIR FLOW IN FRACTURED SOILS AND BEDROCK

Air flow patterns in fractured low permeability soils and in bedrock are very similar. These are actually *dual porosity* media in which the fractures represent a very high permeability stratum which occupies an exceedingly small percentage of the soil volume. The characteristic which distinguishes fracture systems is the blocks of material between the fractures. These are termed *matrix blocks,* and they generally present a very high resistance to air flow. Figure C-2 depicts a matrix block-fracture flow system.

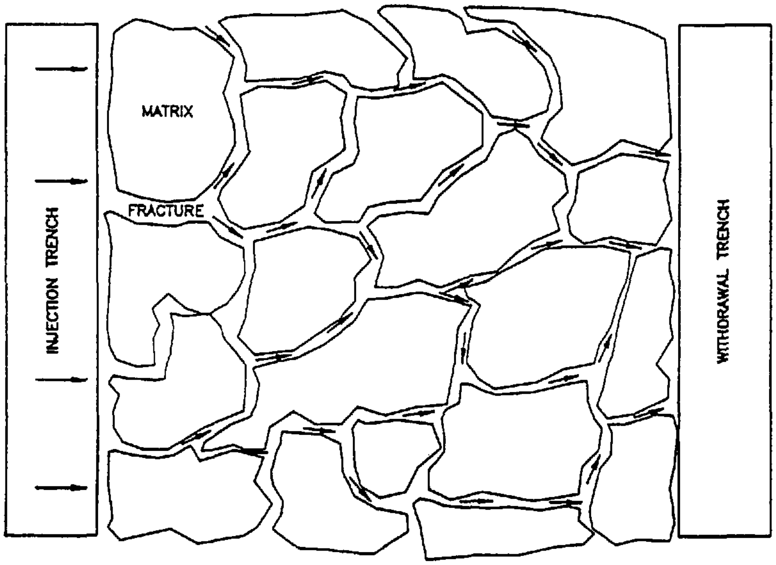


Figure C-2. Cross section of air flow in a fracture-matrix block system

Air flows freely through the fractures, but cannot be induced to flow through the matrix blocks. Contaminant recovery from the matrix blocks in a continuous flow SVE system is limited to diffusive losses from the matrix block into the adjacent fractures. This is an exceedingly slow process. The pulsed operation mode is designed to treat the matrix blocks, as was detailed above.

3.2 DESIGN STRATEGY

The soil vapor extraction design strategy must address several technical barriers inherent in this scenario:

> Low permeability soil - An air exchange rate of 1 soil pore volume per day is typically used in vapor extraction systems optimized for evaporative recovery. Given the very low pneumatic conductivity in this soil, a minimum average pressure drop of 0.1 inch H_2O per foot of travel will be required. For vertical wells where the required air exchange rate is to be induced over a radius of 15 feet, the wellhead vacuum must reach 45 inches of H_2O. A two-well system using the injection-withdrawal strategy still requires a wellhead vacuum of 23 inches of H_2O. A trench-based system inducing air flow between pressure and vacuum trenches requires a vacuum of 0.75 inch of H_2O at 15-ft separation.
>
> High water table - The high water table complicates treatment in this scenario, since the vacuum lift exerted in any of the strategies given above will flood the treatment zone. Even though the water yield rate may be quite low, water which is lifted from below will block the limited air flow pathways and reduce contaminant recovery. The system designer will be required to minimize vacuum levels by opting for a low vacuum configuration, and minimizing distance between air sources and sinks (minimizing total required pressure drop).
>
> Fracture flow - Advective air flows will not contact most of the soils in the treatment zone. The continuous fractures present a high-conductivity pathway which captures virtually all air flow at steady state pressure drop. Treatment of the matrix blocks will be diffusion-limited.
>
> Aqueous-phase recovery - The saturated matrix block soils harbor dissolved compounds which will be inaccessible to the bulk soil air flow.
>
> Diffusion-limited release - Contaminants located in discontinuous fractures and in unsaturated matrix block pores must reach the bulk

soil air flow through gaseous-phase diffusive movement. Contaminants located in water-filled fractures and in saturated matrix block pores must reach the bulk soil air flow through aqueous-phase diffusion.

A design strategy which maximizes the possibility of achieving typical contaminant closure levels in this scenario incorporates the following elements:

- Trench-based air injection and withdrawal - A shift from standard vertical, radial air wells yields significant operational advantages for this scenario: The high vacuum levels required by a radial well system will lift the shallow groundwater and flood fractures in the treatment zone. Unless this water can be removed by the SVE system, the blockage of available air flow pathways can significantly reduce the treatment rate. The trench face distributes air flows over a much broader surface area and minimizes pressure drop to the lowest level possible.

- Three-step air flow optimization - The air flow protocol which maximizes contaminant recovery will change through the life of the project. In the first operational step, product will be recovered from fractures in the standard, continuous air flow pattern with an exchange rate of one pore volume per day. Pressures and vacuums are pulsed in the second step to encourage discharge of product from discontinuous fractures and unsaturated matrix block elements. The final step in the protocol is the creation of a low-flow regime, designed to maintain soil oxygen content at levels which promote biological activity. This final step is aimed at aqueous-phase materials which reside in the matrix block.

3.3 EFFECTIVENESS ISSUES

Each of the following contaminant reservoirs will be affected differently by the soil vapor extraction process. The potential treatment effectiveness and strategies which might optimize performance for these reservoirs is outlined below:

Free product trapped in continuous fractures - This material will yield quickly during continuous air flow operations. Product trapped in continuous fractures should represent the majority of the product released during system operation.

Free product trapped in discontinuous fractures - Product recovery from the discontinuous fractures will be limited by gaseous-phase diffusion during continuous air flow operation. Pulsed operation may improve yield, assuming the soil characteristics which resist pulsed operation (described earlier) are not encountered.

Aqueous-phase product diffused into matrix blocks - This product yields very slowly, limited by aqueous-phase diffusion rates which are much slower than gaseous phase rates. Treatment of this material is probably accomplished most effectively by diffusion of dissolved oxygen into the matrix block which promotes biological breakdown. If the residual material is limited to aqueous-phase compounds, a very low air flow rate sustains biological activity and minimizes operational cost.

Product adsorbed on organic soil material - This material may not be recoverable to a large degree. Recovery of the other product phases is primarily driven by equilibrium processes, and removal is achieved by displacing equilibrium to favor release of the contaminants. Adsorbed product release requires that dissolved phase product first be removed, which is difficult with SVE systems. Residual adsorbed petroleum product may remain at levels above target cleanup standards after soil vapor extraction yields have ceased.

Residual product trapped within matrix pore throats - Given the fact that the matrix blocks are saturated in this scenario, the residual product trapped in the matrix pore throats would be near the matrix-fracture boundary and be recoverable through gaseous-phase diffusion and possibly advection in a pulsed operation. The small cross-sectional area of the pore throats will slow recovery of this material relative to that of the product trapped in discontinuous fractures, although the mechanism of recovery is likely similar.

Free product floating on the water table - Phase-separated hydrocarbons should reside primarily in the fractures and be recovered much like product trapped in discontinuous fractures. Pulsed operations should increase recovery of this material due to flexing of the free water surface and delivery of a portion of the material to the continuous fractures.

3.4 AVAILABLE TECHNOLOGY ENHANCEMENTS

- Vacuum dewatering: Deep-vacuum dewatering may provide a significant yield rate enhancement for recovery of phase-separated hydrocarbons and residual product trapped in pore throats. An effective dewatering program will also free the system designer to operate at greater vacuum levels without allowing the water surface rise to interfere with design air flow pathways.

- Heat Injection: Although this would be at the expense of biological degradation, application of heat to the soils through any of the available strategies should dramatically increase treatment rates and lower achievable endpoint concentrations. This may be the only way to achieve closure levels for aqueous-phase material in the matrix block and contaminants adsorbed to soil organics.

Section 4

REMEDIAL CAPABILITY IN CONTINUOUSLY STRATIFIED LOW PERMEABILITY SOILS

Continuously stratified soil systems, with sharply contrasting pneumatic conductivities, is the second geologic setting addressed in this paper. The basic scenario is as follows:

- The soil is stratified with layers ranging from medium sand to silt
- The soil is relatively dry with continuous air pathways in both the silt and the sand
- The sand behaves like a porous medium with regard to fluid flow
- There are some preferential pathways in the silt and in the sand
- The water table is located 3-4 m below the ground surface
- The effective air-filled porosity is 0.2; the total porosity is 0.3

4.1 AIR FLOW IN STRATIFIED SOILS

Soil systems which are comprised of multiple strata of contrasting air permeabilities are a significant design challenge and have contributed to dramatic failures of the technology to reach treatment targets. It is possible to design SVE treatments which can overcome stratification-induced problems and these are discussed below. This section briefly reviews the air flow patterns which are established in stratified soils.

Figure C-3 depicts a site dominated by low-permeability soils such as silt, with a seam of high permeability soil (sand, for example) at the mid-depth. The sand seam is one-tenth the combined thickness of the two silt layers. A trench-based

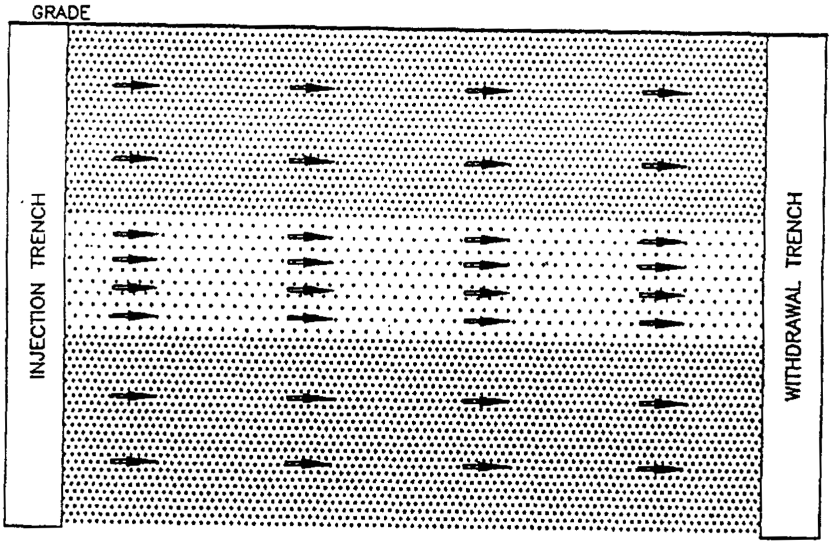


Figure C-3. Depiction of air flow patterns in a stratified permeability site

source/sink layout has been installed and the site surface is sealed. A fixed-displacement pump has been set up to drive the air flow. When the system operates, the following occurs:

- A pressure gradient is established between the two trenches.
- The pressure drop across the two soil types is equal.
- The air flows allocate between the strata in proportion to the pneumatic conductivity of each strata.

If there is a 100-fold difference in pneumatic conductivity between the strata, roughly 90% of the air flow passes through the sand. If biodegradation is ignored, the cleanup time in the silt layers would be roughly 100 times longer than that in the sand.

The pulsed operation strategy, which is described below, offers some relief from the air flow pattern failure in stratified permeability soils. However it may be impossible to create a sufficient pump-down at sites with a high proportion of highly permeable strata.

4.2 DESIGN STRATEGY

The continuous stratification scenario presents a single principle technical barrier which must be overcome to achieve treatment. This is the pneumatic conductivity contrast. Air flows can easily be established in massive formations of either medium sand or silt. But when alternative pathways are available, the induced air flows will overwhelmingly follow the high conductivity pathway. Release of product from the silt strata will be diffusion-dominated in a continuous air flow system. A recovery design which depends on advective air flow through the silt strata will require an exceedingly long remediation time frame.

The soil vapor extraction system designer should incorporate the following design strategy elements to maximize the probability of achieving closure under this scenario:

- Vertical well system - Air flows can be induced effectively in this scenario with vertical wells. Air injection is necessary to provide horizontally dominant pressure drops, and can be either pressurized or passive (1 atm). Passive injection would be utilized during pulsed operation.

- Three-step air flow optimization - As with the previous scenario, recovery rate optimization strategies will change through the life of the project. Early operations will be most effective with continuous air flow, and recovery will be primarily from the sand strata and from the phase-separated hydrocarbons perched on low-permeability lenses. Pulsed operation would be expected to optimize yields during the second step of air flow application, but this strategy may not be as effective as in the earlier scenario. The high conductivity sand strata will allow air to move so freely that it is very difficult to establish significant soil vacuum levels. The site closure objective may not be met until the third step of the protocol is implemented; namely, low flow bioventing.

4.3 EFFECTIVENESS ISSUES

Each of the following contaminant reservoirs will be affected differently by the soil vapor extraction process. The potential treatment effectiveness and strategies which might optimize performance in these scenarios is outlined below:

> Free product trapped on perched, low-permeability lenses - This material should be removed at acceptable rates during both continuous and pulsed air flow operations. Acceptable treatment can be accomplished for this product reservoir, and it would not be expected to be the limiting factor in site closure.
>
> Aqueous-phase constituents diffused into continuous, low-permeability layers - This phase will likely be the most resistant to treatment. The treatment constraints are similar to those expressed for the previous scenario, with dissolved oxygen diffusion into the matrix block pore water and biological breakdown rates determining the pace of recovery.
>
> Residual product in both the permeable and low-permeability layers - Residual product in the high-permeability strata will be recovered quickly during continuous flow operations. The recovery rate for product in low permeability strata will be limited by gaseous-phase diffusion, and will be recovered much more slowly. The pulsed operation phase should enhance recovery rates for this reservoir of material, but the limitation on attainable vacuum levels in the sand strata constrains the degree of treatment improvement due to pulsing.
>
> Free product on the water table, adjacent to a high-permeability layer - Phase-separated hydrocarbons are recovered quickly in this setting. The recovery rate should be accelerated during pulsed operations. This is due to flexing of the water table surface which spreads product into the overlying soils which are subjected to advective air flow.
>
> Contaminant recovery from low permeability isolated lenses rather than continuous layers - Recovery from isolated lenses is limited by the same mechanisms which slow recovery in continuously stratified systems. Treatment will be primarily a diffusion-limited process.

4.4 AVAILABLE TECHNOLOGY ENHANCEMENTS

- Air Sparging: Recovery of contaminants from the capillary fringe may likely be enhanced by injection of air into the underlying aquifer. Since the rate-limiting release for this scenario lies in the aqueous-phase of the silt strata, this enhancement may not be cost-effective.

- Heat Injection: Although at the expense of biological degradation, heat injection can be expected to dramatically improve release rates for the low-permeability strata. The incremental cost for heat injection must be justified by the accelerated time to completion.

Section 5

COST AND COMMERCIAL AVAILABILITY

A standardized treatment scenario has been established to provide baseline cost and treatment duration comparisons for basic technologies and available enhancements. The site conditions for the standard project are : treatment volume of 100 ft x 100 ft x 15 ft, a stratified fine-grained media contaminated with gasoline which has diffused into the low-permeability matrix blocks at a concentration of 1,000 ppm. The target is to meet a 200-ppm closure goal.

5.1 BASIC DESIGN

The site volume lies at the mid to low range of commercial scale applications of soil vapor extraction, with a total volume of 150,000 ft^3. The minimum air flow requirement is 20 scfm, which will provide a nominal air exchange rate of one soil pore volume per day. The pressure drop required to establish the air exchange rate will be controlled by the high permeability strata, and a 14-well network will operate at less than 3 psi injection pressure and less than 6 inches of Hg vacuum. Equipment selection will be driven by the pulsed operation design objective, which requires relatively high pumping rates to establish significant soil vacuum.

The vapor extraction system would be installed with below-grade piping and an impermeable site cover. Allowances have not been made for pavement cutting and repair. The pumping equipment specification includes both pressure and vacuum blowers, individual wellhead flow controls, and water separation.

System operations would begin with continuous air flow for approximately two months, followed by pulsed operation on a cycle optimized by site staff. The total project duration is estimated at 9 months, which is relatively short due to the limited reduction in concentration required for this project.

The five-fold reduction specified for the baseline system will yield approximately 15,000 pounds of gasoline recovery. It is assumed that offgas control would be required in most jurisdictions. Four months of catalytic oxidation control has been budgeted, with the balance of operations through activated carbon.

5.2 COST BASIS

The following costs are representative of commercial projects with a similar scope:

• Pilot Test	$20,000
• Pre-treatment soil sampling	$ 5,000
• Installation	$37,000
• Operations (9 months)	$18,000
• Offgas control	$21,000
• Post-treatment soil sampling*	$10,000
Total	$111,000

*Note: The cost of post-treatment soil sampling is higher than the initial sampling as the cost of the initial drilling is included in the well installation cost.

More aggressive completion standards can be achieved through extension of the project duration, without additional installation costs.

5.3 COMMERCIAL AVAILABILITY

Soil vapor extraction systems capable of achieving this standardized treatment are commercially available. There are, however, significant variations in application of the technology which influence project duration and closure level capabilities.

Section 6

CASE HISTORIES

The case histories presented below are intended to show the results of soil vapor extraction application to a cross-section of petroleum products in massive low permeability soils and in stratified soil sites. These SVE projects have not all achieved their respective treatment objectives to date. They are presented to illustrate the difficulties in achieving closure standards in low permeability settings. It is important to note that the closure levels for these sites are significantly lower than for the baseline design case above.

6.1 JP-4 IN MASSIVE CLAY SITE

JP-4 was lost from an above-ground storage tank piping system in multiple, small-scale releases. The site volume is approximately 3,500 cubic yards, with groundwater at 16 ft. The tank system and approximately 100 cubic yards of grossly contaminated soil was removed prior to treatment system installation. The site closure standard is 50 ppm total petroleum hydrocarbons by a modified EPA 8015 method, calibrated to JP-4.

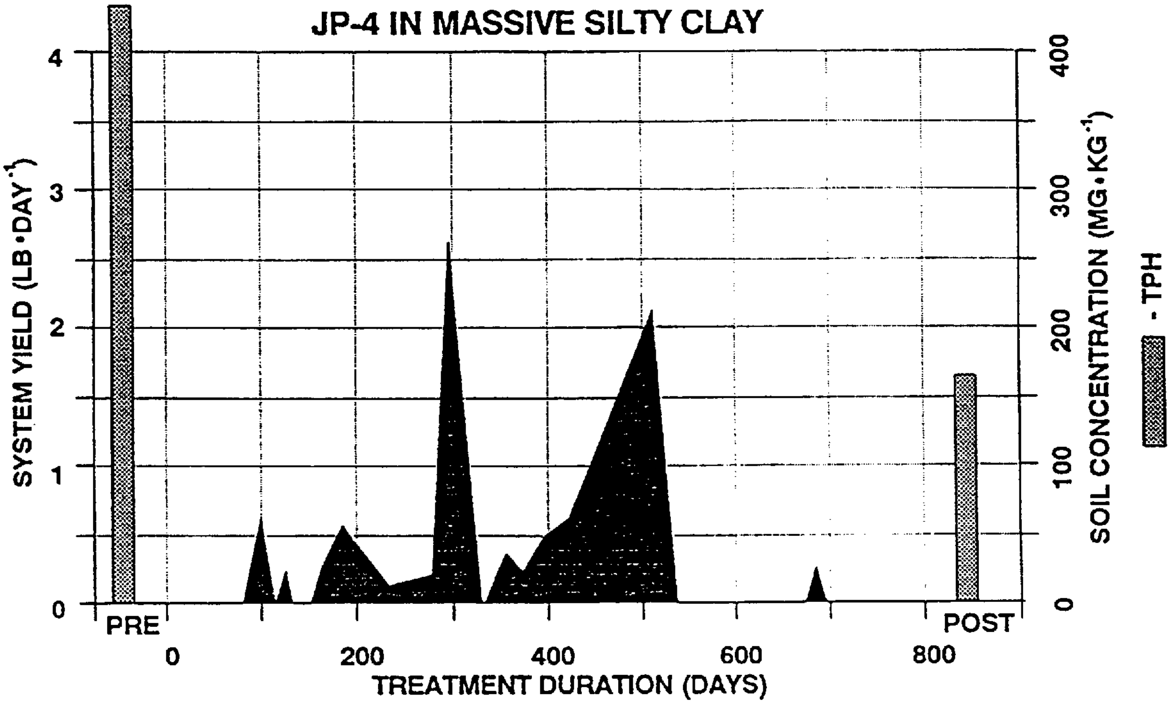
The technical barriers on this site are:

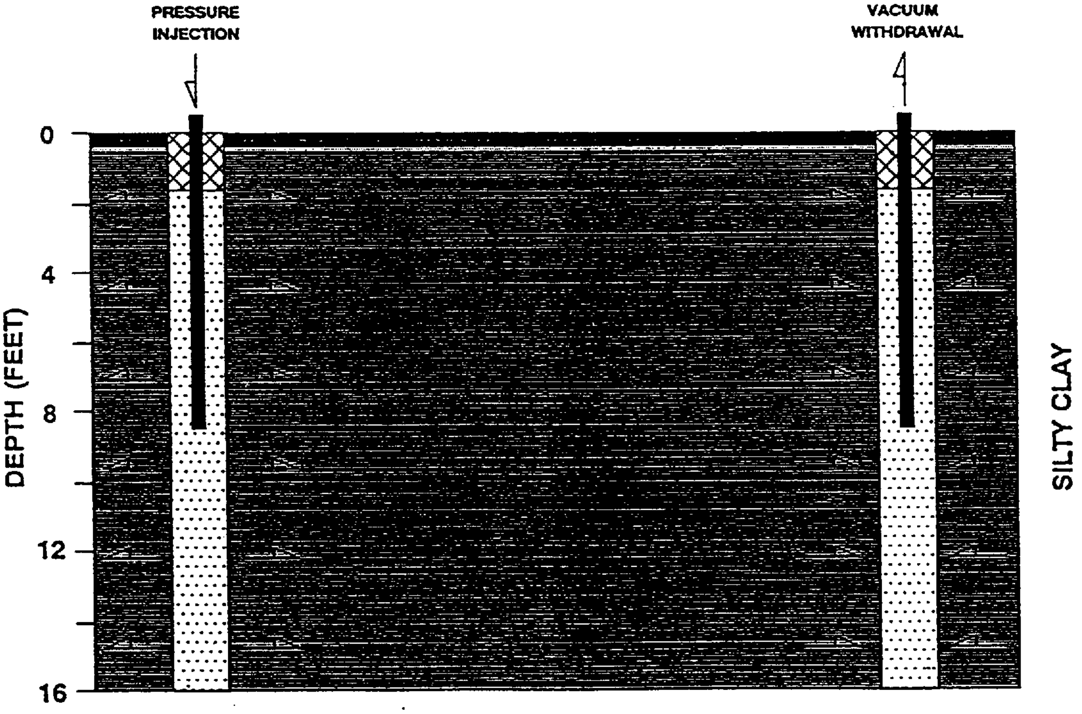
- Massive, low permeability soils
- Low volatility target compounds
- Low closure standard in relation to the mobility of the target compounds

An additional problem encountered at the site is that the basin created by excavation of soil was allowed to fill with water prior to backfilling. This left a highly contaminated, highly saturated volume which has subsequently resisted air flow.

The design strategy is based on a minimum air exchange rate of 1 soil pore volume per day. The treatment mechanism is expected to be a combination of limited evaporative recovery and biological degradation. The design layout and results are summarized in Figure C-4, and are as follows:

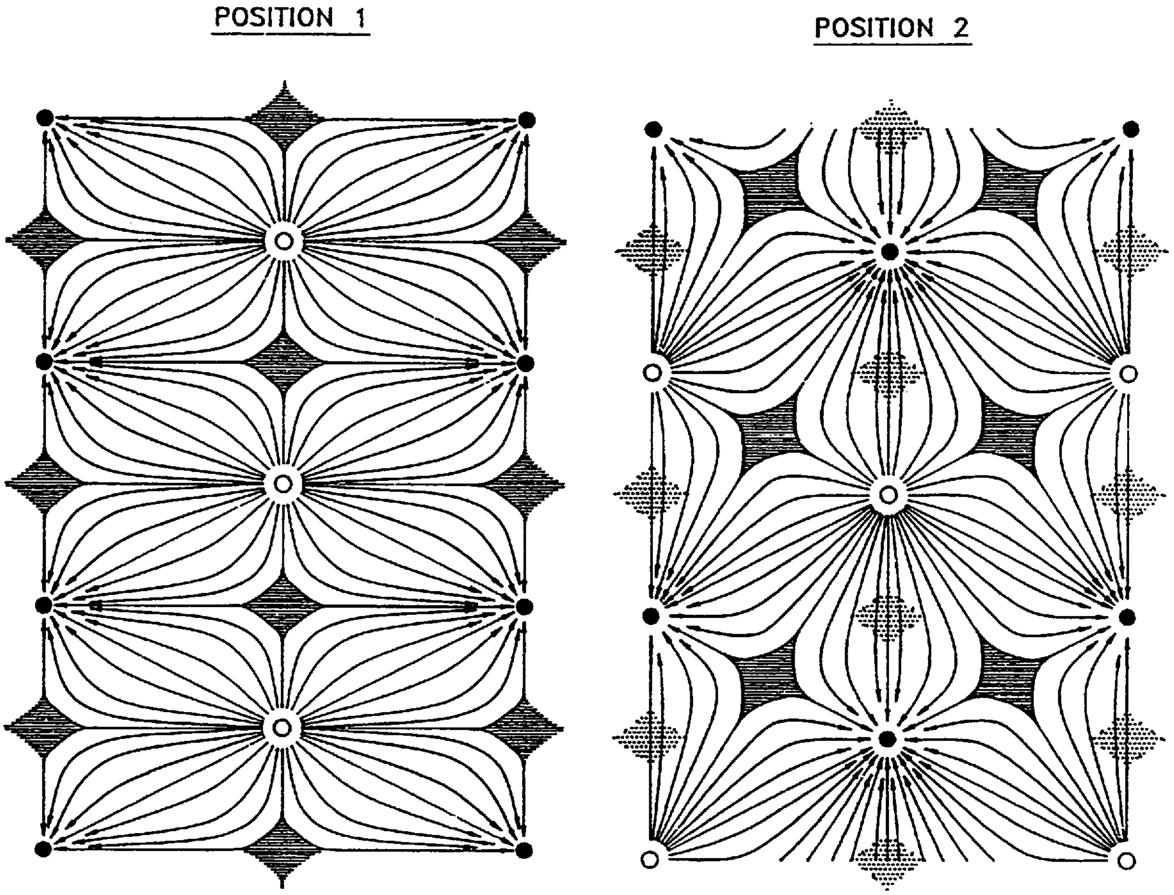
> System layout - The soil vapor extraction system is based on a pressure injection - vacuum withdrawal concept, with wells networked as shown in Figure C-5.
>
> Offgas yield results - As expected, yield rates are very low for this low volatility fuel, with maximum recoveries of just over 2 pounds per day. Many of the monthly samples fall below 0.1 pounds per day. Carbon dioxide production has not been measured at this site.





SOIL STRUCTURE AND WELL CONSTRUCTION STRATEGY

Figure C-4. Case history summary: JP-4 in massive silty clay



EXPLANATION:

○ SVE INJECTION WELL
● SVE WITHDRAWAL WELL
◆ TREATMENT NODE

Figure C-5. Well field rotation concept. Treatment nodes which develop in position 1 are treated during position 2 operations

Soil concentration - Pre-treatment soils averaged 440 mg/kg TPH and samples collected following 700 days of treatment averaged 165 mg/kg. The post-treatment sample average was above the agreed closure criteria due to failure of treatment in the wet soil sector.

The treatment achieved more than 10-fold reduction in the soils which received air flow. The site operators were unable to achieve air flow in the saturated area, which indicates that some form of SVE enhancement will have to be undertaken to reach the site-wide treatment objective.

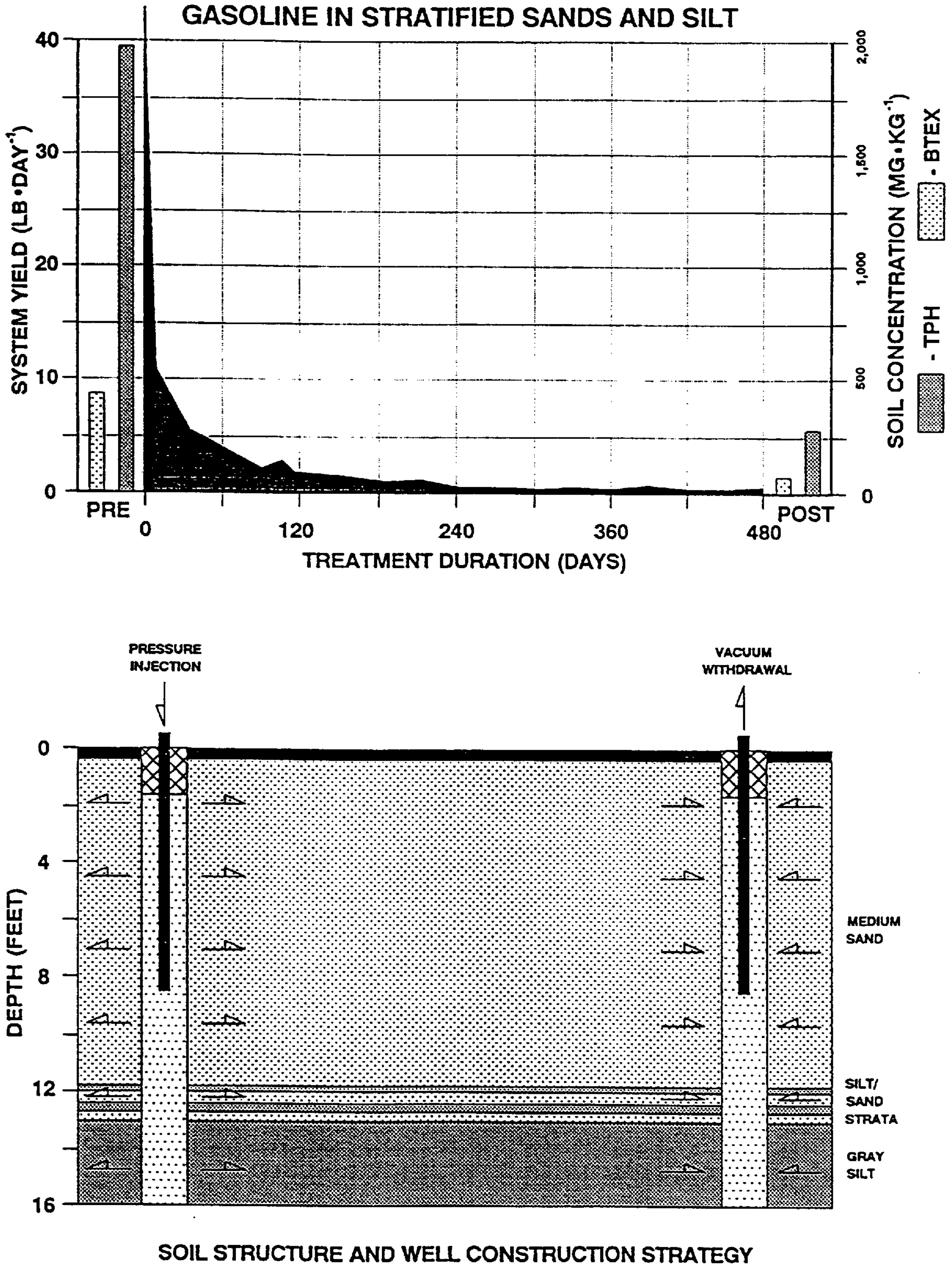
6.2 GASOLINE IN STRATIFIED SAND-SILT

The second of the case history examples is the recovery of gasoline from a stratified sand-silt soil system. The gasoline was released from an underground storage tank system, and contaminated soils under a paved driveway and beneath a warehouse facility. The site volume is approximately 5,000 cubic yards, with groundwater at 14 ft below ground surface (BGS). The contaminant levels are highest in the 10 to 14-foot depth range, which includes the base of a sand unit and a stratified sand-silt sequence. The capillary fringe occurs in the sand-silt sequence. Free-phase hydrocarbons have been observed in the silt-sand sequence and in lower silt stratum. The site will be closed to risk-based soil concentrations for benzene (170 mg/kg), toluene (7 mg/kg), ethylbenzene (10 mg/kg) and xylenes (47 mg/kg). The soil treatment system is operated in conjunction with a groundwater depression and free phase hydrocarbon recovery.

The technical barriers on this site are:

- Contrasting pneumatic conductivity in target soil strata
- Presence of free-phase hydrocarbons
- Fluctuating groundwater surface elevations

The design strategy was based on a minimum air exchange rate of 1 soil pore volume per day. The primary treatment mechanism is evaporative recovery of the hydrocarbon, with the expectation that aqueous-phase diffusion will limit recovery rates in the lower strata. The design layout and results are depicted in Figure C-6, and are as follows:



GASOLINE IN STRATIFIED SANDS AND SILT

SOIL STRUCTURE AND WELL CONSTRUCTION STRATEGY

Figure C-6. Case history summary: Gasoline in stratified sands and silt

System layout - The soil vapor extraction system is based on a pressure injection - vacuum withdrawal concept, with wells networked as depicted in Figure C-5.

Offgas yield results - The system off-gas has followed a log-linear decline, with initial values over 40 pounds per day. After 480 days, the yield is below 1 pound per day. Carbon dioxide measurements are not available for this site.

Soil concentration - Pre-treatment soils averaged above 450 mg/kg total BTEX, with highest concentrations of approximately 3,000 mg/kg. During the 480-day treatment period, average concentrations fell to near 60 mg/kg. Site closure requires an additional 10-fold minimum reduction in benzene concentrations.

The soil zones which now require additional treatment are concentrated in the stratified sand-silt sequence just above the water table. The system operators have modified flow protocols to focus air in the regions of highest residual product, with pulsed operation under consideration to advect contaminants present in the top part of the aquifer into the SVE system.

The treatment system was initially expected to achieve closure objectives within one year. But the silt-sand sequence appears to have developed insufficient air flows in this design. The system performance can be markedly improved by reconstruction of the well points to focus air flow in the lower strata. This will require the addition of vacuum dewatering below each wellhead to control the water table rise.

Initial data collections after re-configuration of air flows indicates that the treatment will be completed following 6 to 9 months of additional recovery.

6.3 DIESEL FUEL IN STRATIFIED, MEDIUM TO FINE-GRAINED SOIL, WITH PHASE-SEPARATED HYDROCARBONS

The third of the case history examples is the recovery of diesel fuel from a stratified sand, gravel and clayey silt site. The diesel fuel was lost in a catastrophic release of 7,000 gallons, which entered the soils below the ground surface. The site volume is approximately 4,000 cubic yards, with groundwater at 15 to 16 ft BGS. Contaminant levels were highest in the lower vadose zone, and substantial free phase hydrocarbon was present at the water table. The initial response action was groundwater depression and free product recovery which yielded approximately

1,000 gallons of product. This was quickly followed by installation of the soil vapor extraction system to initiate soil remediation. The site has been closed to risk-based soil concentrations for benzene (<170 mg/kg), toluene (<7 mg/kg), ethylbenzene (<10 mg/kg), xylenes (<47 mg/kg) and total petroleum hydrocarbons (<642 mg/kg).

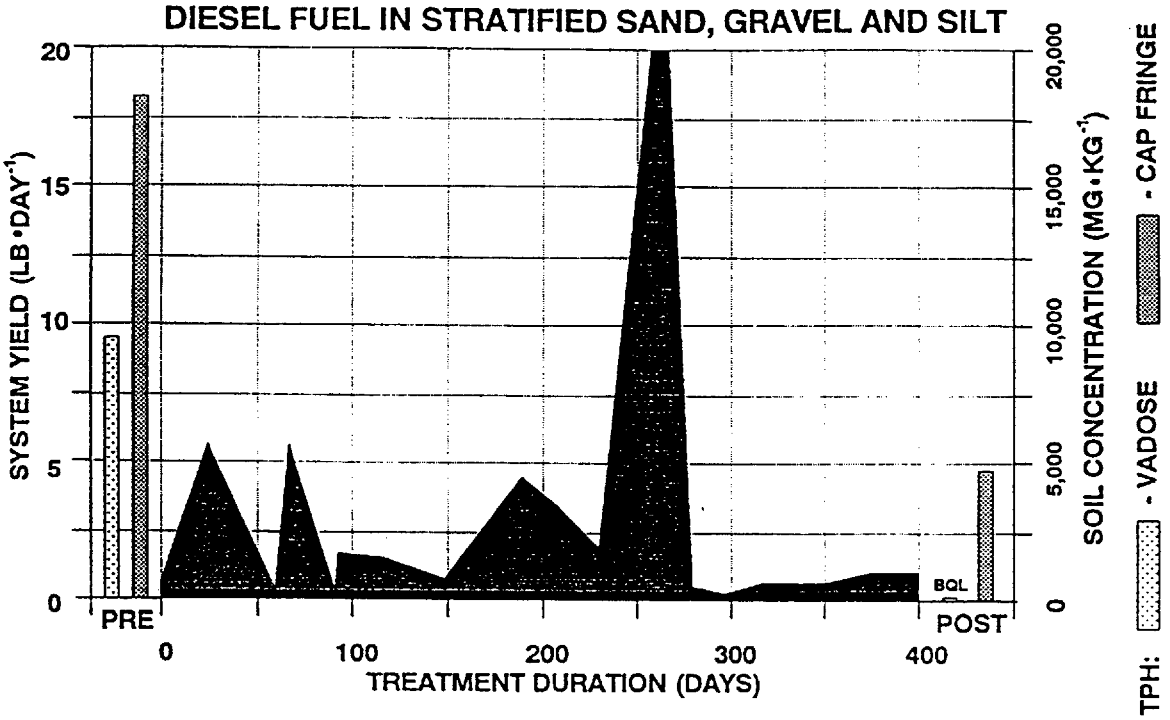
The technical barriers on this site were:

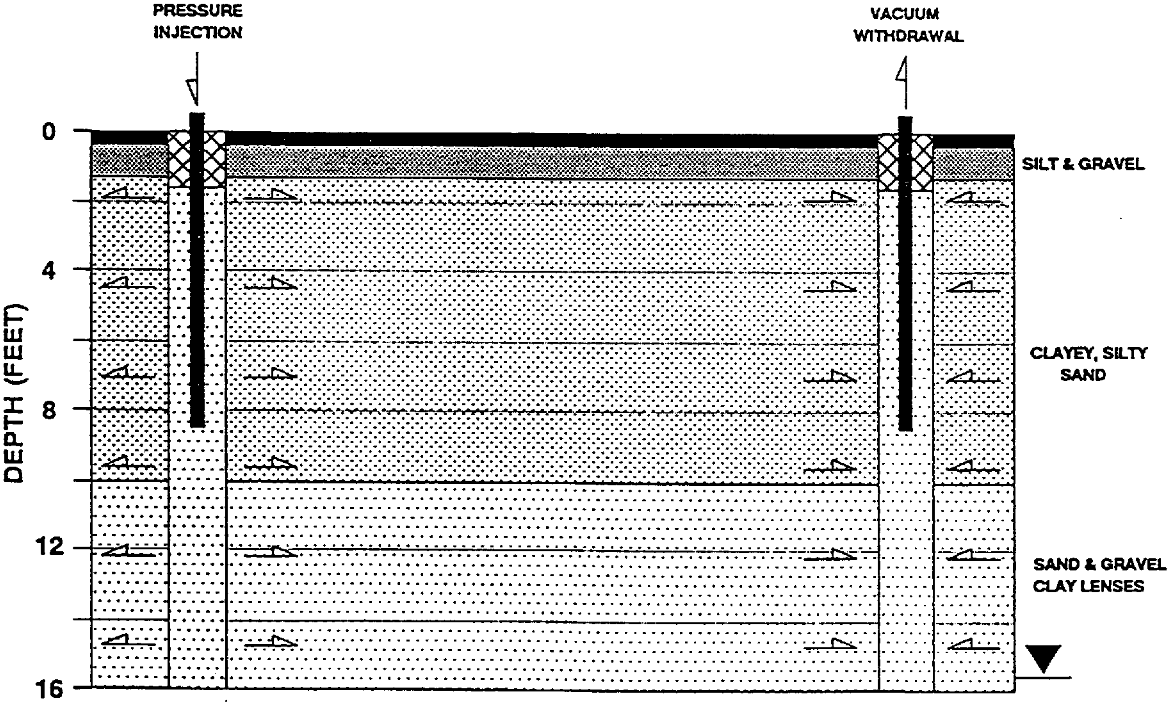
- Contrasting pneumatic conductivities in the target zone soils;
- Presence of free-phase hydrocarbons;
- Low-volatile target compounds.

The design strategy was again based on a minimum air exchange rate of 1 soil pore volume per day. The two primary treatment mechanisms which achieved this recovery were direct evaporation and biological breakdown. The design layout and operating results are summarized in Figure C-7, and are as follows:

> System layout - The soil vapor extraction system is based on a pressure injection - vacuum withdrawal concept, with wells networked as depicted in Figure C-5.
>
> Offgas yield results - contaminant concentrations were erratic in the system offgas, with significant yield spikes during groundwater elevation fluctuations. No carbon dioxide measurements were made during the treatment, but biological breakdown is presumed to have played a major role in the soil cleanup.
>
> Soil concentration - Pre-treatment soils averaged 9,000 mg/kg in the vadose zone, and 17,000 mg/kg in the capillary fringe. After 400 days of treatment, the vadose zone soils were reduced to less than 50 mg/kg average TPH. The capillary fringe and upper aquifer soils were reduced to 4,800 mg/kg TPH, and require continuing treatment.

Despite the contrasting soil permeabilities, this treatment progressed quickly because the lower unit, in contact with groundwater, was the high-permeability zone. This focused the majority of air flow on the most contaminated strata.





SOIL STRUCTURE AND WELL CONSTRUCTION STRATEGY

Figure C-7. Case history summary: Diesel fuel in stratified sand, gravel and silt

6.4 TCE IN STRATIFIED CLAY-SAND SITE

The final case history example is the recovery of TCE from a sharply stratified sand-clay site. An unknown quantity of TCE was lost from an underground storage system, over an undetermined time frame. The site volume is approximately 30,000 cubic yards, with groundwater in the sand stratum at a depth of 10 to 12 ft BGS and the piezometric surface rising 3 ft into the overlying clay. The sand stratum discharges to a wetland, where pre-treatment TCE concentrations reached 45 mg/l in open surface water, 50 feet from the shoreline. Dense, non-aqueous-phase liquid (DNAPL) solvent has been encountered in the sand stratum, and the upper clay is TCE-saturated near the leak points in the underground tank system. The lower clay unit has not been impacted at this time. The applicable closure standard for this site is 20 mg/kg in soils and 1 mg/l in groundwater, but the site is expected to be closed on the basis of a site-specific risk assessment.

The technical barriers at this site are:

- Sharply contrasting pneumatic conductivities between the clay and sand strata;
- Dense, non-aqueous phase material trapped in a thin, confined aquifer.

The design strategy was based on a minimum air exchange capacity of 1 soil pore volume per day, with air wells placed in two strata. A water recovery system was installed in the sand stratum to dewater the source area, and an interceptor trench was installed at the groundwater-surface water interface. The design layout and operating results are summarized in Figure C-8, and are as follows:

> System layout - The soil vapor extraction system was designed to develop air flows in two strata - the low permeability clay and the high permeability sand. The sand was dewatered to allow free air flow in the lower unit.
>
> Offgas yield results - More than 600 gallons of TCE has been captured on activated carbon in 1,300 days of system operation. Several major yield increases were observed, each occurring after additional vacuum wells were constructed in the upper clay stratum.
>
> Soil concentration - No measurements have been made to determine progress toward cleanup. The published standards are quite low, and system production indicates that soil concentrations are still far from closure levels.

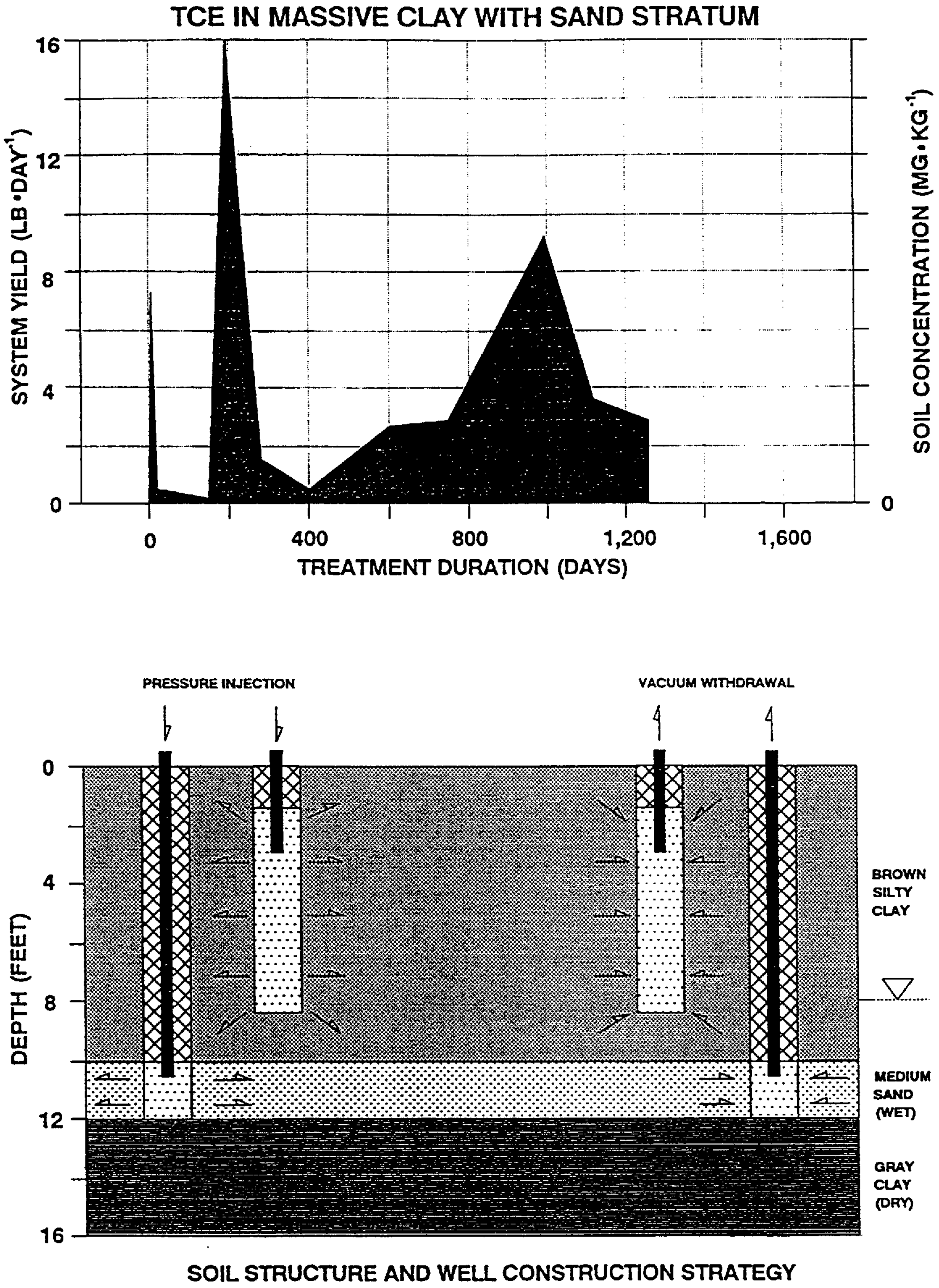


Figure C-8. Case history summary: TCE in stratified clay and sand

This system demonstrates the worst possible site conditions for soil vapor extraction system operation. Despite the high quantitative yield, the site is very unlikely to meet published closure standards. Several specific operational problems have been encountered:

- Air flows - The vacuum and pressure wells in the clay unit are likely short circuiting to the sand stratum very quickly after startup. This will contribute to the sharp but unsustainable yield spikes following each round of new well installations.
- Contaminant distribution - The confined aquifer contains TCE concentrations in the 100 mg/l range, which is diffusing contaminants into the overlying clay, from underneath, over a large soil volume. This material will be exceedingly difficult to recover.
- Site surface seal - The wells were installed through the impermeable site cover, which allows pressure leakage to develop around the wellheads. This problem can be overcome in a below-grade installation.

The long-term strategy for this site is to improve yield through pulsed operation, with a revised project objective of reducing the source loading to levels which reduce concentrations at the groundwater-surface water interface to less than 16 ppb TCE. This objective may be obtained within two years of improved system operation.

Section 7

SUMMARY

7.1 OVERALL STRENGTHS AND WEAKNESSES

The application of soil vapor extraction to recovery of hydrocarbons from soils has grown dramatically since its introduction in the mid-1980's (API, 1984 and 1985). In sandy porous media, the technology has shown many strengths:

- Proven closure capability - Many case studies have shown that soil vapor extraction can be utilized to achieve health-based soil closure standards for volatile and semi-volatile compounds in moderate to high permeability soils.

- Low cost - Soil vapor extraction is often the lowest cost alternative to achieve health-based soil closure standards. It can reach beyond the practical limits of excavation, to great depths and beneath buildings.

- Enhancement ability - The technology can be enhanced through any of several methods which increase its capability for low volatility compounds and low permeability soils.

Several weaknesses in the technology in low permeability settings have also been demonstrated:

- Contrasting Permeabilities: In stratified low permeability settings, the air will follow the path of least resistance through the sand, and cleanup of silty or clayey layers/lenses will be difficult and time-consuming.

- Moisture Conditions: The induced vacuums in SVE systems as well as capillary pressures will mean that the soil above the water table in fine-grained material will be 100% water-saturated over a significant thickness. Unless the SVE system can remove this water, there is no path for the air to flow, and cleanup of soils in this saturated zone will be diffusion-limited.

- Steep Pressure Drops: The wellhead vacuum in low permeability soils will quickly dissipate away from the borehole. Designing an optimized system of vacuum and well spacing is difficult.

7.2 BREAKTHROUGHS REQUIRED FOR ROUTINE APPLICATION IN LOW PERMEABILITY SOILS

There has been very little experience in the application of soil vapor extraction to low-permeability soils. The case studies show that, as expected, it is difficult to achieve published soil closure standards in low permeability soils. Further, no consistent pattern has emerged which explains the successes and failures. Several "breakthroughs" are required to consider soil vapor extraction suitable for routine application to low-permeability soils.

- Basic feasibility - The industry needs a well-documented site closure in each of the low permeability soil scenarios. The level of documentation required is not likely to be developed in a typical commercial application.

- Characterization of fate and transport mechanisms - There are several fate and transport mechanisms which control the rate and extent of contaminant recovery in low permeability soils. These include evaporation, gaseous-phase diffusion, aqueous-phase diffusion, desorption, and biodegradation. The effects of these mechanisms must be determined in a well-monitored set of experiments.

- Cleanup levels - Reasonable risk-based closure objectives must be established for low permeability soils. It is unlikely that soil vapor extraction can achieve the low levels demonstrated for high permeability soils, at any cost.

Section 8

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BIOVENTING IN LOW PERMEABILITY SOILS

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ABSTRACT

This paper describes an in-situ technology that may offer the potential to, at least partially, remediate LNAPL's in silty or clayey soils. The bioventing process is described and its capability to remove product in two types of low permeability settings evaluated. The paper also includes a summary of the commercial availability and typical costs of the technology as well as case histories where it has been applied in low permeability media.

Section 1

DESCRIPTION OF THE TECHNOLOGY

Bioventing is a process designed to provide indigenous soil microorganisms with enough oxygen O_2 to aerobically degrade target contaminants by introducing a supply of air or O_2 to O_2-deficient soils. The technology is applicable to any contaminants found in O_2-deficient soils that are more biodegradable aerobically than anaerobically. Bioventing may be accomplished through the extraction of soil gas, injection of air, or a combination of both. Bioventing is a technology closely allied to soil vapor extraction (SVE), which is a process designed to promote volatilization. Generally, when applied to petroleum hydrocarbons, SVE stimulates some biodegradation and bioventing causes some volatilization. The key differences are air flow rates and vent well configuration. Soil vapor extraction typically utilizes high air flow rates to extract soil gas from the treatment zone; bioventing may inject or extract air at lower flow rates, resulting in soil aeration but minimizing volatilization. Bioventing may be applied in situ in either the vadose zone or the saturated zone (by means of air sparging) or applied ex-situ in soil piles. This paper will focus on in-situ vadose zone applications.

In general air injection is felt to be the preferable means of supplying air for bioventing. Air injection creates an "expanded bioreactor" in situ to maximize biodegradation. When air is injected into contaminated soils, the gas movement pushes volatiles into the surrounding cleaner soils. The volatiles biodegrade in these cleaner soils, thus expanding the volume of soil in which in-situ bioremediation takes place. On the other hand when gas is extracted, the volume of soil in which in-situ bioremediation takes place is limited to the initially contaminated soil. The net result is that, all else being equal, more contaminant is biodegraded when air is injected into a well than when air is extracted from a well.

From a practical point of view, air injection is easier and less costly to engineer. The chief concern related to air injection is safety. When air is injected, care must be taken to prevent migration into buildings or other subsurface structures. The U.S. Air Force Center for Environmental Excellence (AFCEE) is sponsoring a "Bioventing Field Initiative" in which approximately 100 pilot and full-scale bioventing systems have been installed to date. Approximately 90% of these systems utilize air injection only (Miller et al., 1993).

A given vent well at a specific flow rate affects a specific volume of soil, defined as the "radius of influence." The phrase "radius of influence" used in this sense is the radius to which a vent well can provide adequate O_2 to meet the O_2 demand. It appears that aerobic biodegradation of hydrocarbons is not oxygen limited at O_2 concentrations higher than 3 to 5% (Miller, 1990). Thus, a practical definition of radius of influence is the radius to which a vent well can supply 5% oxygen.

Bioventing is potentially applicable to any contaminant that is more readily biodegraded aerobically than anaerobically, such as most petroleum hydrocarbons (Atlas, 1981). To date, most applications have been to remediate petroleum hydrocarbon contamination (Hoeppel et al., 1991); however, specific application to polycyclic aromatic hydrocarbons (PAHs) (Lund et al., 1991; Hinchee and Ong, 1992) and to an acetone, toluene, and naphthalene mixture (Hinchee and Ong, 1992) have been reported.

In most bioventing applications, the key is biodegradability vs. volatility. If the rate of volatilization significantly exceeds the rate of biodegradation, removal takes place more readily through volatilization. Figure D-1 illustrates the general relationship between a compound's physiochemical properties and its potential for bioventing.

In general, low vapor pressure compounds (i.e., below ~ 1 mm Hg) cannot be successfully removed by volatilization. Biodegradable contaminants that exhibit these low vapor pressures are potential candidates for bioventing. Higher vapor pressure compounds (i.e., above ~ 760 mm Hg) are gases at ambient temperatures. These compounds volatilize too rapidly to be easily biodegraded during venting, the compounds being purged from the soil matrix before degradation can occur. Compounds with vapor pressures between 1 and 760 mm Hg may be amenable to either volatilization or biodegradation in a bioventing system. Within this intermediate range lie many of the petroleum hydrocarbon compounds of greatest regulatory interest, such as benzene, toluene, and the xylenes. Figure D-1 shows that various petroleum fuels are more or less amenable to bioventing. For example, some compounds found in gasoline are too volatile to easily biodegrade using an SVE process, but most of the constituents of diesel fuel are sufficiently nonvolatile to preclude volatilization. JP-4 jet fuel falls in an intermediate range.

In order for bioventing to be successfully applied, it is necessary to aerate soils. The ability to aerate soils is very much a function of soil gas permeability. Soil gas permeability is a function of soil grain size and moisture content. For a given soil, soil gas permeability is highest when the soil is dry and decreases with increasing soil moisture. This phenomenon is illustrated in Figure D-2.

Even in a sand, if moisture content is high, adequate gas flow may not be possible. The site must be sufficiently permeable to allow an approximate minimum of 1 soil gas exchange per 1 to 20 days (Hinchee et al., 1993). Typically, permeability in excess of 1 darcy is adequate. When the permeability falls below ~ 0.1 darcy, gas flow

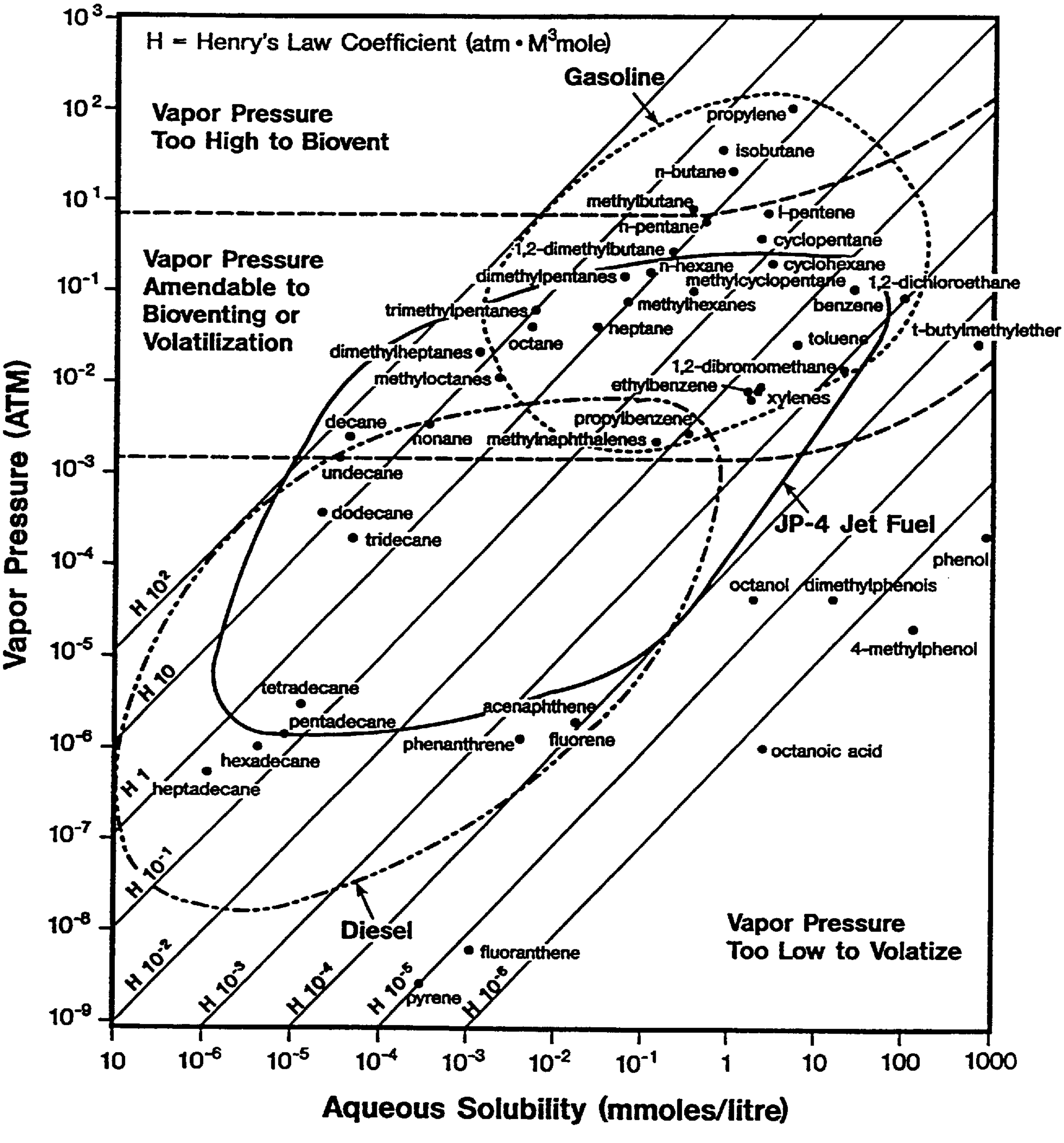

Figure D-1. Impact of Physiochemical Properties on Potential for Bioventing

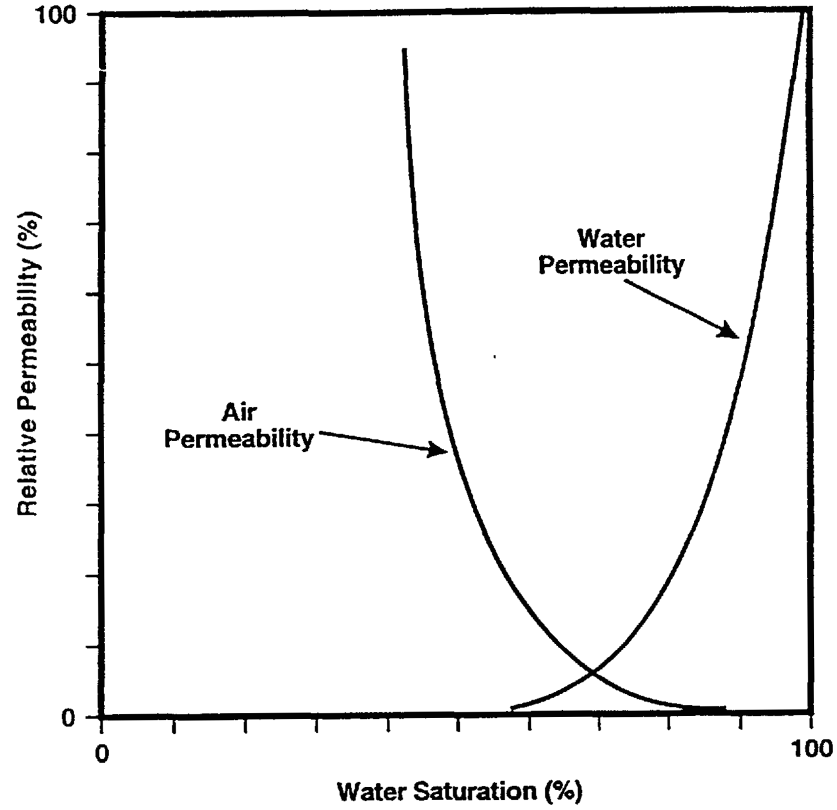

Figure D-2. Air and Water Permeability as a Function of Water Content

typically occurs either through secondary porosity (such as fractures) or through any more-permeable strata that may be present (such as thin sand lenses).

The feasibility of bioventing in these low-permeability soils is a function of the distribution of flow paths, and the diffusion of air to and from the flow paths, within the contaminated area. In a soil with reasonably good diffusion, a maximum separation of 2 to 4 feet between the flow path and the contaminant may still permit bioventing treatment, based on diffusion calculations and acceptable time frames for remediation.

Gas permeability is a very site-specific characteristic. Bioventing has been successful in some low-permeability soils, including a silty clay site at Fallon Naval Air Station (NAS) in Nevada (Battelle unpublished data); a silty site on Eielson Air Force Base (AFB) in Alaska (Leeson et al., 1992); and an alluvial site, which is predominately clay, in California (D. Downey, Engineering-Science, Inc., personal communication of unpublished data).

At a clay site on Tinker AFB in Oklahoma, bioventing has met with less success. The primary difference between the Tinker AFB site and the others appears to be geological. The soils at Tinker consist primarily of a massive wet clay, apparently devoid of sand layers, fractures, or other secondary porosity.

In addition to gas permeability, hydraulic permeability may be important if it is necessary to add nutrients or moisture to soil or if it is necessary to dewater a site.

Section 2
GENERAL TECHNOLOGY CONSIDERATIONS

2.1 EFFECT OF HIGH SOIL WATER CONTENT ON CONTAMINANT REMOVAL

Microorganisms live in soil water and, in general, increasing soil moisture levels increases microbial habitat and the potential for biodegradation. Hinchee and Arthur (1991) found that soil moisture was an important variable in laboratory soil columns that simulated bioventing.

Counteracting this beneficial effect of soil moisture is the reduced air permeability resulting from increased moisture. High soil moisture has several negative effects on bioventing. Lower gas permeability requires greater energy input to stimulate gas flow. Increased channeling of flow through more permeable zones or the secondary porosity is another typical result of high soil moisture. Finer-grained soils tend to hold more moisture at the same tension, which results in an exaggeration of permeability differentials between strata. This, in turn, causes poorer air distribution and lengthens the distances through which O_2 must diffuse, slowing the biodegradation process. The third and perhaps most significant impact of increasing soil moisture is upon the diffusion process itself. As soils become wetter, tortuosity (the path a molecule must follow when diffusion becomes dominant) increases, slowing the rate of diffusion. If soil moisture increases to a level where the air-filled voids are no longer interconnected, diffusion must take place in the aqueous phase. Diffusion in the aqueous phase is approximately 1,000 to 10,000 times slower than in the gaseous phase. The result is that, in a strata where O_2 delivery is dependent on aqueous-phase diffusion, the depth of soil that can be treated at reasonable cost using diffusion drops from a few feet to a few inches or less.

To date, limited field experience involving the application of bioventing to low permeability sites exists and unfortunately, none of the good demonstrations completed to date have been in low permeability soils. The limited information that is available however can lead to some general observations. At a silty bioventing site at Eielson AFB near Fairbanks, Alaska, Leeson et al. (1992) has been attempting to evaluate soil warming using a number of technologies. One of these is warm water application. This has proven a good means of warming the soil and, where oxygen is delivered, biodegradation rates have increased. It has been difficult, however, to maintain adequate oxygenation throughout the site. The treatment plots are 40 feet by 40 feet, depth to groundwater is ~ 8 feet, and water was applied continuously at a rate of ~ 1 gpm. Figure D-3 illustrates average O_2 content in several of the treatment plots. As can be seen, the active plot (the one to which water was added) had consistently lower oxygen levels than the other plots.

During startup of a bioventing system at a sandy site at Tyndall AFB, Florida (Miller et al., 1991), surface water addition was initially varied to optimize the biodegradation rate. Although this was done only rudimentary and was not well documented, it was observed (Battelle unpublished data) that, above a constant application rate of 100 inches/yr, oxygen concentrations declined rapidly in some portions of the plots. At this site, depth to groundwater was ~ 6 feet.

These examples point out the problems encountered with high soil moisture. Unfortunately, there are no known good demonstrations have been completed on low permeability, wet sites. It is likely, however, that low permeability, wet conditions will result in decreased contaminant removal levels, particularly in thicker low permeability strata, such as clay layers supporting perched water.

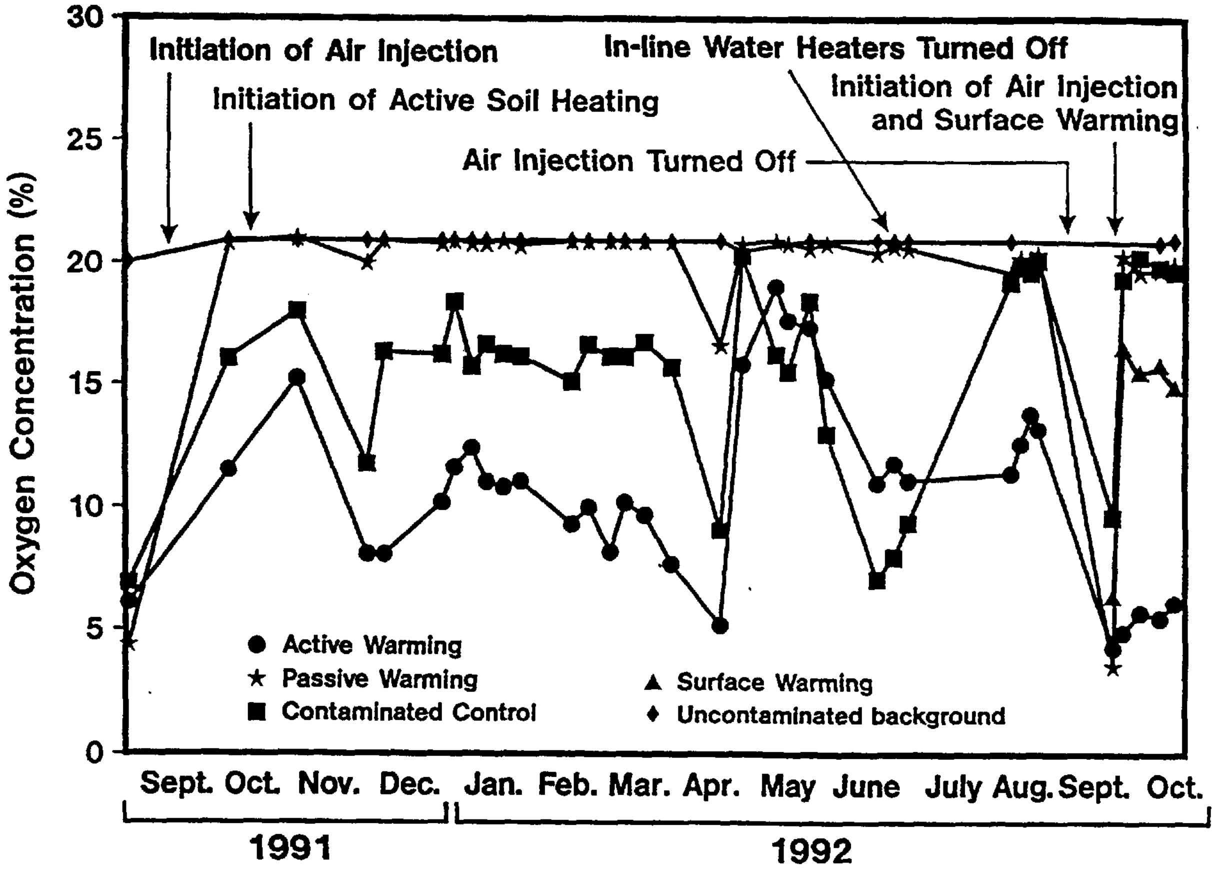

Figure D-3. Average O_2 Concentration in Bioventing Plots at Eielson AFB, Alaska (Based on soil gas collected from 30 to 50 monitoring points per event)

2.2 HOW EFFECTIVE IS THIS TECHNOLOGY AT ACCESSING CONTAMINATION UNDER BUILDINGS AND PAVEMENT?

Bioventing has been successfully applied beneath structures. The degree of success is dependent upon the radius of influence of the vent well. Under stratified conditions, where gas-permeable strata are present, radii of influence of 100+ feet are possible. The technology is known to have been successfully applied under buildings, roads, and runways. One problem with working under buildings is the potential for migration of contaminated soil gas into the building when operating in an air injection mode.

2.3 WHAT IS THE MAXIMUM DEPTH TO WHICH THIS TECHNOLOGY IS APPROPRIATE? IN WHAT SOIL TYPES?

There is no inherent depth limit, so long as continuous air flow channels are present. Bioventing has been applied to depths of 200 feet and there are known deeper applications.

2.4 HOW EFFECTIVELY CAN THIS TECHNOLOGY REMEDIATE PETROLEUM PRODUCTS (OTHER THAN GASOLINE)?

The process is generally more applicable to petroleum products that are heavier than gasoline. Bioventing typically requires more time than soil vapor extraction to remediate a gasoline site, and it is more difficult to design a bioventing system that does not require offgas treatment. With heavier petroleum products, SVE becomes less feasible and offgas emissions become less of a problem.

Bioventing is known to have been successfully applied to gasoline, avgas, JP-4, JP-5, Jet A, diesel, and crude oil contamination (Miller et al., 1993). In general, the heavier the fuel, the slower the biodegradation rate and the lower the cost of application.

2.5 WHAT LIMITATIONS TO NUTRIENT DISTRIBUTION ARE POSED, ESPECIALLY IN A STRATIFIED SOIL WHERE A CONTAMINATED VADOSE ZONE SAND LENS UNDERLIES A SURFACE CLAY OR SILTY CLAY LAYER?

Nutrients probably are not a limiting factor for bioventing and, for most sites, the cost of nutrient addition is not worth the marginal increase observed in biodegradation rates. At the Hill AFB bioventing demonstration site, bench-scale studies conducted by Hinchee and Arthur (1991) indicated that nutrient addition should increase biodegradation rates. However, field application of nutrients to the site did not result in increased rates (Dupont et al., 1991).

Nutrient addition also was studied at the Tyndall AFB demonstration site (Miller, 1990; and Miller et al., 1991). Two side-by-side plots received identical treatment, except that one (V2) received both moisture and nutrients from the outset of the study, whereas the other plot (V1) received neither for 8 weeks, then moisture only for 14 weeks, followed by both moisture and nutrients for 7 weeks. No significant effect from either the moisture or nutrient additions was observed. These findings support field observations made at Hill AFB, that the addition of nutrients does not stimulate biodegradation. Based on acetylene reduction studies, Miller (1990) speculates that adequate nitrogen was present due to nitrogen fixation. Both the Hill and Tyndall AFB sites were contaminated for several years before the bioventing studies, and both sites were anaerobic. It is possible that nitrogen fixation, which is maximized under these conditions, provided the required nutrients. In any case, these findings show that nutrient addition is not always required.

Trying to induce nutrient infiltration through a clay or silty clay into an underlying sand is difficult, if not impossible. There are no known sites where this has been successfully accomplished and documented. Permeability considerations aside, solubility limitations and ion exchange would most likely make transport of phosphorus and ammonia infeasible (Aggarwal et al., 1991).

It is possible that nutrients could be introduced in a dissolved form and transported via water flow in secondary porosity. If the fluid velocity is high, the problem of ion exchange may be overcome as a result of lack of direct contact between nutrient ions and clay surfaces. At a highly fractured site where significant water flow can be introduced in these fractures, this may be feasible although it is not known to have been demonstrated.

2.6 IN WHAT WAYS CAN SPECIFIC LIMITATIONS OF OXYGEN, AVAILABLE NITROGEN, ETC., BE OVERCOME? ARE GAS PHASE NUTRIENTS A VIABLE ALTERNATIVE TO AQUEOUS PHASE SOLUTIONS WITH REGARD TO DISTRIBUTION AND EFFICIENCY?

In low permeability soils, oxygen limitations may be overcome in part by increasing the density of air injection vent wells or the number of withdrawal points. Air injection is felt to be a better means of oxygen supply in low permeability soils. By using numerous narrowly-screened points for air injection rather than a single broadly-screened well, better oxygen distribution can be achieved.

In concept, gas phase nutrients appear to be an attractive alternative to waterborne nutrients for bioventing. Potential advantages include the ability to move nutrients horizontally, a possible reduction of channeling through more permeable strata, greater diffusivity, and possibly fewer permeability problems due to high soil moisture. The difficulty is in identifying candidate gases. Some bench-scale work has been performed in Battelle's laboratories with ammonia gas and colloidal dusts. To date, a high degree of success in achieving migration through soils has not been achieved. Ammonia tends to dissolve in soil water and form ammonium ions that do not move readily through the soil. The colloidal dusts probably are removed by impaction and do not appear to migrate adequate distances.

Section 3

REMEDIAL CAPABILITY IN NATURALLY-FRACTURED MASSIVE TIGHT SOILS

To demonstrate remedial capability in naturally fractured massive tight soils, consider the following scenario:

- The clay is extensive and is 30 to 50 m thick
- The upper 2 m of the clay is highly weathered due to desiccation
- The fractures are spaced 1 to 100 cm apart, primarily vertically
- The fractures have 10 to 40 mm apertures
- The clay blocks between fractures are saturated (i.e., there are no continuous air pathways)
- The depth to the water table is 1 to 3 m
- The effective air-filled porosity is <1%.

3.1 APPLICATION DESCRIPTION

A possible design for a site as in this scenario would be close placement (perhaps, on 4 ft centers) of small, narrowly screened air injection points. Construction might consist of 6-inch x 1/2-inch diameter screens placed at depths of 3.5, 2.5, and 1.5 m in each hole. Each screen would be placed in ~1/3 m of gravel and separated from the overlying screen by ~2/3 m of wetted bentonite. The 1.5 m injection point would be grouted from the gravel to the surface. The screens would be connected to 1/4-inch tubing, each brought separately to the surface. Air injection might be at pressures of 5 psig at 3.5 m, 4 psig at 2.5 m, and 2.5 psig at 1.5 m. (Lower pressures are used in the shallower wells to prevent fracturing of the overlying bentonite seal.) With this scheme it is possible that aeration could be achieved; however, pilot testing would be required to verify this on the site.

3.2 REMOVAL EFFECTIVENESS

3.2.1 Free Product in Continuous Fractures

In fractures into which air flow is induced, contaminant removal by bioventing could be achieved. However, no known well-documented demonstration exists for a site of this kind upon which to quantify these comments. Two mechanisms can operate to remove these contaminants: volatilization and biodegradation. Volatile contaminants are removed in the gas passing through the fracture. Free product probably does not biodegrade in pure phase; it must become dissolved in the aqueous phase to be bioavailable. Water and free product coexist in contaminated soils. Typically, the water with its greater surface tension will wet the soil particles, and free product will occupy the larger pore spaces. The free product biodegrades by dissolving into the aqueous phase to become bioavailable, and in the presence of oxygen, by being metabolized.

3.2.2 Free Product in Discontinuous Fractures

If no air flow is induced into the channel, removal would be dependent upon aqueous-phase diffusion — a very slow process.

3.2.3 Aqueous-Phase Product Diffused into Matrix Blocks

Oxygen molecules are smaller and more diffusive than most hydrocarbon molecules. If air flow can be induced into the fracture from which the hydrocarbon diffused, treatment in a time frame similar to the age of the spill may be expected. (Note that this does not contradict the very much longer time frame for remediation vs age of spill derived in the McWhorter paper (McWhorter, 1995) in this series of focus papers. The McWhorter paper assumed remediation was due solely to reverse aqueous phase diffusion from the matrix to the fractures, and did not allow for biodegradation due to oxygen diffusion into the matrix.) If air flow is not induced into the "parent fracture," treatment would probably be much slower.

3.2.4 Product Adsorbed onto Organic Soil Material

As stated previously, treatability would depend upon proximity to air flow channels. For contamination more than a few inches from fractures with air-flow, removal would be exceedingly slow.

3.2.5 Residual Product Trapped within Pore Throats

As with product adsorbed onto organic matter or diffused into matrix blocks, the amenability to biodegradation of product in pore throats will be limited by the proximity of air flow channels and diffusion rates.

3.2.6 Free Product Floating on the Water Table

In general, any vapor extraction-based technology has limited application in the capillary fringe. Gas flow is difficult to induce in this situation due to high moisture content, and treatment will become diffusion-limited. Dual phase extraction, especially the application of *bioslurping* (see Figure D-4), does however appear to have promise for free phase product removal (Kittel et al., 1994).

3.3 COMPLEMENTARY TECHNOLOGIES

As bioventing is an emerging technology, particularly with application to low-permeability soils, very little work of this kind has been done; therefore, the response to the question of complementary technologies must be speculative. The following are technologies which are believed to have the potential to be complementary:

- Pneumatic Fracturing - Battelle is currently working with pneumatic fracturing technology at a site similar to the one described here at Tinker AFB.
- Electro-osmotic Dewatering - This has the potential to reduce the moisture content of these soils and allow improved air flow (Casagrande, 1957 and 1962).
- Large-Diameter Auguring - This approach has been used on low permeability soils at Kelly AFB, Texas. However, this data is not available at this time.

Section 4

REMEDIAL CAPABILITY IN CONTINUOUSLY STRATIFIED LOW PERMEABILITY SOILS

This section presents an assessment as to the potential effectiveness of bioventing at a hypothetical site. Site conditions are as follows:

- The soil is stratified with layers ranging from medium sand to silt
- The soil is relatively dry, with continuous air pathways in both the silt and the sand
- The sand behaves like porous media with regard to fluid flow
- There are some preferential pathways in both the silt and the sand
- The water table is located 3 to 4 m below the ground surface
- The effective air-filled porosity is 0.2; the total porosity is 0.3.

4.1 APPLICATION DESCRIPTION

This site is amenable to a conventional treatment design. With vent wells screened from approximately 1 to 4 m, air could be injected, withdrawn, or both. It may be necessary to place some narrowly screened vent wells in the silt layers to allow selective air injection into these strata. The radius of influence in the sand would probably exceed 30 feet, and vents wells could probably be installed on 30-foot centers.

4.2 REMOVAL EFFECTIVENESS

To date, a well-documented bioventing demonstration has not been published for a site of this kind.

4.2.1 Free Product Trapped on Perched, Low-Permeability Lenses

The high soil moisture and resulting low gas permeability will result in diffusion-limited, very slow removal rates at a site of this type.

4.2.2 Aqueous-Phase Product Diffused into Continuous Low-Permeability Layers

Assuming this contamination diffused from a location into which gas flow can be induced, removal in a time frame similar to the age of the spill is possible (see Section 3.2.3).

4.2.3 Adsorbed Product on Both the Permeable and Low-Permeability Layers

In the permeable strata, high levels of oxygenation can be achieved and good removal is expected. In less permeable strata, removal becomes diffusion-limited. However, if the diffusion path length is less than 2 to 4 feet and the soil gas is continuous, removal in a reasonable time frame (a few years) can be expected. If the diffusion path lengths are greater, or aqueous-phase diffusion controls, removal will be much slower.

4.2.4 Residual Product in Both the Permeable and Low Permeability Layers

Residual product remediation would be largely diffusion-limited. In the more permeable layers it would be likely to occur more rapidly than in the low permeability layers. In the dryer, less permeable layers, oxygen diffusion from the permeable layers can occur in the gas phase. Where the layer is less than a few (<2-4) feet thick, removal in a reasonable time frame (a few years) can be expected. If the low permeability layers are thicker, or are too wet for gas phase diffusion to occur, removal will be much slower.

4.2.5 Free Product on the Water Table Adjacent to High-Permeability Layer

As stated previously, contaminant removal in the capillary zone will most likely be limited by aqueous phase diffusion, and will be very slow.

4.2.6 Contaminant Recovery from Low Permeability, Isolated Lenses Instead of from Continuous Layers

As discussed above, contaminant recovery will depend on the low permeability lens thickness and the degree of saturation. Thin (2 to 4 ft thick), dry layers will remediate in reasonable time frames; thicker, wetter lenses will remediate more slowly.

4.3 COMPLEMENTARY TECHNOLOGIES

The following are technologies which have been found, or are believed to be, complementary:

- Bioslurping - This is the use of a suction dewatering system to recover free product, control water table elevation, and aerate soils simultaneously. Battelle is currently conducting a demonstration of this technology on a site at Fallon NAS, Nevada (see Figure D-4).

- Soil Warming - This can increase biodegradation rates.

- Dewatering - This can increase the size of the vadose zone as well as air flow through the contaminated soils.

Section 5

COST AND COMMERCIAL AVAILABILITY

Consider a hypothetical site 100 ft x 100 ft x 15 ft in stratified fine-grained media, contaminated with gasoline diffused into the low-permeability matrix blocks at a concentration of 1000 mg/kg:

a. What is the cost (capital and operating) to remediate down to the 200 mg/kg level?
b. What is the estimated time to remediate?
c. To what extent is this technology commercially available?

5.1 DESIGN ASSUMPTIONS

- 25 vent wells screened from 5 to 15 feet
- 5 three-level monitoring points
- Air injection of 20 cfm with 4-hp blowers
- Aboveground plumbing
- Monitoring consists of
  - 25 pre-treatment soil samples
  - Initial flux monitoring to verify no surface emissions problems
  - Quality in-situ respiration tests for first year, annually thereafter
  - 25 post-treatment soil samples
- Power is readily available
- Permitting costs are not included.

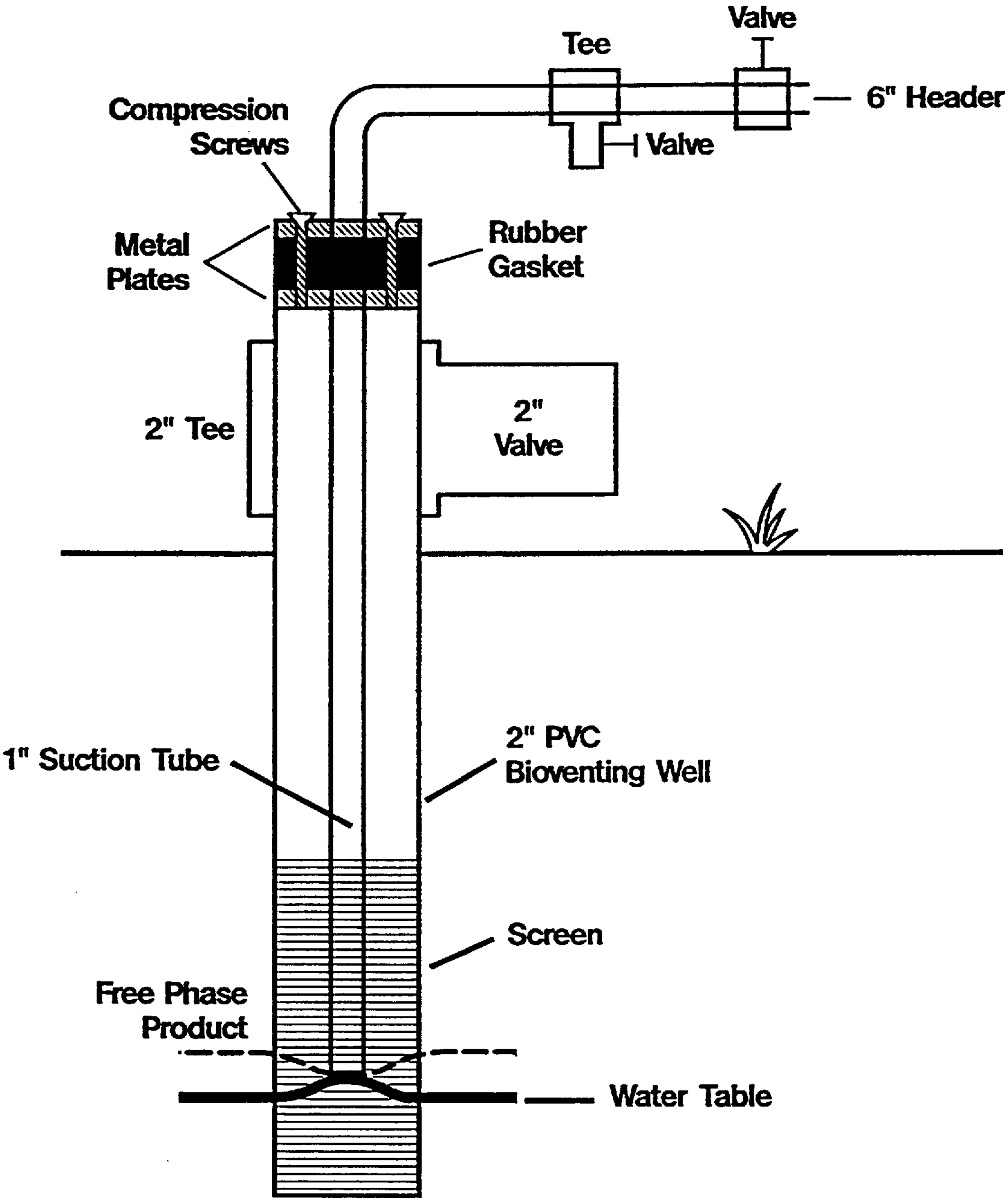

Figure D-4. Typical Bioslurping Well Design

5.2 COST ESTIMATE

Pilot Study	
Soil gas permeability test	$10,000
In-situ respiration test	$10,000
Installation	
Design	$10,000
Vent Well Installation (25 x $1000)	$25,000
Monitoring Point Installation (5 x $1000)	$ 5,000
Blower Acquisition/Installation	$ 7,000
Monitoring (2 years)	
Pretreatment Soil Sampling	$ 5,000
Flux Monitoring	$ 8,000
In Situ Respiration Testing (5 x $5000)(a)	$25,000
Post-treatment Soil Sampling(b)	$10,000
Power	$ 2,000
Total Estimated Cost:	$117,000

(a) The $5,000 cost for quarterly in situ respiration testing includes mobilization and reporting.

(b) The cost of final soil sampling is higher than the cost of initial sampling as the cost of the initial drilling is included in vent well and monitoring point installation.

5.3 TIME TO REMEDIATE

A reasonable average biodegradation rate would be 2 to 5 mg/kg per day. Using this figure, 160 to 400 days would be required to reduce 1,000 mg/kg to 200 mg/kg. A reasonable estimate of the total time to achieve cleanup is 2 years.

5.4 TO WHAT EXTENT IS THIS TECHNOLOGY COMMERCIALLY AVAILABLE?

Bioventing is commercially available. It is, however, a new and emerging technology that is not yet widely understood or accepted, particularly with regard to low permeability site applications.

Section 6
CASE HISTORIES

To date, no well documented case histories have been published for low permeability bioventing sites. Several are under way, however, and will be published within the next couple of years. In general, experience has found that the technology appears to be applicable to stratified sites with more permeable lenses and strata where gaseous diffusion can aerate less permeable strata. The only complete failure known to exist is in the massive clay sites at Tinker AFB. Battelle is currently investigating ways of improving air distribution at those sites by pneumatic fracturing and by using numerous tightly spaced, narrowly screened injection points.

Section 7
SUMMARY

7.1 STRENGTHS OF THE TECHNOLOGY

- Low cost relative to other technologies examined in this volume
- Widely applicable, robust technology
- Relatively low technology

7.2 WEAKNESSES OF THE TECHNOLOGY

- Applicability to low-permeability soils less well known
- Relatively slow (2 to 5 years at most sites)
- Limited applicability to saturated soils

7.3 ARE THERE ANY SPECIFIC BREAKTHROUGHS THAT MUST BE ACHIEVED BEFORE THIS TECHNOLOGY CAN BE ROUTINELY APPLIED AND RELIED UPON FOR SUCCESS?

No one obstacle is preventing widespread application of the technology. It is believed that at this time it can be routinely applied to sites with soil gas permeabilities greater than 1.0 darcy. More experience on a variety of sites and well documented demonstrations are needed.

Applicability to low permeability sites is less well understood and documented. More applied field research is required.

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HYDRAULIC AND IMPULSE FRACTURING FOR LOW PERMEABILITY SOILS

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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 to increase the effective permeability and change paths of fluid flow in soil. The discussion is limited to two methods of creating fractures by injecting liquid; fracturing methods involving gas injection or detonation of explosives are omitted. The most well-known method, hydraulic fracturing, involves injecting fluid at modest rates and pressures during several tens of minutes. A new method, termed *impulse fracturing,* involves injecting fluid at fast rates and great pressures during several tenths of a second. The paper also includes a summary of the commercial availability and typical costs of the technology as well as case histories where it has been applied in low permeability media.

Section 1

DESCRIPTION OF THE TECHNOLOGY

1.1 HYDRAULIC FRACTURING

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. A solid compound has been developed at the University of Cincinnati (Davis-Hoover and others, 1991), which slowly releases oxygen. This can be injected into hydraulic fractures along with slowly dissolving nutrients to stimulate in-situ aerobic degradation of organic compounds in soils. A new project has just been initiated at the University to investigate the feasibility of filling hydraulic fractures with electrically conductive material, particularly graphite, to enhance electroosmosis and perhaps electrical heating techniques. In addition, it is feasible to fill hydraulic fractures with metal catalysts, such as iron particles, which Gillum and Burris (1992) have proposed as a method of degrading a wide range of halogenated organic compounds.

During the past several years, more than 100 hydraulic fractures have been created by the University of Cincinnati in silty clay at seven locations in the midwestern United States. 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.

1.1.1 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.

In fine-grained soil, hydraulic fractures are created 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. E-1). Stacks of gently dipping hydraulic fractures have been created with vertical spacing of 0.5 to 1 ft using the driven casing method. Vertical spacings of less than 0.5 ft 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 (Fig. E-2), at the beginning of injection during a test at 5 ft depth, the pressure increased abruptly to 64 psi, but then decreased sharply when the fracture began to propagate. Injection pressure was between 15 and 20 psi during propagation. Slightly greater pressures are required to create fractures at greater depth.

1.1.2 Fracture Form

Details vary considerably, but hydraulic fracturing generally produces a single parting of the soil (multiple fractures require repeated operations), and there are two typical forms of hydraulic fractures created in soil. 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. Using techniques described above,

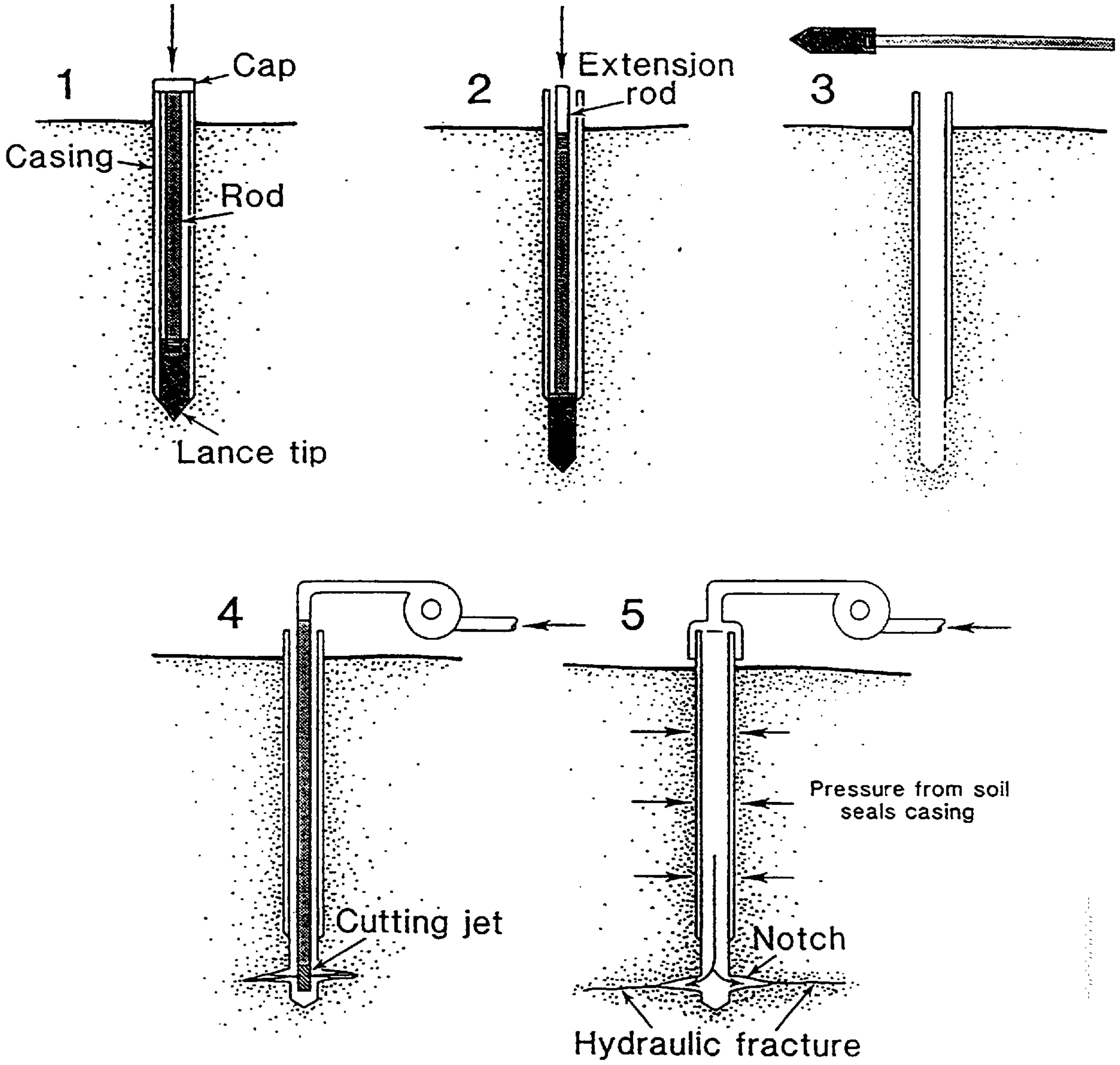

Figure E-1. Method of creating hydraulic fractures in soil. 1. Drive casing and inner rod to depth. 2. Advance rod. 3. Remove rod. 4. Cut notch with water jet. 5. Inject fluid to create fracture. Rod is inserted, casing driven to greater depth and another fracture is created.

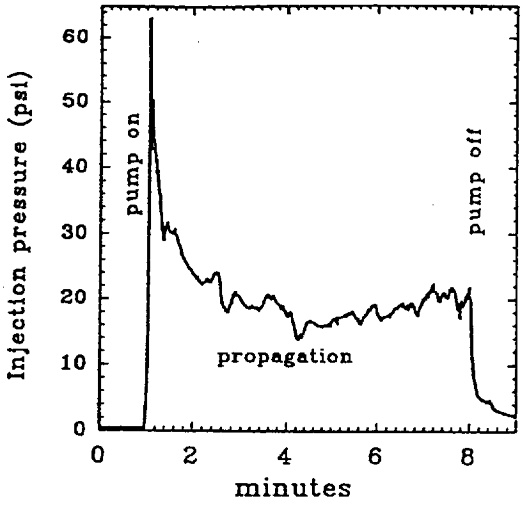

Figure E-2. Injection pressure as a function of time during hydraulic fracturing.

it is felt that vertical fractures in soil are of limited size and probably of limited value to remediation when used with vertical wells.

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 nearly flat-lying in the vicinity of the borehole and the dip increases to approximately 20° at some distance away (Fig. E-3), whereas in other cases the fractures appear to maintain a roughly uniform dip from the borehole to the termination.

In nearly every case, the fracture has 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 typically downslope. Vehicles have been used to load the

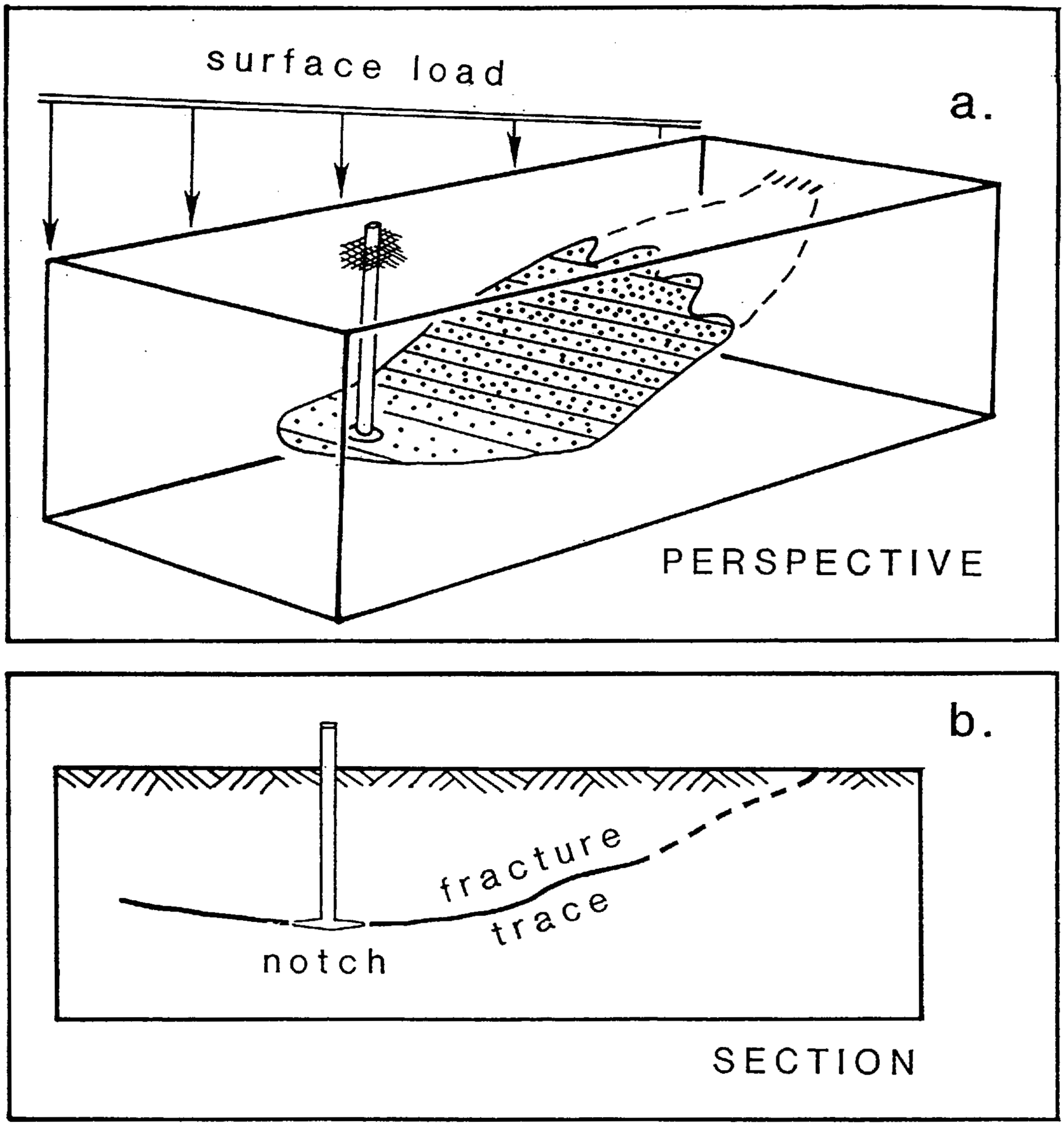

Figure E-3a. Idealized hydraulic fracture created at shallow depths in overconsolidated silty clay. 3b. Trace of idealized fracture. Dashed line is path taken by continued pumping.

ground surface and influence the propagation direction away from the vehicles.

Hydraulic fractures have been created between 4 ft and 30 ft below the ground surface. All of them have been in silty clay, and most have been in glacial drift that probably was overconsolidated, meaning at one time it experienced a greater vertical stress than at present. The maximum length of the fractures increases with depth, but is in the range of 20 to 35 ft. Between 5 and 12 ft^3 of sand (1 ft^3 = 100 lbs) are injected into a fracture. The average thickness of sand in a fracture ranges from 0.2 to 0.4 inches. The largest fracture that has been characterized was 55 ft along the major axis of the elliptical fracture plane, the most voluminous contained 44 ft^3 of sand, and the thickest was approximately 1 inch.

The maximum dimension of a hydraulic fracture depends on the volume of fluid injected into it. But this dimension is not without bounds because the fracture climbs and will vent or reach the ground surface with continued injection. Some remedial technologies are insensitive to whether the fracture vents, but others, such as soil vapor extraction, may benefit if the fracture is confined to the subsurface.

The volume of injected slurry then becomes critical; a small volume will reduce the chance of reaching the ground surface but limits the size and effectiveness of the fracture, whereas a larger volume will produce a more effective fracture but increases the chance of reaching the ground surface. A simple theoretical analysis has been developed based on principals described by Murdoch (1993) to analyze basic features. Numerical analyses of fracture propagation is being pursued 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.

1.1.3 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. E-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 (Fig. E-4) can be used to infer the location of the fracture at depth. 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. Those generalizations are based on 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).

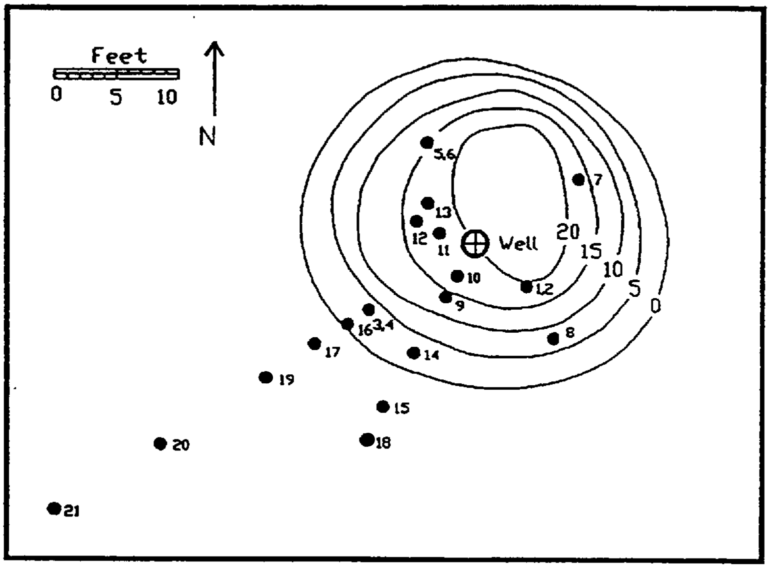

Figure E-4. Contours of uplift in mm of ground surface over a hydraulic fracture at 5 ft depth. Numbered dots are locations and identification numbers of pneumatic piezometers.

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. Recently Phil Cluxton of the University of Cincinnati has developed a laser-based device that measures uplift every few seconds at a variety of locations to provide real-time monitoring of the uplift accompanying fracturing. Tiltmeters are another method of monitoring the deformation associated with hydraulic fracturing.

1.1.4 Limitations

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.

1.1.4.1 Geologic Conditions. The state of stress in soil appears to play a dominant role in determining the orientation of a hydraulic fracture. 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. That ratio can be greater than unity in other soils, particularly so-called overconsolidated soils (Brooker and Ireland, 1966), that have been consolidated under a great load, such as a glacier, or that contain swelling clays. Accordingly, it is expected that hydraulic fractures in 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.

Hydraulic fracturing of soil is regarded as most useful in overconsolidated soils. There are several mechanisms that will produce overconsolidation. Most work to date 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.

The distributions of major glaciated areas and major areas containing vertisols in the U.S. are given in Figure E-5. Keep in mind several points:

> 1) Vertisols may occur locally outside the areas shown on the map, so the state of stress favoring gently dipping hydraulic fractures may occur locally in areas not shown on the map.
>
> 2) Soils other than vertisols may be overconsolidated by shrinking and swelling, so the state of stress favoring gently dipping hydraulic fractures may occur in major areas not shown on the map.
>
> 3) Some sediments in glaciated areas, such as those deposited as a glacier retreats or reworked by processes following glaciation, will not be overconsolidated.
>
> 4) A relatively high lateral stress will occur in bedrock underlying most of the U.S.

Bedding, preexisting fractures, cobbles and other discontinuities appear to play a secondary role in determining the overall fracture geometry. At one location where detailed excavations were made, hydraulic fractures cut across bedding and around cobbles, resulting in features with the same form as hydraulic fractures in massive silty clay.

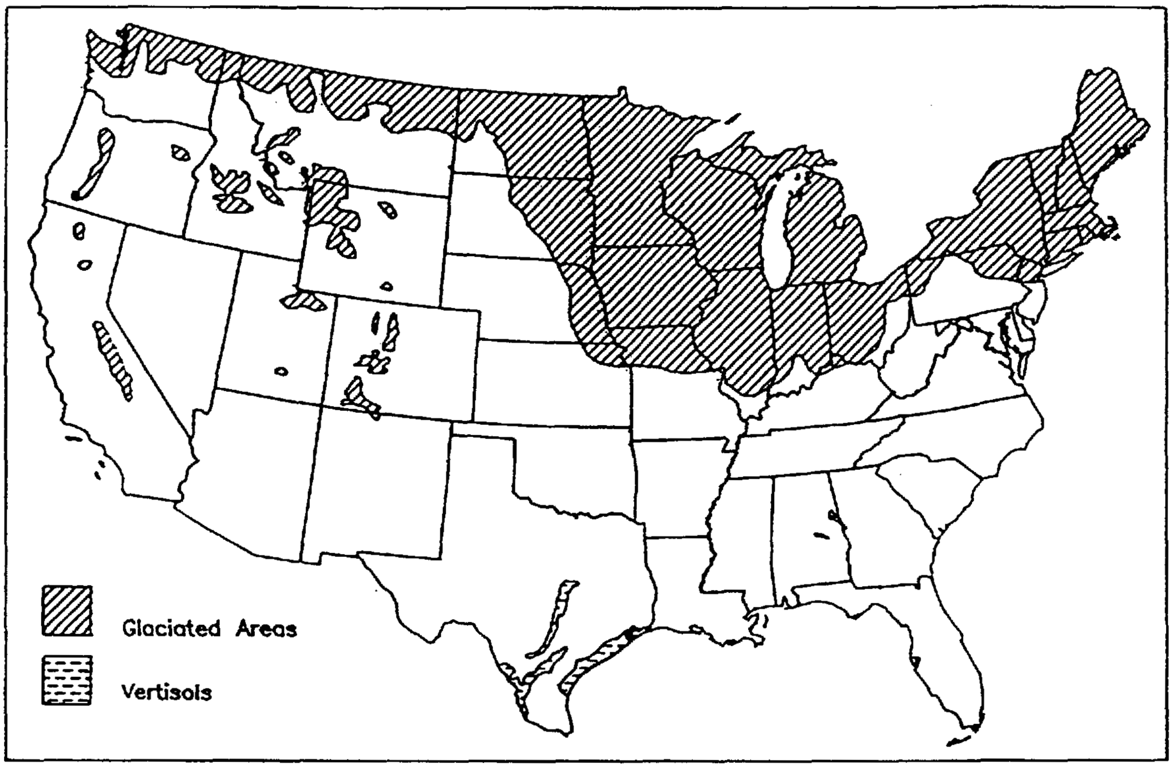

Figure E-5. Areas that have been glaciated (based on Flint, 1971, fig 18-11), or that are underlain by vertisols (based on USGS Sheet 86).

Very recently, remarkably large, nearly horizontal hydraulic fractures were created by the University of Cincinnati staff in soft interbedded clays, silt and fine-grained sand in eastern Texas. The geotechnical evaluation of these sediments has yet to be completed, but the soft character of this material suggests that it is normally consolidated. The preliminary interpretation is that bedding caused the hydraulic fractures to remain horizontal at this site. This preliminary interpretation is mentioned here because it suggests that overconsolidation is not necessarily a requisite to create gently dipping hydraulic fractures at all sites, which implies that more sites could be candidates for this technique than formerly realized.

1.1.4.2 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 (6 to 10 depth, for example) in soil typically forms a broad dome roughly 1 inches in amplitude and 30 ft across, and structures overlying the hydraulic fracture should be capable of accommodating these soil displacements. At the ground surface, vertical fractures in soil or pavement are commonly dilated during the doming that accompanies fracturing.

1.2 IMPULSE FRACTURING

To address the limitations that the state of stress plays on hydraulic fracturing, a new method of creating sand-filled fractures with high pressure impulses of water has been developed. This investigation is in its early stages and the results are preliminary; nevertheless, the results indicate that impulse fracturing should be a versatile and effective tool in low permeability soils.

1.2.1 Method

Impulse fracturing involves deforming soil with pulses of water generated by a hydraulic intensifier. The device (Kinnan, 1986) consists of a large piston with a sealed nitrogen charge on one side and hydraulic fluid on the other. A shaft extends from the large piston into the hydraulic fluid, through a seal and onto a small piston (Fig. E-6). A fast-acting valve allows pressurized

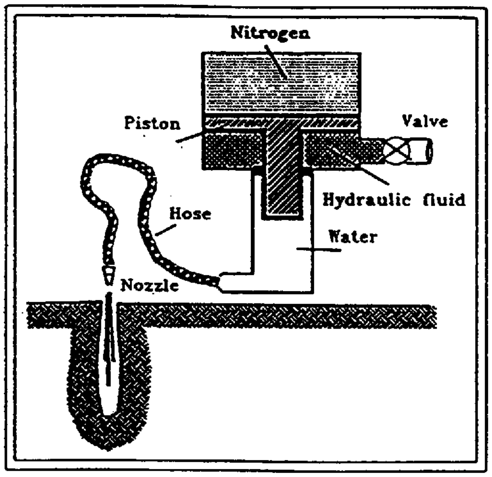

Figure E-6. Schematic of the hydraulic intesifier.

hydraulic fluid to be rapidly released. An injection fluid (e.g. water, gel, grout) is circulated beneath the lower piston through high pressure hoses and to a nozzle adjacent to ground that is to be fractured.

To arm the intensifier, the pressure of the hydraulic fluid is increased to 2500 psi, compressing the nitrogen to a similar pressure. During discharge, the hydraulic fluid is rapidly released through the valve and the large piston is advanced by the expanding nitrogen. The pressure exerted by the small piston on the injection fluid is intensified, according to the ratio between the areas of the large and small pistons and the size of the nozzle. In its current configuration, the impulse intensifier creates a pulse of fluid of approximately 0.5 L, which is discharged in less than 300 milliseconds. Injection pressure increases sharply to 8500 psi in 12 milliseconds (Fig. E-7), and then decreases to atmospheric pressure during the following 275 milliseconds. Velocities of the fluid at the leading edge of the impulse are on the order of 500 ft/s to 1500 ft/s.

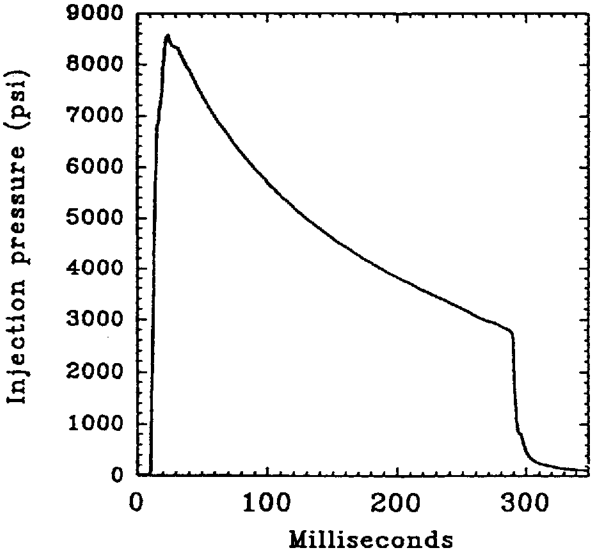

Figure E-7. Injection pressure as function of time during impulse fracturing.

Granular material, such as sand, is introduced into the fluid pulse and carried into the subsurface. Configurations have been evaluated that allow granular solids to be emplaced in impulse fractures while the nozzle is pointed vertically downward at the ground surface or below an open borehole, or while the nozzle is inclined to the axis of either a vertical or a directional borehole.

1.2.2 Fracture Form

The general deformation created by a single impulse includes a cylindrical hole and fractures either parallel or normal to the axis of the hole. In detail, many fracture forms apparently can be created. Here, the results of two early field tests will be described: one where the nozzle was directed vertically downward at the ground surface, and another where the nozzle was inclined to the axis of a directional borehole. The vicinity of the ground in each test was excavated to map the resulting deformation.

During the vertical tests, five pulses from the intensifier created an axial hole as much as 2 inches in diameter and 50 inches deep. Two planar fractures were created parallel to the axis and extending along the full length of the hole. They extended approximately 12 inches into the soil on either side of the hole (Fig. E-8). Coarse-grained sand to gravel (0.2 to 0.3 inch diameter) was injected with each pulse, completely filling the axial hole and filling most of the fracture as well.

The other test consisted of firing pulses as a nozzle was pulled along a directional (nearly horizontal) borehole in normally consolidated silty clay loam. The nozzle was inclined to the borehole axis and oriented in the horizontal plane, and eight pulses were spaced along the borehole (Fig. E-9). A bentonite slurry was injected to mark the resulting fracture. This procedure created an open cavity several cm thick within 12 inches of the borehole. A horizontal, bentonite-filled fracture extended from the open cavity to approximately 4 ft from the borehole. The results of this test are particularly significant because they showed that impulse fracturing can produce a horizontal fracture in normally consolidated material.

1.2.3 Comparison to Other Methods

Impulse fracturing straddles middle ground between hydraulic fracturing and jet cutting. Filled fractures are created by impulse fracturing, just as they are by hydraulic fracturing. The features created by impulse fracturing alone appear to be smaller than those created by hydraulic fracturing. Impulse

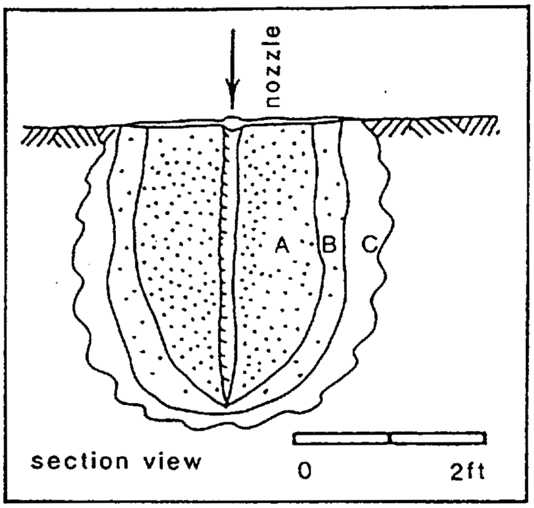

Figure E-8. Fracture created by firing downward with the impulse intensifier. Zone A is fracture filled with gravel to thicknesses of 0.2 to 0.4 inch. Zone B is sparsely filled with gravel. Zone C is filled with water, but no gravel.

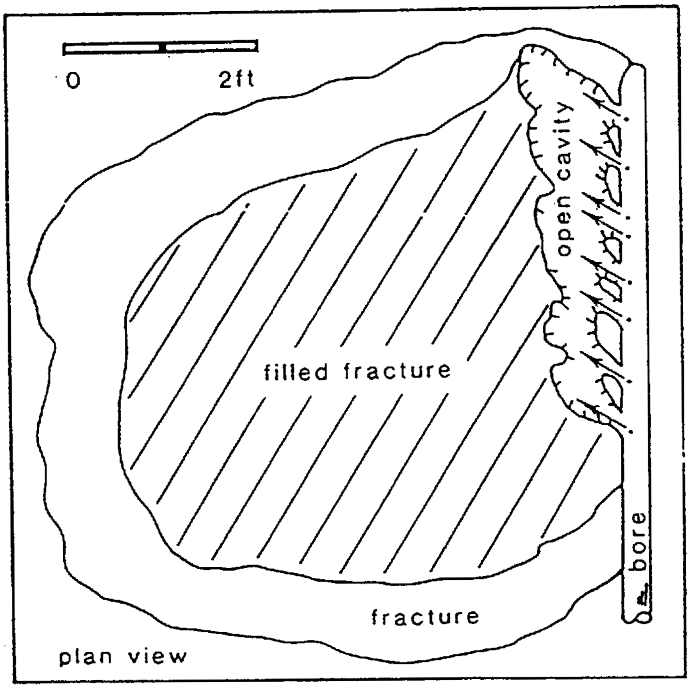

Figure E-9. Deformation created by a series of pulses of bentonite slurry at various points along a horizontal bore. Nozzle was oriented horizontally and produced an open horizontal cavity and fracture. The cavity was 1 to 2 inches high and approximately 12 inches deep.

fracturing, however, is more versatile than hydraulic fracturing because its use appears to be less dependent on the state of stress of soil in the vicinity of the wellbore.

Continuous water jets operating at the peak pressures of the impulse intensifier can be created using available pumps, and those jets will cut cavities and create fractures that are similar to the ones from the impulse intensifier, according to unpublished tests at the University of Cincinnati. Relatively large volumes of fluid are required for a continuous jet, however, potentially causing problems with disposal or offsite migration at contaminated sites.

Section 2

GENERAL TECHNOLOGY CONSIDERATIONS

The following section addresses specific questions related to hydraulic and impulse fracturing.

2.1 WHAT ARE THE EFFECTS OF SOIL WATER CONTENT?

Water content appears to have negligible effect on hydraulic fracturing in tight soils. Hydraulic fractures have been created under saturated and partly saturated conditions, and no effect related to the water content has been detected. The fluid injected to create hydraulic fractures is remarkably stiff, so the leakage out of the fracture and interaction with pore fluids during propagation is limited. All of the current impulse fracturing has been limited to partly saturated soils.

Water content has a strong effect on recovery rates during soil vapor extraction using hydraulic fractures. At several sites recovery rates decrease and in-situ suctions increase as water content increases following rainfall events. Elsewhere, dewatering of a saturated site was required before vapor extraction could be initiated.

2.2 LIMITATIONS BY ACCESS BENEATH BUILDINGS?

Both hydraulic fracturing and impulse fracturing techniques have been conducted out of directional boreholes, which are ideally suited to accessing beneath structures that are either technically or logistically difficult to penetrate with vertical drilling techniques.

Hydraulic fractures will deform overlying materials, lifting a dome in uniform soils that is 0.5 to 1 inch high and 25 to 35 ft across. Many buildings, slabs, or other structures can accommodate some displacement, and the effect of uplift accompanying hydraulic fracturing should be evaluated during an initial feasibility study. 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. <u>In general, caution must be exercised in applying hydraulic (or pneumatic) fracturing in proximity to underground piping or fuel storage tanks until more experience is gained with the technology</u>.

2.3 LIMITATIONS DUE TO DEPTH AND SOIL TYPE?

Hydraulic fractures can be created at depths far below those possibly required for environmental applications. Shallow depths will limit shallow applications, particular in weathered soils. A substantial fracture was created at a depth of 3 ft in fresh till, but depths of 5 to 6 ft were required to contain fractures in weathered till.

Coarse-grained soils may inhibit fracture propagation as the liquid phase of the injected slurry leaks off into the soil and leaves the granular material behind. However, hydraulic fractures have been mapped cutting from clayey silt through coarse sand and there was little apparent effect of the stratigraphy (Murdoch and others, 1991).

During a recent project nearly flat-lying hydraulic fractures were created in soft, interbedded sediments apparently because the fractures propagated along stratigraphic contacts. The details of that project are still being evaluated, but they do suggest that bedding may play a more important role than previously recognized.

Soils containing swelling clays will favor the creation of gently dipping hydraulic fractures, assuming that the soils have experienced cycles of shrinking and swelling to produce a relatively high lateral stress.

2.4 EFFECTS OF NATURALLY OCCURRING FRACTURES?

Naturally occurring fractures were poorly developed at locations where excavation studies were conducted, so detailed field evidence of the effects of naturally occurring fractures is unavailable. Recently however, hydraulic fractures were observed along slickensides in swelling clay during a field test in Texas. In the laboratory (Murdoch, 1993) it was found that the fracture toughness (resistance to fracture propagation) of silty clay is quite low. This means that relatively little energy is required to actually break soil compared to the energy required to dilate the fracture walls. For this reason, it appears that in most cases the state of stress will be the dominant control of the path of a hydraulic fracture relative to controls by naturally occurring fractures. At sites where naturally occurring fractures are particularly abundant, however, or where the in-situ stresses are similar, the naturally occurring fractures can play an important role in determining the propagation path of a hydraulic fracture.

Hydraulic fracturing could be particularly effective at sites containing naturally occurring vertical fractures in overconsolidated silty clay. Here it is expected that gently dipping hydraulic fractures will cut across, and provide access to, many of the naturally occurring fractures. In some cases, naturally occurring fractures at the ground surface were seen to be dilated by several mm during doming caused by a hydraulic fracture at depth. This dilation presumably increases the conductivity of the vertical fractures and may improve access to contaminants adsorbed along fracture walls.

2.5 HOW EFFECTIVELY CAN THIS TECHNOLOGY REMEDIATE PETROLEUM PRODUCTS OTHER THAN GASOLINE?

Fracturing technologies in general will increase yields and provide for the delivery of solids. As such, they should enhance remedial techniques, such as bioventing, that are known to degrade heavier petroleum fractions provided oxygen can be delivered to the subsurface. The degree of enhancement, and whether it is sufficient to warrant implementing the technique, can only be evaluated on a site-by-site basis at this time.

A variety of electrical techniques, ranging from electroosmosis through joule heating and vitrification, have been proposed as remedial actions for a wide range of contaminants. These techniques typically make use of point or line electrodes and they experience large losses of electrical potential in the vicinity of the electrodes. A new project, termed *Lasagne,* has been initiated with industry-government sponsorship to evaluate the feasibility of enhancing these electrical techniques by filling hydraulic fractures with electrically conductive material, particularly graphite, to form sheet-like electrodes.

Recent work has suggested that some petroleum products can be degraded when in contact with solid compounds, such as metals or biological nutrients and electron receptors. It appears to be feasible to enhance the versatility of these solid compounds by delivering them in-situ using hydraulic or impulse fracturing.

2.6 WHAT TESTS WILL HELP ESTABLISH THE SUITABILITY OF HYDRAULIC FRACTURING AT A SITE?

Hydraulic fractures can be created in all the soils that have been tested, and they probably can be created in any soil. Gently dipping fractures will be the most useful orientation, however, and they can only be created at some sites. Evaluating the state of stress appears, at this time, to be the most viable method of predicting the orientation of hydraulic fractures in soil.

Geotechnical engineers have developed a variety of methods for estimating the state of stress in soils, typically to aid in the design of foundations, tunnels or other subsurface construction projects. Consolidation tests can be performed on high-quality soils cores in the laboratory to give some indication of the state of stress. In-situ tests are also available using a variety of devices, including the borehole pressuremeter (Baguelin and others, 1978; Briaud, 1986), dilatometer (Powell and Uglow, 1986; Marchetti, 1980), or stepped blade (Handy, 1988). Small hydraulic fractures have also been used to estimate the state of stress in soil (Bjerrum and Anderson, 1972; Massarch, 1975 and 1978).

Geotechnical engineers express the results of those tests as the ratio of the horizontal to vertical effective stress, K_0. In general, values of K_0 greater than 1.0 will favor flat-lying hydraulic fractures, and the larger the value of K_0 the more the flat-lying orientation will be favored. Most geotechnical consulting companies should be capable of measuring K_0. Although an in-situ stress test is the most viable method, it is by no means a certain indicator of the viability of hydraulic fracturing. Therefore, it is only suggested conducting such a test if the cost of doing so is less than the cost of conducting a feasibility test of hydraulic fracturing itself.

Published information on in-situ stress testing in the area of interest should be obtained prior to any field testing. For example, the data published by Mahar and O'Neill (1983) show that K_0 in the Beaumont soils, a montmorilonite-rich vertisol that occurs in the vicinity of Houston, Texas, is greater than 1.0 at depths less than 10 m. These data strongly indicate that gently dipping hydraulic fractures could be created in the Beaumont soils, and recently a field test was completed that confirmed this indication.

K_0 is by no means a standard parameter obtained during an environmental site investigation. The number of blows required to drive a split-spoon 6 inches, which is a standard measurement, is a reasonable predictor of the orientation of hydraulic fractures in silty clay, glacial formations. If the blow counts are less than 5, hydraulic fractures probably will be steeply dipping, whereas if they are greater than 15, hydraulic fractures probably will be gently dipping. Please keep in mind that this is strictly an empirical finding, and its validity to areas underlain by other formations is unknown.

Hydraulic fractures in shallow bedrock settings should behave slightly different than in soils. In most shallow bedrock settings, where the rock has been uplifted following deep burial, the ratio of lateral to vertical stress will be significantly larger than in soils. Moreover, the fracture toughness of most rocks is several orders of magnitude greater than soil, so there will be more of a tendency for hydraulic fractures in rock to follow discontinuities, such as bedding surfaces or joints. As a result, it is expected that the dominant orientation of hydraulic fractures in shallow bedrock will be horizontal, particularly when the bedding is horizontal.

The effect of heterogeneity, such as bedding or vertical fractures, appears to be site-dependent. At one location hydraulic fractures cutting across bedding in glacial drift have been mapped, suggesting that bedding plays only a minor role. Elsewhere, however, preliminary evidence suggests that bedding may cause hydraulic fractures to be flat-lying in the absence of relatively large lateral compression, although the data from this site are still being evaluated. Accordingly, well-developed contrasts in the toughness of adjacent stratigraphic units may be sufficient to create flay-lying hydraulic fractures at sites where in-situ stress measurements indicate that the lateral stress is approximately equal to the vertical stress.

Section 3

EFFECTS ON REMEDIATION IN DIFFERENT GEOLOGIC SETTINGS

In the following section the remedial effects of hydraulic and impulse fractures will be estimated by addressing several questions pertaining to the remediation of two site conditions, a massive silty clay and a stratified deposit. Field tests conducted using hydraulic fracturing during remediation have thus far been limited to systems using vapor extraction or liquid injection for bioremediation. Accordingly, responses to the questions will be based on best judgment, with some of the answers unsupported by field data.

3.1 MASSIVE SILTY CLAY

Assume the following conditions: An area underlain by massive, silty clay 30-50 m thick that contains natural fractures. The upper 2 m is highly weathered and desiccated. Natural fractures are vertical, spaced 1 to 100 cm, with 10-40 micron apertures. The contaminated area is saturated so that the pneumatic conductivity is negligible and the air-filled porosity is less than one percent.

How effective is the technology at removing:

1. Free product in continuous fractures?
2. Free product in discontinuous fractures?
3. Aqueous phase product diffused in matrix blocks?

4. Product adsorbed on organic soil material?
5. Residual product trapped in pore throats?
6. Free product floating on the water table?

3.1.1 Evaluation of Conditions

Gently-dipping hydraulic fractures could intersect many vertical, naturally occurring fractures, and they should increase the recovery of free product residing in the natural fractures. It is expected that recovery from continuous fractures should increase substantially, particularly from fractures that overlie the hydraulic fracture and can drain by gravity as well as suction. Moreover, it is expected that recovery from discontinuous fractures that are cut by the hydraulic fracture should also increase, compared to recovery without a hydraulic fracture.

One strategy that could be effective at improving recovery of product that cannot be mobilized by advection (either because it has diffused into matrix blocks or is adsorbed onto organic material) is to create a stack of hydraulic fractures with close vertical spacings (Fig. E-10). Applying suction will remove product from the fractures, thereby increasing the concentration gradient and promoting diffusion toward the fractures. Cycling the suction head applied to the fractures could induced compressibility-driven advection out of matrix blocks (Fred Payne describes this process in more detail in the Soil Vapor Extraction paper in this volume).

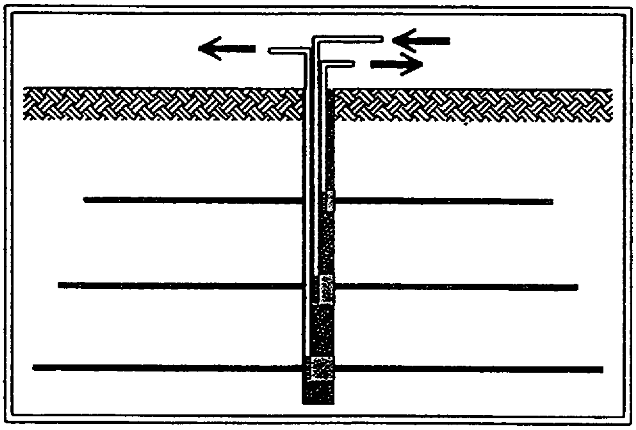

Figure E-10. Section view of a stack of vertical fractures and a multi-level completion. Various combinations of positive or negative pressure are applied to the individual fractures to change the pattern of flow in the subsurface.

The recovery of free product floating on the water table should be more effective with wells that have been stimulated by hydraulic or impulse fracturing. A vertically extensive fracture, similar to that obtained by the impulse fracturing technique and shown in Fig. E-8, would be particularly suited to floating product recovery because the fracture would be in contact with the product as it moves up or down in response to fluctuations in the water table.

3.1.2 Complementary Technologies

Hydraulic fracturing itself is intended to complement in-situ methods of remediation, such as soil vapor extraction, pump and treat, bioremediation, electroosmosis, etc. by increasing the ability to control subsurface fluids. There are other techniques, such as creating a horizontal well, that can be used either alone or with hydraulic fracturing to further improve the ability to control fluids.

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. Both hydraulic and impulse fracturing have been conducted from directional bores, so the techniques described here can be combined with directional drilling.

Most methods of directional boring will create a skin of relatively low permeability material around a well, particularly when the bore penetrates fine-grained sediments. Both fracturing techniques will penetrate a low permeability skin and could be used to reduce the detrimental effects of the skin. Hydraulic fractures have been created from directional wells, although the effect that fracturing had on the borehole skin was not evaluated during these studies.

3.2 STRATIFIED CLAY AND SAND

Assume the following conditions: Relatively dry soil composed of beds and lenses ranging from permeable, medium-grained sand to tight silt. A water table occurs at 3 to 4 m.

How effective is the technology at recovering:

1. Free product perched on silt lenses.
2. Aqueous phase product in continuous, low permeability beds.
3. Product in isolated silt lenses.
4. Adsorbed product in permeable and tight beds.
5. Residual product in permeable and tight beds.
6. Free product on water table in permeable bed.

3.2.1 Evaluation of Conditions

One problem in this scenario is that vapor flow will occur preferentially from high permeability layers that are intersected by a vertically extensive well screen. This problem could be partly addressed by using multi-level recovery wells, which consist of several screened intervals separated by sealed intervals. This would allow combinations of recovery and air inlet at different intervals to induce vertical flows through low permeability beds intersected by the well.

Multi-leveled well completions have been used to access gently dipping hydraulic fractures and induce vertical flows through low permeability material between the fractures. In the stratified scenario described above, however, well yields may be sufficient so that hydraulic fracturing is unnecessary (the sand beds behaving similarly to a hydraulic fracture).
It may be possible to create hydraulic fractures in silt beds that are greater than approximately 30 cm thick. Where the beds are thinner and well yields are substantial, however, the effects of hydraulic fracturing are expected to be limited.

Section 4
COST AND AVAILABILITY

The cost of remediating any site to a specific concentration is beyond the scope of current evaluations of fracturing technology. The requirements for creating hydraulic fractures themselves, however, has been evaluated. Using currently available methods, it is possible to create 4 to 6 fractures per day with a three-person crew.

Associated costs are approximately:

Labor	$1600/day
Materials (sand, fluids)	$ 950/day
Equipment usage	$2000/day
Drilling support	$1200/day

Assuming that the site requires several dozen fractures to be created, a cost of approximately $900 to $1400 per fracture is estimated using current methods and including costs of drilling support. Specialized requirements at individual sites, well completion costs, monitoring requirements, mobilization, or other factors could cause this cost estimate to increase. Streamlining the fracturing method (as it rapidly moves beyond the research stage), eliminating the costs of drilling support, and reducing the amount of monitoring will cause this estimate to decrease.

The approach to estimating the requirements for hydraulic fracturing at a hypothetical site containing overconsolidated silty clay till begins with a feasibility test to determine the geometry of hydraulic fractures created at the site. If gently-dipping fractures are created, then hydraulic fracturing can proceed; if not, then impulse fracturing may be more appropriate for this site. It is assumed that the contaminants have a relatively high vapor pressure, so that they can be recovered by soil vapor extraction. Using conventional blowers, 1 inch of water suction head between 20 and 30 ft from recovery wells at a test site in silty clay has been observed. Assuming that this suction is sufficient to transport the contaminants, then the area could be recovered with a 3 by 3 grid of wells. Fractures have been created at 6, 10 and 15 ft depths from single boreholes at several sites, and this configuration is both straightforward and appears to provide reasonable coverage with depth. Typically, each fracture is screened individually so that they can be used either for recovery or as an air inlet.

An estimate of the cost to create the 27 fractures and complete the nine wells is on the order of $25,000 to 30,000.

As of this writing, hydraulic fracturing of soil has been conducted at seven sites for research investigations. A few companies are now providing hydraulic fracturing services for site remediation purposes. Several oil field service companies routinely create hydraulic fractures at great depths in rock, and they could extend their service to cover near surface conditions.

SECTION 5

CASE HISTORIES

Pilot-scale demonstrations of the effects of hydraulic fracturing have been evaluated by the US EPA SITE program. Highlights of two of the demonstrations will be described below, with the details available in the SITE report.

5.1 AIR FLOW STUDY

A preliminary vapor extraction test at the US EPA Center Hill Research Facility was conducted using fractured wells and conventional wells in uncontaminated ground. The site is underlain by stiff, brownish-gray, silty-clay till, which contains rock fragments below 10 ft. The surface of the site is barren or covered by a thin layer of coarse gravel, so that the air at the ground surface is presumably maintained at atmospheric pressure. Hydraulic fractures were created at depths of 5, 10 and 15 ft, although the fracture at 15 ft was not used during the tests described here. The hydraulic fractures extended to radial distances of 10 to 15 ft, according to the results of uplift monitoring (Fig. E-4; more details of the fractures in Murdoch and others, 1992). A multi-level recovery well was completed with separate casing for each fracture (Fig. E-10). Another well was created in unfractured ground as a control using the same completion techniques as described above.

Pneumatic piezometers were installed at various depths and locations. Some piezometers were installed within fractures, whereas others were installed above the upper fracture (Fig. E-4).

Vapor extraction was conducted at the fractured and unfractured wells using conventional 1 Hp blowers, which were set up to provide 38 inches H_2O of suction head at the beginning of the test. Pressure head and flow rate were monitored for 40 days beginning in late January, 1992. Shorter duration tests were conducted using a positive displacement pump capable of generating suction heads of 150 inches H_2O.

5.1.1 Distribution of Suction Head

Suction diminishes abruptly with distance away from the conventional well (Fig. E-11a), whereas it decreases relatively gradually with distance from the fractured well. For example, 1 inch of H_2O suction head occurs between 2 and 3 ft from the conventional well, whereas it occurs 25 ft from the fractured well. The distribution of suction also varies with precipitation; suction head increased after rainfall. The data shown are typical values.

5.1.2 Well Yield

The yield of the conventional well remained roughly constant at 0.3 cfm throughout the duration of the test (Fig. E-11b). In contrast, the yield of the well intersecting hydraulic fractures was between 3 and 4.5 cfm for most of the test, roughly an order of magnitude more than from the conventional well. Yield from the fractured well decreased abruptly following rainfall and then increased after water was removed from the recovery well. This dependence of yield on rainfall was seen at all the sites where tests were conducted, although the magnitude of the effect shown in Figure E-11 was reduced by installing a system to regularly dewater the vapor extraction wells.

5.1.3 Air Flow Modeling

A theoretical, steady state analysis of the flow of air to a fracture was conducted using AIRFLOW, a 3-dimensional code developed by Craig Joss and Art Baehr of Drexel University. It was assumed that the fracture was

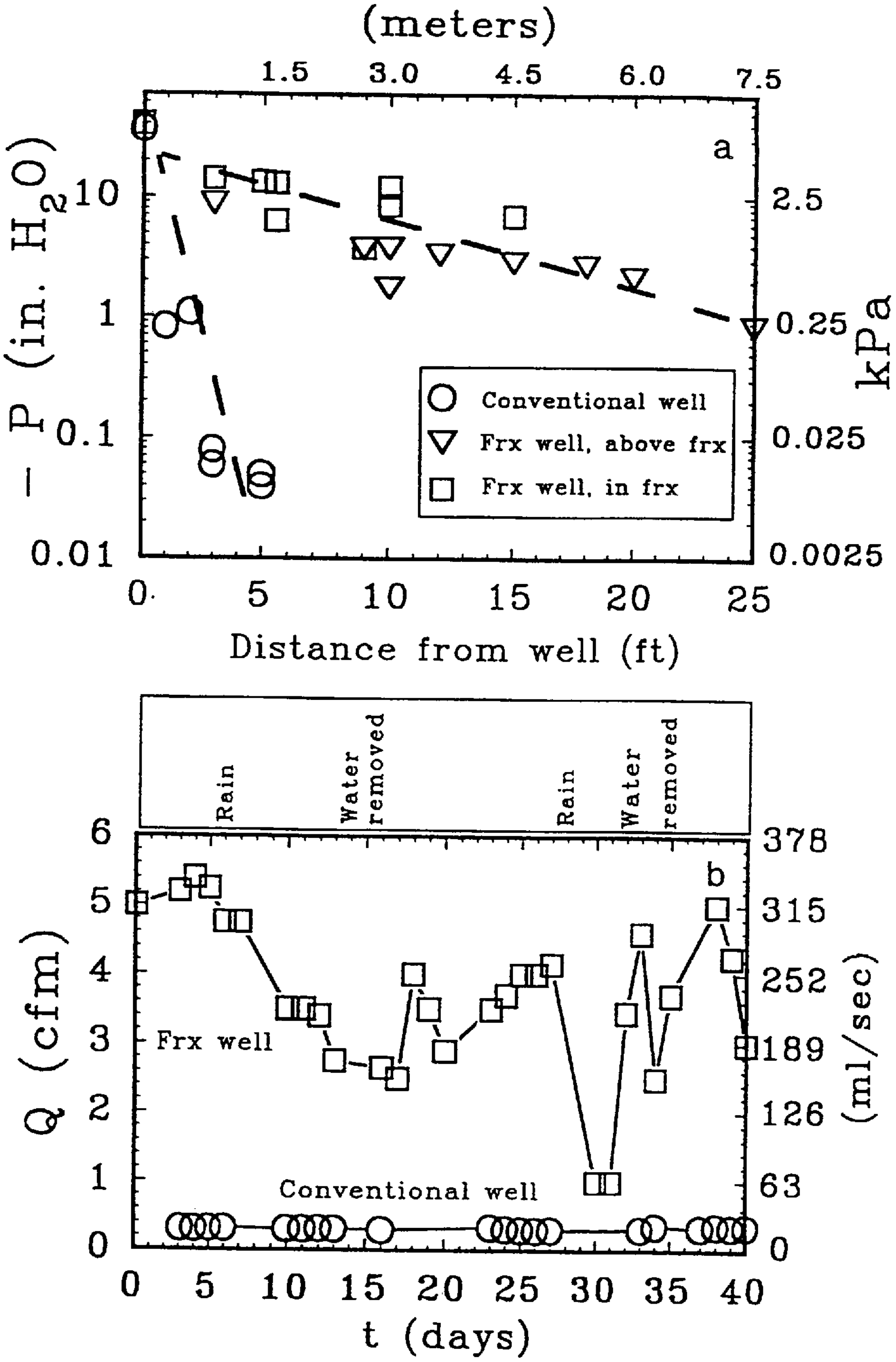

Figure E-11a. Suction head as a function of radial distance from a conventional well intersecting hydraulic fractures. 11b. Volumetric yield as a function of time for conventional and fractured wells. Major rain events and times of dewatering recovery wells are indicated.

shaped like a flat-lying circular disk, 5 ft below the ground surface, and that it was 10 ft in radius, 0.25 inch thick and filled with coarse-grained sand (the actual fracture tapered near its periphery and was slightly greater in radius). The ground surface was assumed to be at atmospheric pressure, and an impermeable layer was assumed to be at a depth of 20 ft. The permeability of the till was estimated at 10^{-9} cm^2, based on calibration simulations using a conventional well screened at 5 ft. The permeability of the fracture was unknown, so a wide range of permeabilities was evaluated. The results of the simulation are shown along with field data obtained by applying 100 inches of suction head to the fracture at 5 ft depth (these data differ from the ones given above).

Both well yield and the distribution of suction are strong functions of the permeability of the fracture (Fig. E-12). The suction head observed in the field is predicted approximately by a fracture whose permeability is between 3 x 10^{-6} and 5 x 10^{-6} cm^2 (Fig. E-12a). The observed suction is slightly greater than predicted at radial distances greater than 15 ft, but the uplift data indicate that the fracture is probably bigger than the assumed 10 ft. The yield observed in the field was approximately 7 cfm, which is predicted for a fracture whose permeability is 7 x 10^{-6} cm^2 (Fig. E-12b). A permeability in the range of 3 x 10^{-6} to 7 x 10^{-6} cm^2 is consistent with clean sand to gravel, according to Bear (1979).

The results of the analysis indicate that the effects of a sand-filled hydraulic fracture on the flow of air in the subsurface can be explained using accepted methods of analyzing air flow to a permeable layer.

5.2 SOLVENT RECOVERY STUDY

A pilot-scale test of hydraulic fracturing during vapor extraction was conducted at a site in the Chicago area containing a multi-component mixture of solvents. The site is underlain by silty clay glacial drift that contain local zones of perched water. The maximum total concentrations of solvents found in a suite of exploratory borings was contoured to estimate the initial distribution (Fig. E-13). Four locations within the 10 ppm contour were selected for the test. Wells RW3 and RW4 each contained three hydraulic fractures (6, 10 and 15 ft depth) that were screened separately, whereas well

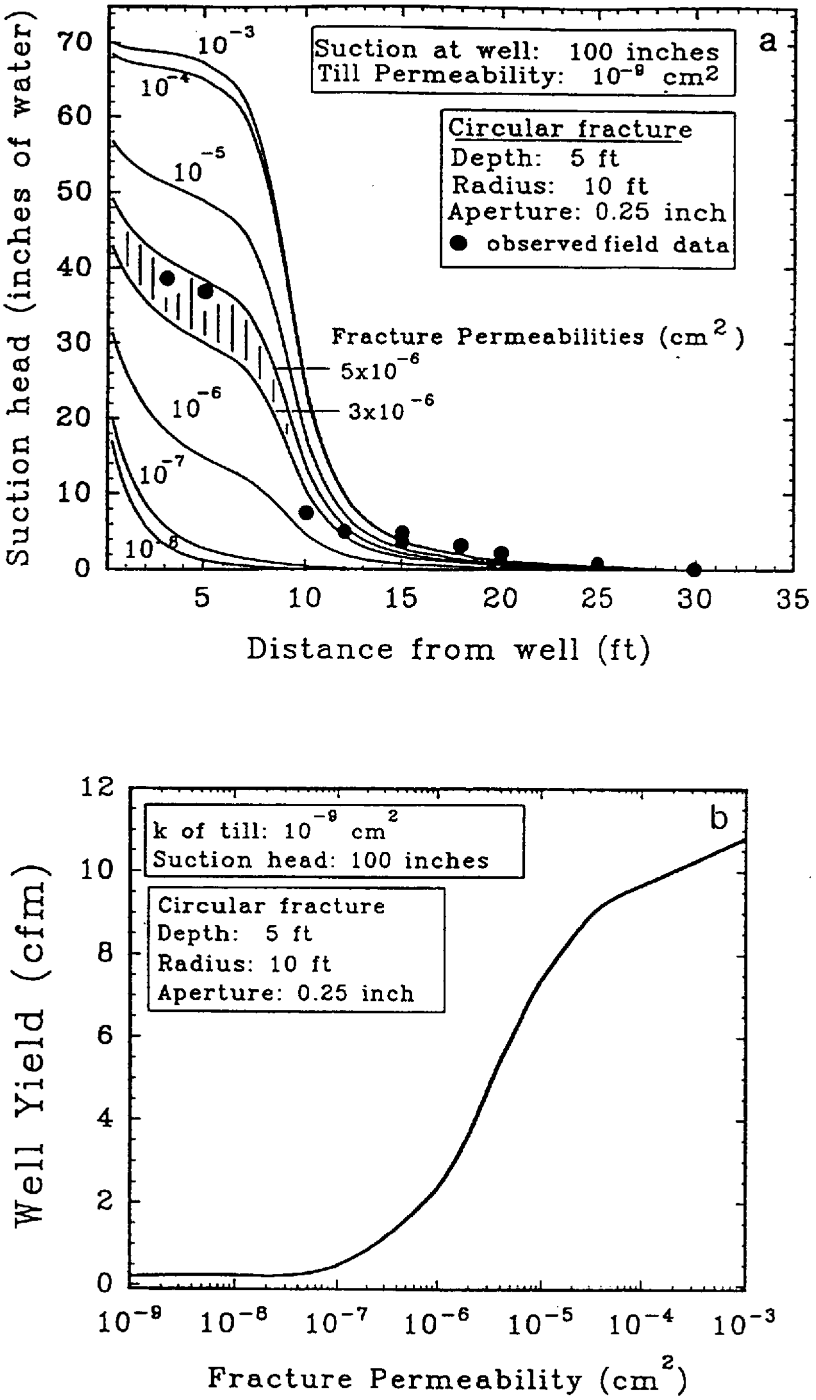

Figure E-12a. Suction as a function of radial distance at a depth of 4 ft, showing field data and theoretical results for various permeability of fracture. 12b. Yield as a function of fracture permeability. Yield without a fracture is 0.23 cfm.

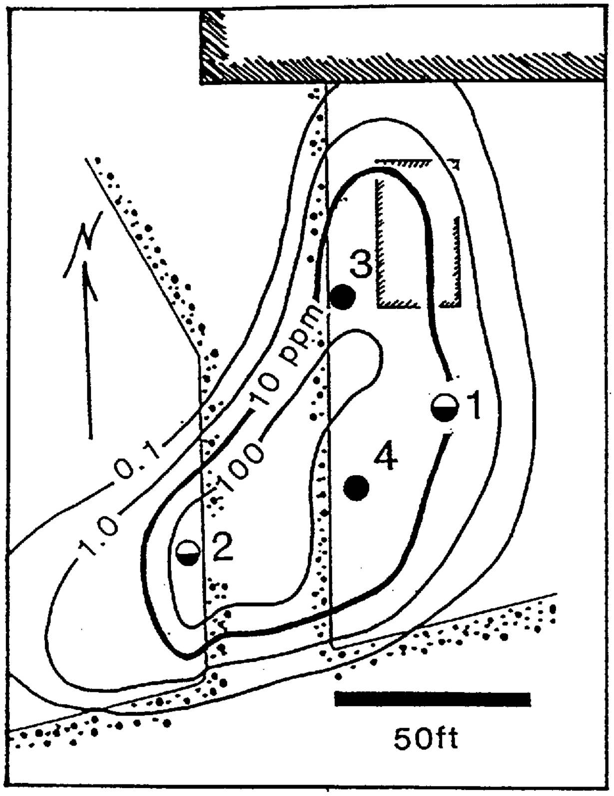

Figure E-13. Map of the solvent recovery site. Contours are concentration of solvent in soil. Filled circles are wells intersecting hydraulic fractures, half-filled circles are conventional wells. Stipled area is paved, grass-covered elsewhere. Small hatched box is former location of tank, larger hatched area is a building.

RW1 was a conventional well screened from 5 to 15 ft, and RW2 contained three screened interval similar to RW3 and RW4. The seal around RW1 failed, so it will be ignored.

Well yields, pressures, and contaminant concentrations were obtained approximately three times a week for 21 weeks beginning in July, 1992. Suction heads applied to the well ranged from 140 to 300 inches of water. The volumetric yields varied markedly with time, just as they did at the Center Hill site, with the yield of RW4 ranging between 30 and 40 cfm, and RW3 between 10 and 20 cfm. The yield of RW2, which lacked hydraulic fractures, was roughly 1 cfm, although in many cases the yield from that well was considerably less 1 cfm and could not be resolved using the flow meter at the site.

The wells intersecting hydraulic fractures yielded contaminants at rates that were roughly an order of magnitude greater than the control well. Mass yield of approximately 0.23 lbs/day was observed from RW3 early in the test. Mass yield diminished with time at RW3 and was approximately 0.18 lbs/day late in the test. Mass yield from RW4 was similar to slightly less than that value throughout the test. In contrast, the average yield from RW2 was approximatly 0.018 lbs/day. Figure E-14 illustrates these results.

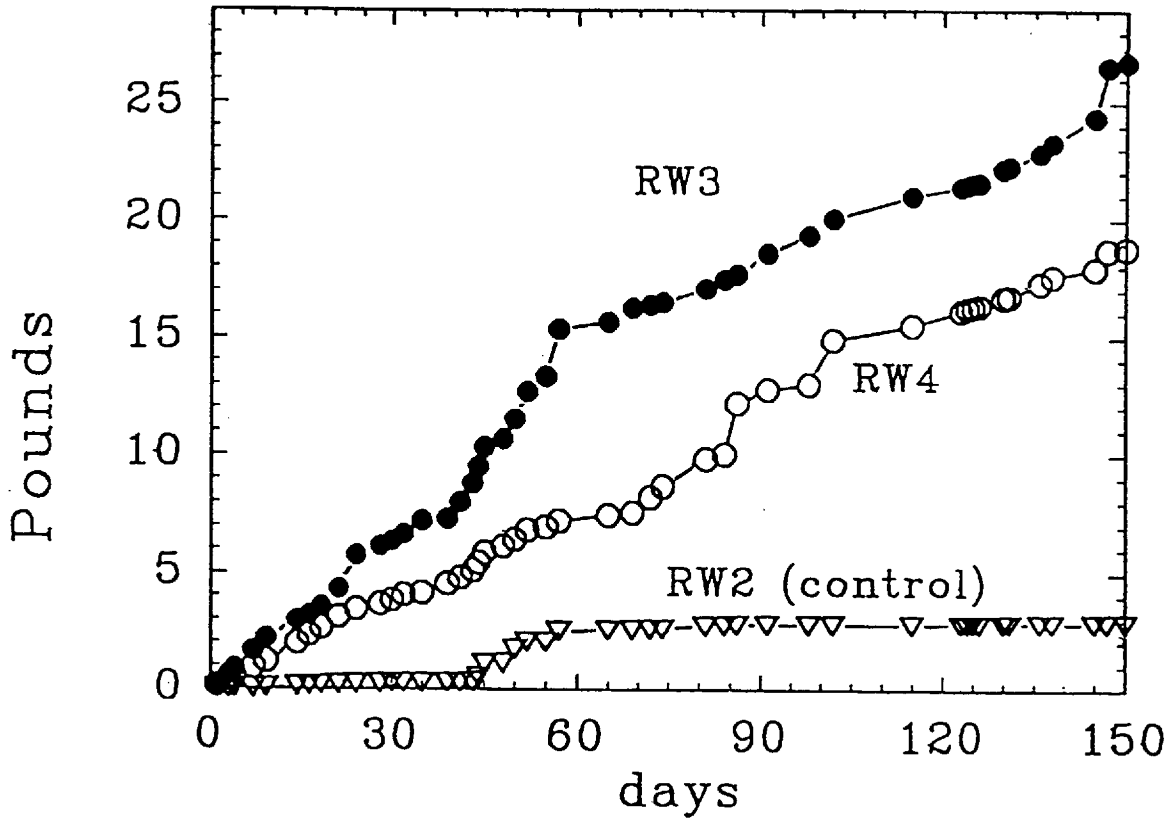

Figure E-14. Estimated mass of solvents recovered as a function of time from fractured wells (RW3 and RW4) and from a conventional well (RW2). Based on data obtained by on-site consulants.

These results were obtained by assuming an average molecular weight for the multi-component mixture of contaminants. More accurate results are obtained by using the molecular weights of individual components to calculate total mass yield, although these data were unavailable at the time this manuscript was prepared. Revised calculations indicate slightly different values of mass yield, although the relative values for the different wells are similar to those cited above.

Vapor extraction was conducted intermittently for several months prior to the data shown here, so the large mass yields that occur in some vapor extraction operations immediately after the onset of recovery may have occurred prior to the time period shown here.

Section 6

SUMMARY

Hydraulic and impulse fracturing techniques are capable of creating sand-filled fractures in soil. During hydraulic fracturing, the most widely known of the two techniques, fractures are created by injecting sand-laden slurry at modest rates and pressures. In contrast, during impulse fracturing, fluid is injected at high rates and pressures to crack subsurface formations. The fractures produced by hydraulic fracturing in favorable conditions can be 20 to 35 ft or more, whereas the fractures produced by impulse fracturing are currently limited to a several ft in maximum dimension. However, the effectiveness of hydraulic fracturing depends on soil conditions: relatively large, gently dipping hydraulic fractures will be created in formations where the lateral stress exceeds the vertical stress (e.g. overconsolidated tills, and moist swelling clays), elsewhere hydraulic fractures in soil may be relatively small and vertical. In contrast, impulse fracturing appears to be much less dependent on soil type and consolidation history, so its application should be more widespread than hydraulic fracturing.

Hydraulic fracturing is particularly suited to sites underlain by relatively uniform, low permeability soils, where the fracture can markedly change the pattern of flow in the subsurface. Field data indicate that hydraulic fractures can increase both the volumetric yield and the mass yield of vapor extraction wells by an order of magnitude of more. Yields vary temporally, typically decreasing after rainfall, but there is no evidence of a decrease in yield due to clogging, embeddment, or closure of the fracture with time. At one unconfined site, a suction head of 1 inch of water occurs more than on order of magnitude further from a fractured than from a conventional well (25 ft compared to 2.5 ft).

The effect of a hydraulic fracture on subsurface air flow depends on fracture dimensions, aperture, permeability, and location, according to the results of steady state analyses using standard numerical methods. Preliminary simulations using values of those parameters that approximate known site conditions are able to predict both the yield and distribution of suction observed in the field. Flows induced by various combinations of suction and air inlet to multiple hydraulic fractures are currently being analyzed, and it is expected that these analyses will be used to design the location and suction scheduling of hydraulic fractures during forthcoming remedial actions.

The results of impulse fracturing are currently limited to physical investigations of fracture geometry; the effects of those fractures on subsurface flow have yet to be evaluated. However, it follows that the effect will be similar to a sand-filled hydraulic fracture of modest diameter.

In general, caution must be exercised in applying any type of soil fracturing technique (hydraulic, impulse or pneumatic) in the vicinity of underground piping or storage tanks until more experience is gained with the technologies.

Section 6

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Section 8

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PNEUMATIC FRACTURING FOR LOW PERMEABILITY SOILS

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ABSTRACT

Meager rates of fluid flow are a major obstacle to in-situ remediation of low permeability soils. This paper describes a method designed to avoid that obstacle by creating fractures to increase the effective permeability and change paths of fluid flow in soil. This method, known as pneumatic fracturing, involves the injection of air under modest pressure to open fissures, which tend to remain open for a period of many months, and in many cases a year or more. As such, this technique is an alternative to hydraulic fracturing, which is discussed elsewhere in this series of papers. The paper also includes a summary of the commercial availability and typical costs of the technology as well as case histories where it has been applied in low permeability settings.

Section 1

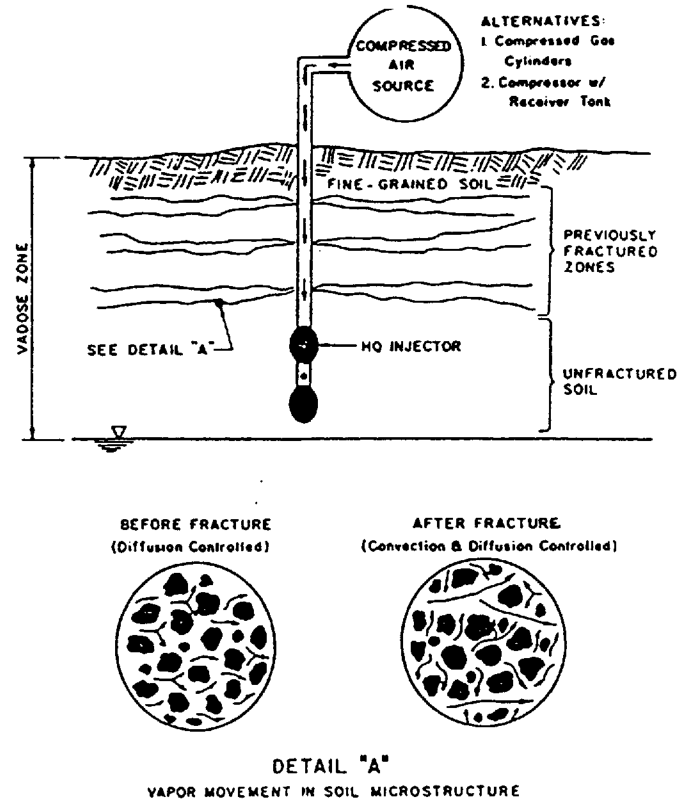
DESCRIPTION OF THE TECHNOLOGY

1.1 INTRODUCTION

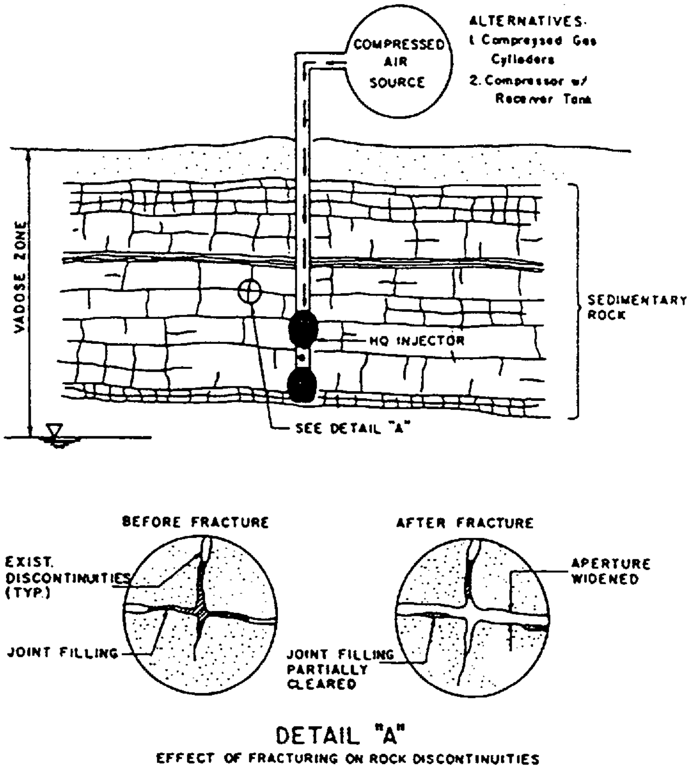
Pneumatic fracturing is an innovative technology which enhances the in-situ removal and treatment of contaminants in low permeability soil and rock formations. The process may be generally described as injecting air (or another gas) into a contaminated geologic formation at a pressure which exceeds the natural in-situ stresses, and at a flow rate which 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 soil vapor extraction, bioventing, thermal injection, and pump-and-treat. Initial applications focused on enhancing treatment of the vadose zone, but recently the technology is being extended into the saturated zone. The pneumatic fracturing system has also been modified to deliver biological supplements (e.g. nutrients, buffers, and microorganisms) directly into the fractured formation to enhance in-situ bioremediation.

The effects of pneumatic fracturing on various lithologies are shown conceptually in Fig. F-1. For formations containing significant amounts of silt and clay, the process creates new convective pathways in the formation which increase permeability, and shorten diffusive distances (Fig. F-1a). In sedimentary rock formations such as sandstone and shale, the process can dilate and extend existing discontinuities, thereby increasing permeability and improving interconnection (Fig. F-1b). The pneumatic fracturing equipment can also be used in more permeable formations such as sand and gravel for rapid aeration, and for injection of biological supplements.



(a) Fine-grained Soil Formations



(b) Sedimentary Rock Formations

Figure 1. Pneumatic Fracturing Concept

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/recovery system for remediating contaminated sites.

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 1.2 and 1.3 which follow.

1.2 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 (1956) 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 (Narendran 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 to the lack of stratification and overconsolidation in these formations.

It is speculated that existing stratification and fractures play a more important role in determining the direction of pneumatic fractures than hydraulic fractures. The reason is that pneumatic fracture propagation is much more rapid, and there is no pre-notching of the formation as in hydraulic fracturing. The formation therefore responds more brittlely, and fractures will favor existing weakness planes.

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 a effective density or unit weight, γ, and an apparent tensile strength, t_a (which is generally a small value and is determined in the laboratory), the fracture initiation pressure, P_i, at a depth, z, may be estimated by:

$$P_i = C\gamma z + t_a + P_o$$

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 depths (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 either 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 to 2000 scfm are sufficient to create satisfactory fracture networks in low permeability formations.

1.3 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 the 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 asperities present along the fracture plane, as well as 'block shifting' of the soil 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.

Over time, pneumatic fractures will tend to close due to overburden stress. However, data from pneumaticaly fractured sites indicates that such fractures in overconsolidated deposits tend to stay open for more than six months, in some cases exceeding a year.

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:

$$Q \sim b^3$$

where ~ 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 incorporated into 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 that a small 'hairline' open fracture will have the same air flow potential as a much larger sand-filled fracture.

Once a fracture network is established in a low permeability formation, aqueous and residual products in the vicinity of the fracture are 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/matrix interface are kept low enough to cause outward diffusive gradients. The spacing of the pneumatically-induced fractures will vary according to geology, but experience to date has shown the minimum spacing between adjacent fractures to be about 2 ft. Fractures tend to merge together at smaller intervals.

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 remediating the blocks completely.

Section 2

GENERAL TECHNOLOGY CONSIDERATIONS

2.1 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 Studies', 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, 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/often available from past site evaluations)

Rock Formations:

- Detailed visual examination of sample to assess lithology, joint frequently 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 tests, vapor extraction, pumping tests (highly desirable/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. The goal of the pilot test is to determine fracture orientation and dimensions as well as the degree to which air permeability can be increased. Excavation of the fractures is generally not performed, mostly because of the difficulty in finding the fractures which have no sand proppant and which will be affected by the excavation process.

2.2 EFFECT OF SOIL WATER

Pneumatic fracturing was originally conceived as a technology for the vadose zone, although more recently the technology is being extended into perched and saturated ground water zones. Field testing, coupled with laboratory analysis of soil samples, have led to the following observations on the effects of soil water:

2.2.1 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.

2.2.2 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. 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 is still limited, and further research and testing are necessary.

2.2.3 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.

2.2.4 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.

2.3 DEPTH RANGE

The effective depth range of pneumatic fracturing with present process equipment is estimated at 3 to 50 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) which 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/depth gradient to initiate fractures, the depth limit with the present system is approximately 50 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 28 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.

2.4 EFFECTIVE RADIUS

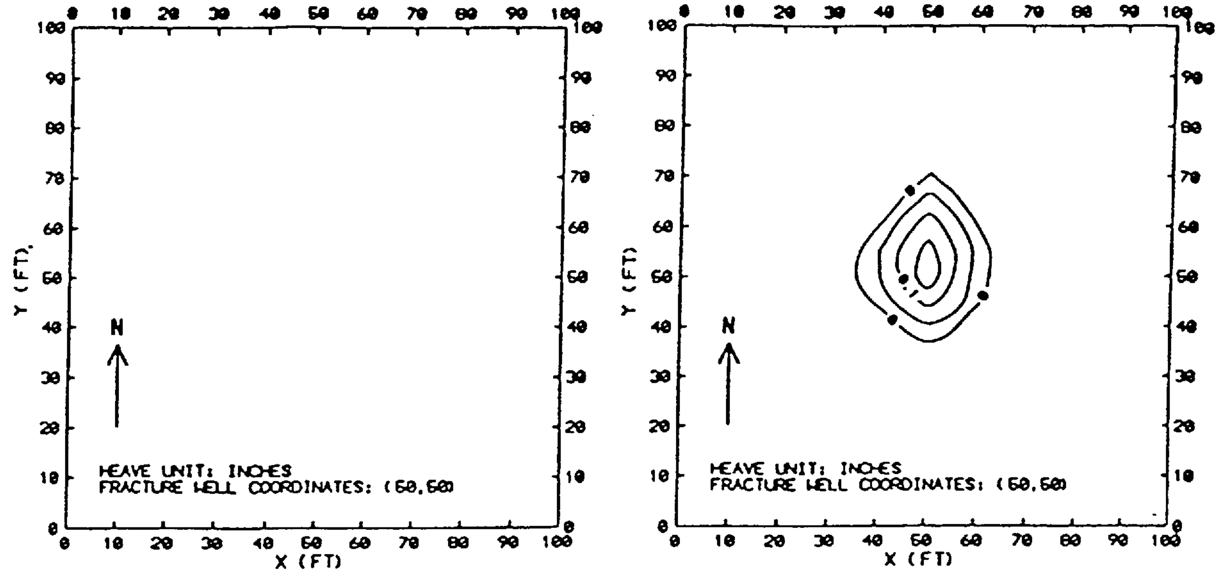
The radial extent of fractures has been monitored by: (1) air communication with outlying monitoring wells; and (2) ground surface heave. Available field data indicate that the effective radius of pneumatic fractures with the present system have typically ranged between 10 and 25 feet measured from the 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 formation 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. F-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 which is apparently related to site geology. Other factors which can affect fracture direction are surface structures and buried utilities.

More experience is required before fracture direction can be adequately predicted. Field tests of a directional nozzle which "forces" fracture propagation in a specific direction are underway. It should also be 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.

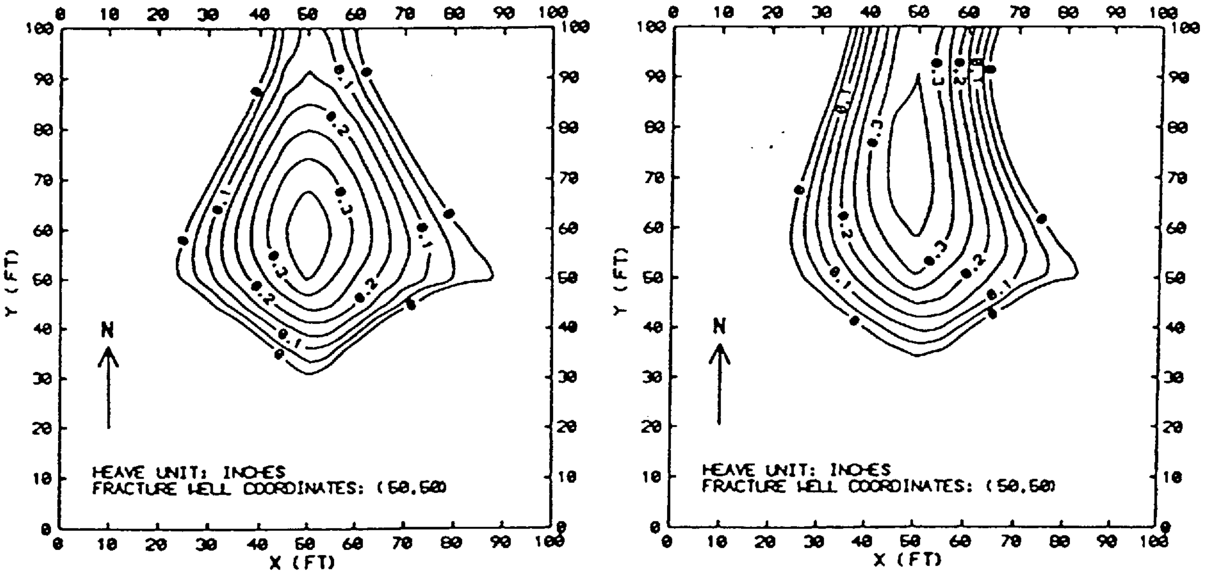
2.5 CONTAMINANTS TREATABLE

Since pneumatic fracturing is an enhancement technology, the types of contaminants which are treatable depend on which other technologies are being used. For example, soil vapor extraction is applicable to volatile and semi-volatiles organic compounds, while bioremediation is theoretically capable of degrading volatile and non-volatile compounds. Integration of pneumatic fracturing with these technologies will not change their basic applicability, but it may extend the



TIME = 0 SEC

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

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 now be 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.

2.6 APPLICABILITY NEAR STRUCTURES 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 has 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 a lesser 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. Some observations on amounts of surface heave and effects on structures are summarized below in Table F-1.

Formation and Fracture Depth	Nearby Structures/ Utilities	Heave During Injection (in.)		Residual Heave (in.)		Remarks
		Max.	Aver.	Max.	Aver.	
Stiff Silty Clay 7 - 11 ft.	Abandoned tank farm over injection area. 6 in. thick reinforced concrete pad with 12 in. thick sidewalls.	1.06	0.35	0.19	0.05	Minor effects on concrete pad and wall. Slight widening and extension of existing cracks.
Fractured Sandstone 9 - 17 ft.	New asphalt pavement over injection area. Buried sewer pipeline approximately 20 ft. away.	0.16	0.12	0.03	0.02	No observable effects on pavement or sewer.
Fill Overlying Silt, Sand and Clay 4 - 7 ft.	One-story warehouse building approximately 9 ft. away. Block masonry on concrete footing.	0.86	0.35	0.34	0.05	No observable movement or effect on building structure. Surface heave data indicated that fractures "reflected" away from building.

Table 1. Summary of Pneumatic Injections Near Structures and Utilities

Section 3

REMEDIAL CAPABILITY IN NATURALLY-FRACTURED MASSIVE LOW PERMEABILITY 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%
- Petroleum hydrocarbons

3.1 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 depths 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 NAPL trapped in the natural fractures, thereby increasing removal rate. Removal of NAPL floating on the water table could similarly be enhanced. Removal of contaminants which 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.

3.2 COMPLEMENTARY TECHNOLOGIES

At this site, pneumatic fracturing could be integrated with any of several in-situ technologies. One approach might be to fracture the formation, and then apply soil 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.

Section 4

REMEDIAL CAPABILITY IN 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)
- Petroleum hydrocarbons

4.1 REMOVAL EFFECTIVENESS

Pneumatic fracturing can potentially be quite effective in this formation, provided air can be made to flow through the induced fractures rather than the sand layer. This will be a function of the thickness of the silty layers; the smaller the dimension, the more likely that air will 'short circuit' through the sand. The silt layer itself will exhibit brittle behavior due to its low moisture content, and fracture patterns should be predominantly horizontal owing to the stratified nature of the formation. Assuming they do not immediately intersect the sand, the induced fractures should improve access to the contaminants, and shorten diffusive paths. These fractures could also accelerate removal of trapped aqueous product. Furthermore, the high pressure injection may also cause some shifting and disturbance of the sand, resulting in air flow improvement in the coarser zones. 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.

4.2 COMPLEMENTARY TECHNOLOGIES

At this site, pneumatic fracturing could be integrated with any of several in-situ technologies. Soil 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.

Section 5

COMMERCIAL AVAILABILITY AND COST

5.1 COMMERCIAL STATUS

Pneumatic fracturing has been pilot tested at several sites over the last 2 1/2 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 already been recommended in several clean-up plans, but has not yet been applied on a production basis to remediate an entire contaminated site. 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, which is Accutech Remedial Systems, Inc (ARS) of Keyport, N.J. It is a non-exclusive license, and discussions are presently underway with other potential licensees. 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 25 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.

5.2 PRODUCTION CONSIDERATIONS

Pneumatic fracturing is a productive process which 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 extraction/injection wells during their construction; (2) flow enhancement in 'dead' zones with low permeability; and (3) flow directionalization. In some cases, it may be necessary to re-fracture the formation at a later time, depending on formation geology and project 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 25 fractures per day is considered attainable with one rig, although pilot studies typically proceed at a much slower rate to allow time for more precise measurements.

5.3 ESTIMATED TIME AND COST TO REMEDIATE A 100' X 100' X 15' SITE

Consider a hypothetical site 100' x 100' x 15' in stratified fine-grained media containing gasoline which has diffused into the low permeability matrix blocks at concentrations of 1000 ppm. The concentration must be reduced to 200 ppm.

5.3.1 Design and Cost

For this situation, assume that wells will be installed on a 20 ft grid, for a total of 25 wells. The primary extraction method will be soil 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 depth 3 to 15 ft. The following is an estimate of the *incremental cost of pneumatic fracturing in excess of primary remediation.*

No. of Pneumatic Injections = 25 wells X 6 injections per well X 1.5 (to allow for multiple injections at selected levels)

= 225 injections

Production Time = 2 days mobilization + $\frac{\text{225 injections}}{\text{20 injections per day}}$ + 1 day demob.

= 15 days (assumes one rig) = 3 weeks

Production Cost = 3 weeks x $ 13,200 per week

= $39,600

Unit Cost = $39,600 / ((100'x100'x15') / 27 = $8.91 per cu yd

Notes: (1) Weekly cost includes $7,200 for equipment and $6,000 for labor.
(2) Monitoring will be performed for operational purposes only.

5.3.2 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 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.

Section 6

SUMMARY

Pneumatic fracturing is an innovative technology which 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 which 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. Fracture initiation pressures for shallow pneumatic fractures are relatively modest: 50 and 150 psi for soil and rock, respectively, at a depth of 20 feet. 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 28 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. However, since a full production clean-up with pneumatic fracturing has yet to be completed, 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.

In general, caution must be exercised in applying any type of soil fracturing technique (pneumatic, hydraulic or impulse) in the vicinity of underground piping or storage tanks until more experience is gained with the technologies.

Section 7

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Section 8

CASE HISTORIES

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: Trichloroehylene (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 extraction 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 the 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 VOC's which had only been detected in trace amounts before fracturing. This suggested that pathways were opened to new pockets of contamination.

Table C1 - 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.

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 ($MeCl_2$)and Trichloroethane (TCA)

Technology: - Enhancement of vapor extraction

- One central extraction well and four peripheral monitoring wells. Separate fracture well.

Duration: 3 days

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 montioring wells and heave sensors)

Comments: Concete slab and containment wall located over injection area. Minor widening and extension of existing cracks noted in concrete.

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

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.

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.

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 effects rainwater infiltration. After experiencing some initial partial closure, fractures still remained viable after 27 weeks with permeabilites 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 inversly proportional to moisture content.

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. An 8 month study was performed to examine fracture longevity.

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, which was subjected to car and truck traffic throughout the study period.

THERMAL TECHNOLOGIES IN LOW PERMEABILITY SOILS

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ABSTRACT

Various thermal technologies, including hot water, heated air, steam, electrical resistance, and radio frequency heating are described and their capability to remove product in two types of low permeability settings evaluated. Of the five processes, steam is given the most attention, primarily because of the experience of the author with this particular technology and its successful application at a field site in California. The paper includes a summary of the typical costs of steam injection as well as case histories where it has been applied in stratified porous media.

Section 1

DESCRIPTION OF THE TECHNOLOGY

Thermal technologies are used to accelerate the in-situ removal of volatile and semi-volatile contaminants by increasing the vapor pressures and thus the evaporation rates. Increasing temperature also results in a decrease in interfacial tension between non-aqueous phase liquid contaminants and water, and an increase in water wettability. In permeable regions, steam injection can lead to the dilution and displacement of pore water (Udell and Stewart, 1992, Vaughan, et al., 1993), thereby removing non-volatile contaminants in aqueous solution. The boiling or displacement of the water during the application of some thermal processes also increases the contact of the contaminant with a gas which can act as a carrier for sweeping volatile and semi-volatile compounds from the soil (Udell and Stewart, 1992). Since desorption of contaminants from solid surfaces also occurs during heating, thermal processes aid in the recovery of compounds adsorbed on the soils. While the drying of the soil during the application of some technologies may lead to increased sorption, the desorption due to an increase in temperature appears to dominate as evidenced by the use of thermal regeneration to remove hydrocarbons from carbon filters.

There are five thermal technologies that have been suggested for the cleanup of subsurface contamination: (1) hot water injection, (2) hot air injection, (3) steam injection, (4) electrical resistance heating, and (5) radio-frequency heating. Radio-frequency (RF) heating and electrical resistance (ER) heating require large electrical power sources at the site to convert electrical energy into subsurface thermal energy. Steam injection, hot water injection and hot air injection require a fuel source and a heater/boiler to add thermal energy to the injected fluid. The differences in energy sources between the various thermal processes impact the costs of each technique. To heat a typical soil from ambient temperature to just below the boiling point of water requires about \$5/yd^3 of electrical energy. For typical soils with a water saturation of 40%, additional electrical costs of \$5/yd^3 are required to evaporate the water. In the case of steam, fuel for the heater/boiler to raise the temperature to 100∞C will cost about \$3/yd^3.

The applicability of each of these thermal technologies is determined by the soil type, water content, and permeability of the soil containing the contaminant. For hot fluid injection, the soil must have a high enough permeability to allow relatively high injection rates to deliver thermal energy to the subsurface. The use of RF or ER heating on the other hand, do not require fluid flow paths to deliver the energy to the subsurface and thus are more applicable to low permeability soils. However, sufficient permeability must exist to allow contaminant removal by soil vapor extraction. Hot air injection, steam injection (followed by vacuum extraction) and electrical heating techniques can also dry the soils, thus increasing contaminant transport to flow paths leading to the recovery system. All thermal techniques require additional wells or surface covers to collect contaminated water, gases, or displaced free product. Each technique must be applied for a sufficient period of time to bring the soil temperature near the extraction wells to values such that the contaminant will not re-condense or become immobilized.

Section 2

GENERAL TECHNOLOGY CONSIDERATIONS

The injection of heated fluids into permeable media will produce different physio-chemical interactions with the contaminant depending on the nature of the injected fluid (gas, liquid, or condensing gas), and the thermodynamic properties of the contaminant. Likewise, the applicability of electrical heating techniques will depend on the character of the contaminated soil, the thermodynamic properties of the contaminant, and the water content of the soil. Each technique has limitations as well as advantages and should be discussed individually before general comparisons are drawn.

2.1 HOT WATER INJECTION

Hot water injection is broadly practicable as long as the soils are permeable. As compared to ground water pumping, hot water injection will lead to an increase in contaminant recovery due to the lowering of interfacial tension and contaminant viscosity (allowing improved free product removal) and the desorption of contaminants from the soils. There is no constraint on initial water content, nor on depth of application. In general, there would be little to gained in the use of hot water to remediate contaminants above the water table and there may be some concern as to the spread of contamination due to leaching. The one advantage of its use in the vadose zone is that the heat remaining in the soils after gravity drainage of the injected water would accelerate remediation by vacuum extraction due to the higher vapor pressures. There is no constraint on its use under buildings or under pavement. However, a significant enhancement in the removal of petroleum products from low permeability soils by hot water injection beyond that of ground water pumping is not to be expected.

2.2 HEATED DRY AIR INJECTION

Hot dry air injection is appropriate above the water table and in soils having sufficient permeability to allow high injection rates. Additional energy costs are needed to operate the compressors. As hot air enters the soil, it is quickly cooled to the local soil temperature, releasing its thermal energy to the porous material. If heated to temperatures significantly above the boiling point of water, a dry zone will evolve near the injection wells and expand with time into the high permeability flow paths. The air will vaporize the interstitial water at the interface between the dry zone and moist zone ahead, carry it downstream, where it will condense as the air moves into regions of lower temperature. The drying of low permeability materials adjacent to the high permeability zones will be diffusion-controlled and slow. Since the heat capacity of air is small, subsurface temperatures will rise slowly. Drying of the soils would be expected only near the injection wells. There is no constraint on the applicability of heated air injection below buildings nor under concrete pavement. The injection of hot air is not limited by depth and could occur below the water table or into soils with high water content. However, limited drying would be expected if hot air were injected below the water table due to water inflow to the heated zone.

The effectiveness of heated air injection to remove petroleum hydrocarbons is similar to that of vacuum extraction, except that the increase in temperature and removal of interstitial water would improve recovery rates. If hot, dry air flows through fractures, drying of the soil near the fracture surface would occur, increasing the gaseous phase saturation, providing a gaseous phase flux from the matrix to the fracture, and increasing the local temperature. All of these effects may lead to significant enhancements in the recovery of dissolved contaminants that have diffused into the bulk soil matrix.

2.3 STEAM INJECTION

Steam injection is applicable both above and below the water table. The permeability of the soil or fracture network must be sufficiently high to allow significant injection flow rates. The heating of the soil by the injection of steam is the fastest of all injection technologies for a given permeability and injection pressure due to the high enthalpy flux of steam compared to hot air or water injection. Furthermore, steam injection has been found to physically displace separate-phase liquid hydrocarbons (Stewart and Udell, 1988) due to high pressure gradients near the steam condensation front.

The technology can be used below buildings if the contaminant is far enough underground to preclude steam from entering the crawl space or floor of the structure. As with any extraction technology, the placement of wells near or under buildings would be problematic. Concrete or asphalt pavement at the surface is considered to be an attribute rather than an obstacle in the implementation of steam injection. No practical limit on depth is envisioned for contaminant cleanup. Oil field experience has shown that steam can be injected to depths exceeding 3000 ft (Konopnicki, et al., 1979). Under typical conditions, steam would be injected at a pressure of about 0.5 psig per foot from the surface to the top of the steam injection interval if fracturing is not desired. Increased depths of operation allow greater operational pressures and greater well spacing. Pressures in the range of 1.0 psig per foot of depth to the top of the injection interval could lead to soil fracturing and upheaval.

Recovery rates of petroleum products decrease as the distillate range increases for all thermal and isothermal vapor phase recovery technologies. Field and laboratory studies have shown that gasoline can be recovered quite readily by steam injection (Basel, 1991, Hilberts, 1985), while diesel recovery rates are significantly slower (Basel, 1991, Van Sickle, 1992). Mid-range distillates such as jet fuel are amenable to steam injection (Volek and Pryor, 1972, Lord, et al., 1987). Recovery rates are enhanced by the drying of the soil during the depressurization occurring after steam injection is ceased (Udell et al., 1991).

The applicability of steam injection to fractured clays and tills is not known. Steam is not expected to readily enter the low permeability bulk matrix. Thermal stresses created by the heating of the confined fractured matrix may also serve to decrease the fracture permeability. On the other hand, if steam were to enter the fractures within the material and if the time of steam contact were large, there is a potential for enhanced recovery of the dissolved contaminant in the bulk soil matrix if the fracture spacing were relatively small. This would occur during the depressurization or vacuum extraction phase of the process where a drying front would propagate into the bulk soil from the fracture face. The vaporized water would serve as a carrier for the vaporized contaminant resulting in high recovery rates.

The benefit of soil upheaval during high pressure steam injection is that new fractures can be created and existing open and dead end fractures can be opened to flow. If properly designed, propped horizontal fractures connected to vertical fractures may be created. The fluid paths could be accessed by the steam during high pressure injection. If steam injection wells were used alternatively as recovery wells, the same fracture system would provide contaminated fluid recovery paths. The use of steam fracturing for contaminant recovery has not been demonstrated in laboratory or field experiments.

The disadvantages of steam injection include (1) the need for relatively high liquid pumping rates to recover the steam condensate, (2) the preferred expansion of the steam zone into high permeability, hydraulically-connected regions, (3) the requirement for relatively close spacing of injection and recovery wells in near-surface installations, and (4) the potential inability to inject steam into lower permeability material at an adequate rates to provide timely heating.

2.4 ELECTRICAL RESISTANCE HEATING

Electrical resistance heating is used to heat low permeability soils that do not have adequate fluid flow paths. To implement this technology, electrodes are placed at regular intervals and voltages on the order of several hundred volts are applied to the electrodes. Power dissipation drops as the distance from the electrode to the fourth 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 DOE Lawrence Livermore design) or six-phase power applied to a hexagonal electrode pattern (the DOE Pacific Northwest Lab 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 provide electrical current paths for the 'injected' electrical energy. ER heating therefore is well suited for low permeability soils. Also as the soil temperature increases, electrical conductivity increases. Thus, for a given voltage difference applied across two electrodes, the current and the heating rate increase with time. However, as temperature increases to the point where the interstitial water begins to boil, the current will drop as the electrical conductivity of the soil decreases. Since the power input due to ER heating is greatest near the electrodes, provisions for electrode cooling are needed.

Recovery wells are required for the removal of volatilized hydrocarbons. The wells would be similar to those installed during soil vapor 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 lower electrical resistivities. Low moisture soils may be problematic since the electrical resistivity is high. 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 safety concerns include the potential for lethal electrical shock and the fire danger from electrical arcs in a situation where hydrocarbon vapors are present. There is no limit on the depth of application.

The ability to remediate higher distillation range petroleum products using ER heating is limited if their boiling point is above that of water. Given the large power requirements to vaporize all the pore water, and the fact 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 will result in an increase in contaminant vapor pressures by factors as high as 40 and ER heating could augment soil vapor extraction in assisting in the removal of volatile components.

2.5 RADIO-FREQUENCY HEATING

Radio-frequency heating is also applicable to low permeability soils (Dev, 1986). The effectiveness of the heating process is greatest in regions near the transmitters where the applied energy is highest and in soils with the largest energy sinks. Since low moisture clays have larger heat sinks than low moisture sandy soils, it is expected that the lower permeability regions will be preferentially heated. However, the presence of pore water has the greatest effect on energy loss and for high water content materials, the energy sinks of various soils will not be significantly different. More importantly, the amplitude of the energy sink decreases orders of magnitude as the soil becomes dry. Therefore, for equal energy input, drying of the soil near the transmitters will increase the rate of energy input to moist soils further away from the dried-out region. The primary mode of contaminant removal is by the vaporization of the soil water and volatile components which can be removed with a soil vapor extraction system.

RF heating implementation would be similar to an ER heating design with respect to the placement of recovery wells and the need to provide vapor collection and cooling equipment. Safety concerns and limitations similar to those listed for the use of ER heating are expected.

Section 3

REMEDIAL CAPABILITY IN NATURALLY-FRACTURED MASSIVELY TIGHT SILTS & CLAYS

To demonstrate remedial capability in naturally fractured massive tight soils, consider the following scenario:

- The clay is extensive and is 30 to 50 m thick
- The upper 2 m of the clay is highly weathered due to desiccation
- The fractures are spaced 1 to 100 cm apart, primarily vertically
- The fractures have 10 to 40 mm apertures
- The clay blocks between fractures are saturated (i.e., there are no continuous air pathways)
- The depth to the water table is 1 to 3 m
- The effective air-filled porosity is <1%.

The scenario presented is one where techniques amenable to shallow remediation are most applicable. Depending on the extent of ground water fluctuation since the time of the spill, any separate-phase hydrocarbon in this scenario would be trapped in near-surface fractures, with perhaps some diffusion into the low permeability matrix blocks. Since capillary suction of a liquid hydrocarbon into the moist tight clay found so close to the water table does not seem likely, the expected transport mechanism is gas phase and/or aqueous phase diffusion of the more volatile and/or soluble compounds into the low permeability matrix.

Given the aqueous-phase solubility of gasoline in water (110 ppm) and a modest organic carbon content of the soil, the soil concentration of the contaminant held in aqueous solution or adsorbed on the grains would not be expected to exceed 50 ppm based on the wet soil weight (Hunt, et al., 1988). Thus the primary target of the cleanup is the free product found in the fractures within the capillary fringe that extends from about 37 cm above the water table to about 1.5 m above the water table. Depending on the local height of free product hydrocarbon floating on the water in the fracture, the free product could extend to soils nearer to the surface. (See sketches of Figure G-1). Surface material weathering and the probable existence of root networks would lead to a greater number of occasionally desiccated channels that would provide additional paths of transport of the hydrocarbon phase deeper into the low permeability material.

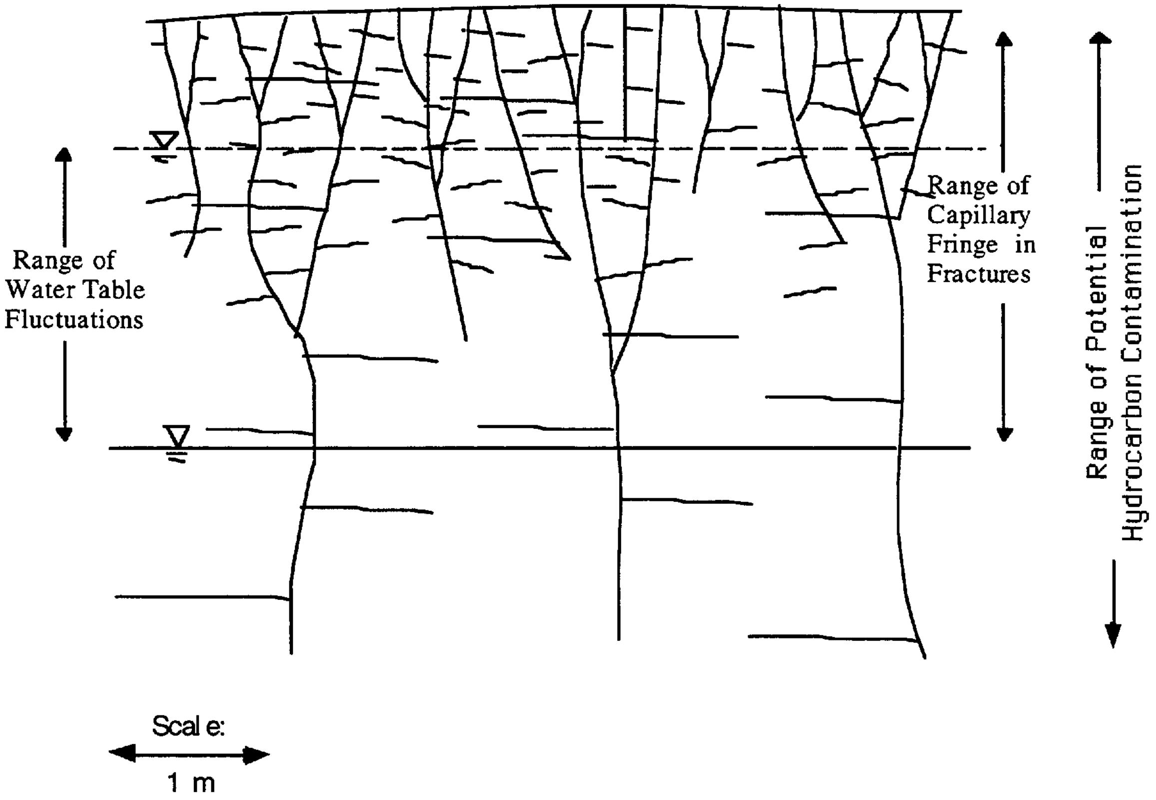

Figure G-1 Sketch of Relationship of Range of Water Table Fluctuation, Capillary Fringe Height, and Hydrocarbon Contamination

There are several workable thermal technologies for this scenario. The application of any one technology would lead to some enhancement in recovery. Combinations of these techniques offers many potentially effective designs. For instance, by placing arrays of RF transmitters or ER electrodes in the soil, and by applying vacuum to the system to recover vapor hydrocarbons and water from the soil, some enhancement in contaminant recovery rates would be gained. Co-injection of heated or unheated air (possibly in the same wells as for electrode cooling) could be an effective complement. However, additional safety equipment, the expense of the RF or ER components, and the energy and equipment required to inject compressed air would be added costs.

The thermal process that is the most intriguing is steam injection combined with induced pneumatic or hydraulic fracturing of the soil. A design might include the combined use of the injection wells as liquid and vapor recovery wells, and a vapor recovery system near the surface (see Figures G-2 and G-3). The cost of installing and operating steam injection through fractures is expected to be somewhat higher than that of hot air or hot water injection through fractures (because of the higher steam-generating costs), but lower than that of electrical heating.

The effectiveness of high pressure steam injection in near-surface fractured media has not been demonstrated in the laboratory or the field. Thus, one can only speculate as to its efficacy. However it seems to offer the potential to recover, at a minimum, free product in the continuous fractures both above and below the current water table. If the continuous fracture network is closely spaced (so that diffusion path lengths are small), it may also be possible to efficiently remove adsorbed and dissolved contaminants in the matrix blocks.

Section 4

REMEDIAL CAPABILITY IN CONTINUOUSLY STRATIFIED LOW PERMEABILITY SOILS

The second geologic scenario to be considered is as follows:

- The soil is stratified with layers ranging from medium sand to silt
- The soil is relatively dry with continuous air pathways in both the silt and the sand
- The sand behaves like a porous medium with regard to fluid flow
- There are some preferential pathways in the silt and in the sand
- The water table is located 3-4 m below the ground surface
- The effective air-filled porosity is 0.2; the total porosity is 0.3

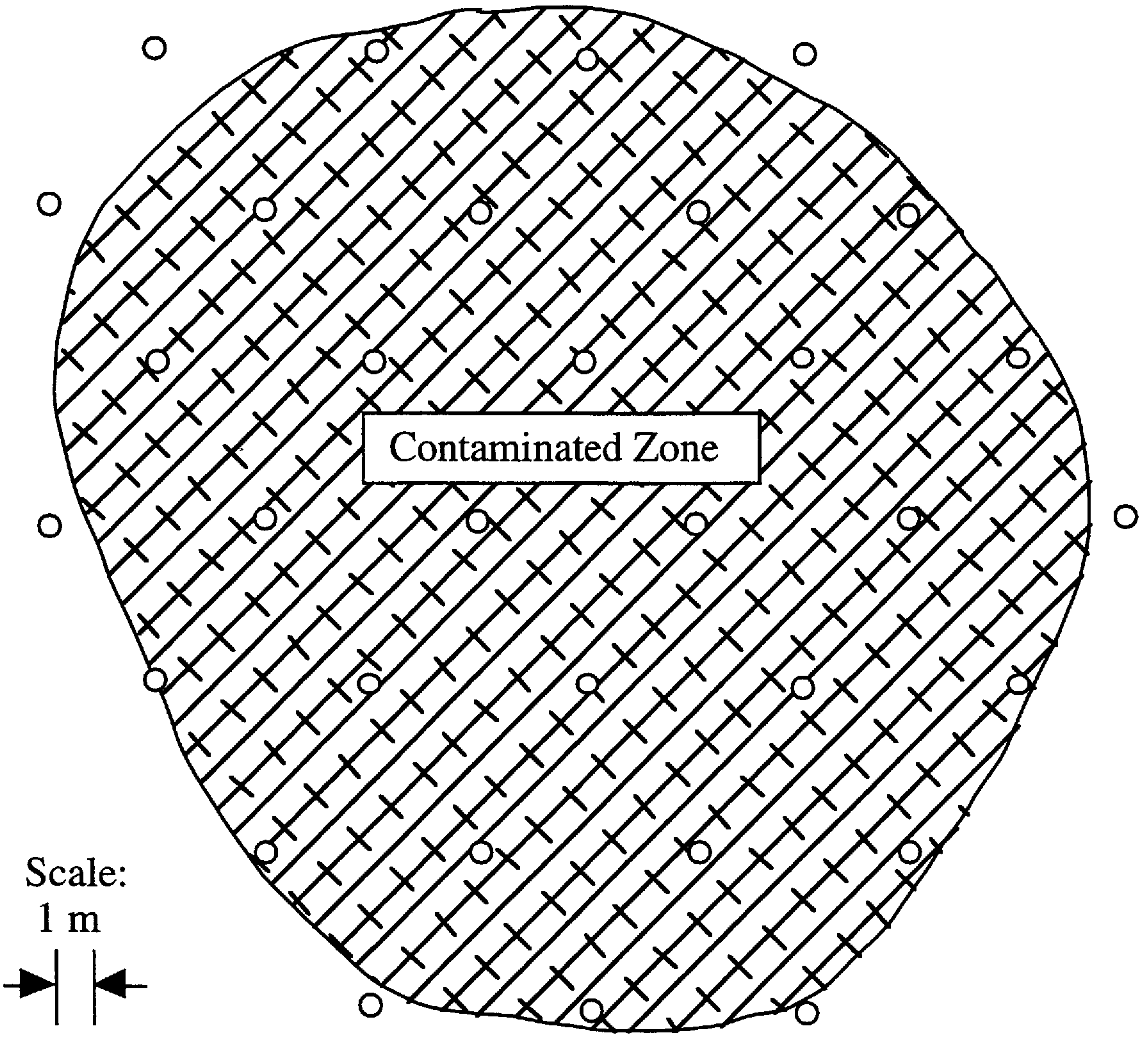

Figure G-2. Layout of Injection/Recovery Wells for High Pressure Steam Injection

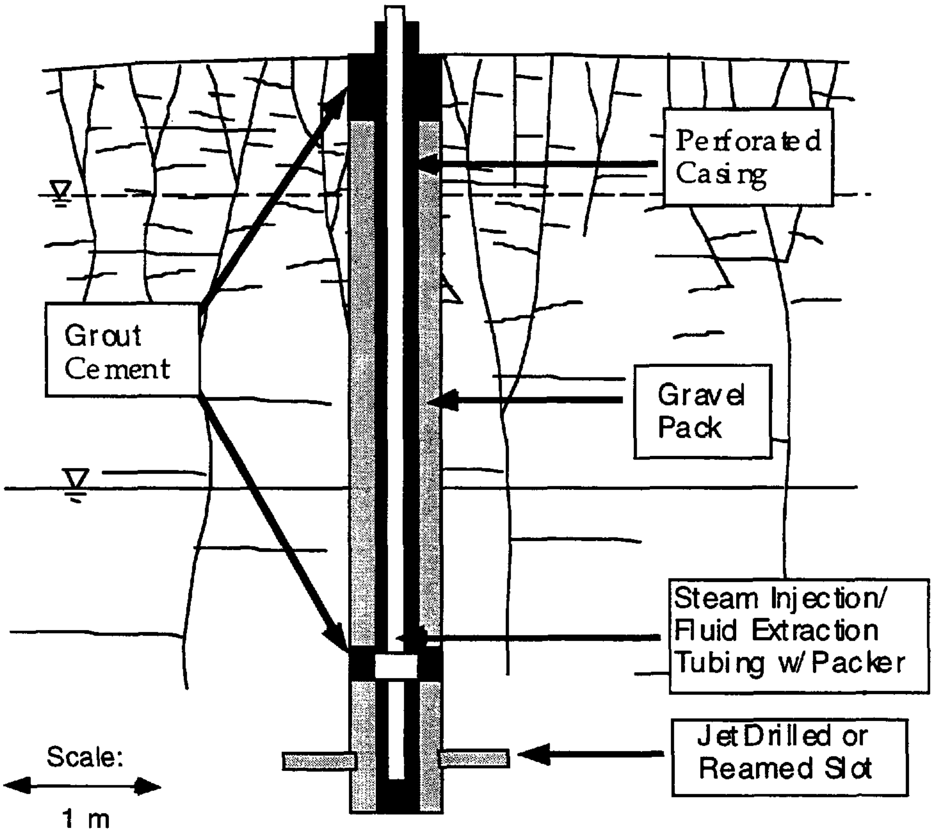

Figure G-3 Conceptual Injection/Recovery Well Design

The scenario presented is typical of many hydrocarbon spill sites. Vacuum extraction at ambient temperature would be the simplest of applicable techniques. The effectiveness of thermal technologies should be gauged against that benchmark. Again, all thermal technologies would provide some degree of enhancement in the recovery rate of the contaminant. Hot water injection is not very promising however since only marginal incremental recovery of mobile NAPL would be expected. Furthermore, the accompanying increase in soil water content would not be desirable for effective removal of the hydrocarbons in the gaseous phase. Heated air injection, with or without ER or RF heating would provide enhanced vaporization rates. Likewise, steam injection would allow mobilization of the NAPL and enhancement of the hydrocarbon vaporization rates. However moisture addition from the accumulation of steam condensate would be a disadvantage.

This site is not as problematic as the previous scenario. The use of any thermal technology would be appropriate if the hydrocarbon mixture is not particularly volatile at ambient temperature. If that were the case, hot air or steam injection should be considered. RF or ER heating could be added for additional enhancement in the hydrocarbon recovery rate. However, the choice of technology is dependent on the hydrocarbon composition, the extent and distribution of contamination, and the surface constraints.

Section 5

COST AND COMMERCIAL AVAILABILITY

Consider a hypothetical site 100' x 100' x 15' in a massive clay fractured formation containing gasoline which has diffused uniformly from the fractures into the low permeability matrix blocks at concentrations of 1000 ppm. The concentration must be reduced to 200 ppm.

The use of high pressure steam injection combined with soil fracturing is used as the basis for cost estimation following the design presented in Figures G-2 and G-3. The volume of contaminated soil is estimated to be about 5,500 yd^3. The number of wells chosen for full-field cleanup is 32, based on radius of influence per well on the order of 4 m. The duration of the cleanup system operation is 50 days, assuming a cleanup rate of approximately 15-20 mg/kg-day. The manpower required for the operation and monitoring of the process is assumed to be, on average, two trained technicians/engineers at the site on a 24-hour basis. The following is an estimated cost breakdown for implementation:

Labor	3 Man-months for Design	$21,000
	16 Man-months Installation/Operation	$112,000
	Labor Total	$133,000
Consumables		
Well installation	(32 wells @ $3200/well)	$102,400
Fuel	(5,500 yd^3 Steam and Flush)	$ 17,000

Treatment System:	Rentals and Purchases	$ 50,000
Monitoring System:	(Temp. Gauges, Data Loggers Tilt Meters, Cameras)	$ 40,000
Total Installation, Utility and Equipment Costs		$209,400
	Total Cost	$342,400

All equipment is commercially available. Some custom installation will be required.

Section 6

CASE HISTORIES

Public data on the use of thermal technologies at the field scale are relatively scarce. Three steam injection studies (Udell and Stewart, 1989, Van Sickle, 1992), three ER heating tests and one RF heating field study (Dev, 1986) were identified. A field demonstration on the combined use of steam injection and electrical heating is currently in progress at Lawrence Livermore National Laboratory (LLNL) and is probably the most valuable experience to consider for the purpose of this paper. Rather than summarize all the other studies, only general observations on them are made.

Field experience with the use of thermal technologies to remove hydrocarbons from the subsurface is extensive from petroleum production operations. The use of thermal technologies to recover hydrocarbons from the subsurface following spills is limited. The use of hot water or hot air injection to augment ground water pumping or vacuum extraction has been shown to provide small incremental recovery rates of free product or vapor hydrocarbons, respectively. The use of RF heating in the field for spill cleanup is limited, but a study of its use at a pilot scale involved very close well spacing (of the order of a few feet) (Dev, 1986). Cost data were not provided. High temperatures above the boiling point of water were measured in the subsurface and excellent recovery of high distillation fraction compounds were reported. Steam injection has been used several times in the

Netherlands, and three times in this country (Udell and Stewart, 1992). The data show that the steam zone expansion in the subsurface is controlled by the subsurface geology. In all field projects, the petroleum products are preferentially recovered in the gaseous phase carried with the flowing steam or non-condensable air.

The LLNL project is focused on the removal of gasoline found both above and below the water table. The subsurface geology consists of alluvial deposits, with layers of high permeability interspersed with clays and clayey silts. A thick gravel layer was found below the water table from about 35 m to 42 m in each surveyed well. The gasoline was found as a separate phase in an area about 30 m in radius. The vertical distribution ranged from 20 m below the surface to about 35 m, with significant smearing due to major ground water elevation fluctuations. Separate phase gasoline was found in the deep water-bearing zone nearly 8 m below the water table. This contaminant distribution rendered the use of technologies such as ambient temperature vacuum extraction or ground water pumping impractical in terms of duration to meet cleanup targets.

There appeared to be two major high permeability layers at this site: the deep gravel layer and an upper unsaturated zone consisting of intermingled sands, silts, clays and gravels. A clay layer of variable thickness separated the two permeable zones. Six injection wells were placed around the perimeter of the area contaminated by separate phase gasoline; two recovery wells were completed near the center of the zone. The injection wells were constructed to allow separate injection into the upper and/or lower permeable regions. The recovery wells were completed over the entire height of the contaminated zone.

In late November, 1992, 3-phase electrical heating began and was operated intermittently for about two months, resulting in the input of 202 MW-hrs of thermal energy in a site with a diameter of about 200 ft and a depth to 150 ft. The energy dissipation was non-uniform spatially. The continuity of low permeability layers was an important element in the distribution of current. Preferential heating was observed in the low permeability zone. Figure G-4 shows a temperature log in a region of effective electrical heating. The single broad temperature peak was observed in a region determined to be clay from geological logs.

Beginning in February 4, 1993, steam was injected below and above the water-table in an effort to remediate gasoline-contaminated soil within the water-bearing zones. After the first 34 days of continuous steam injection, 8.6 million kilograms of steam had been injected into the subsurface, and the steam zone had expanded to an estimated volume of 50,000 m^3. Steam was injected first into the lower gravel layer below the water table for 14 days. Steam broke through at the recovery wells at about 10 days. After 14 days, the injection of steam began 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 at about 23 days. 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.

Temperature logs in each of the 11 temperature monitoring wells were obtained daily. Sample temperature profiles inside the ring of injection wells at various stages of steam injection are shown in Figures G-4 through G-7. The temperature logs from wells outside the injection ring showed similar development of the steam zone in that region. However, with the exception of one location, the steam zone outside of the injection pattern was limited to the well-defined high permeability flow paths.

Figure G-4 shows the temperature profile of a location equi-distance between two injection wells and an extraction well 10 days after the beginning of steam injection into the lower zone. For reference, the lithology log is superimposed to show the correlation between the geologic features and the movement of the steam zone. The broad peak centered at 21 m was due to electrical heating that occurred for 30 days prior to steam injection. The sharp peak at about 37 m is the measured temperature response to the presence of steam in the lower gravely sand layer.

Figure G-5 shows a temperature log at a location directly between an injection well and a extraction well after about 21 days of steam injection. Here one can see four different steam layers that are mostly correlated with the high permeability zones as taken from the geologist logs. However, steam did appear in regions where one would not expect significant flow such as the peak at about 26 m. (This possibly was

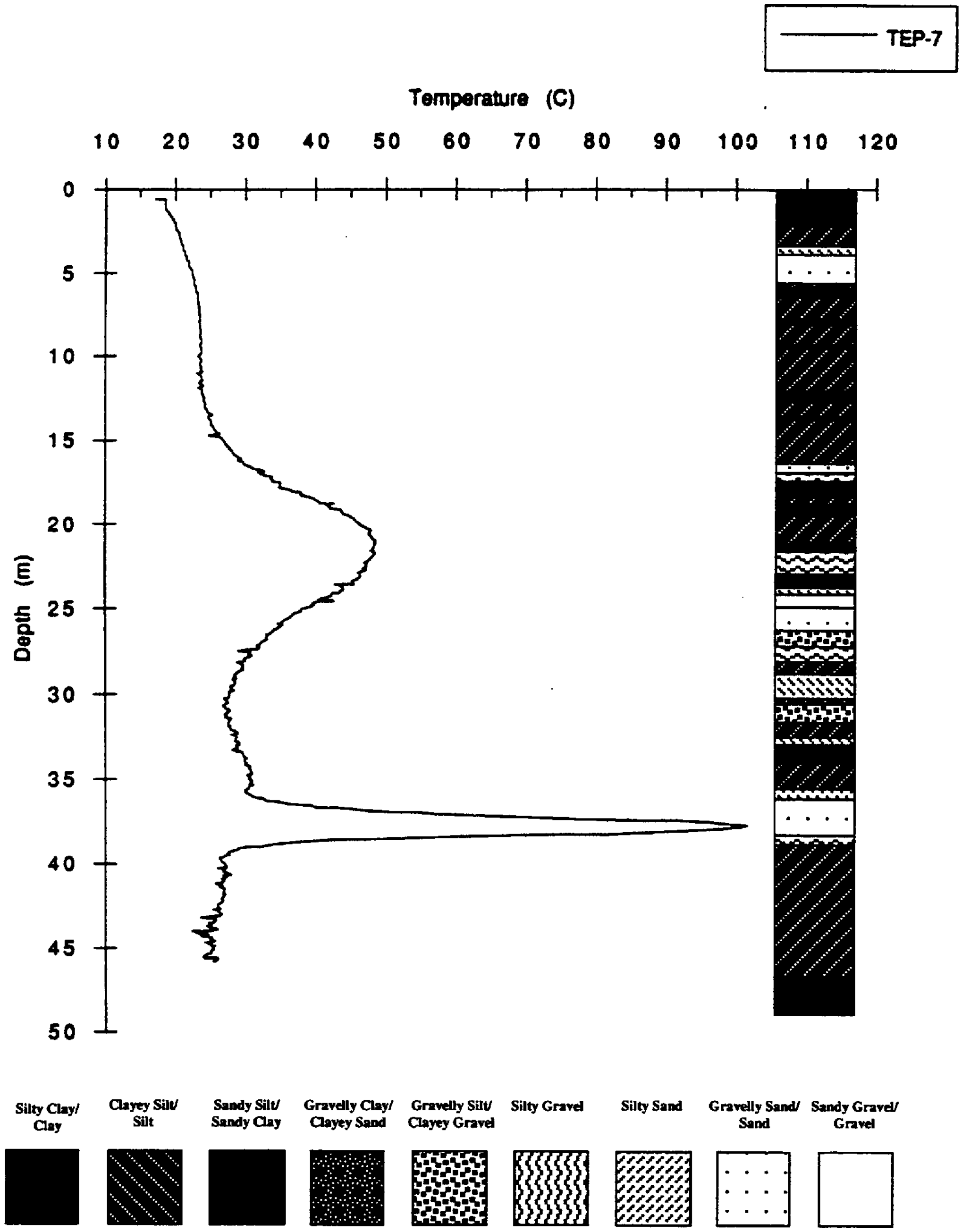

Figure G-4 Temperature log in interior monitoring well (TEP-7) taken 10 days after the initiation of steam injection. The broad peak centered at about 21 m is due to a month of electrical heating. Electrical heating occurred preferentially in the low permeability regions. The sharp peak observed at 37 m is the response to the flow of steam through the gravel layer below the water table.

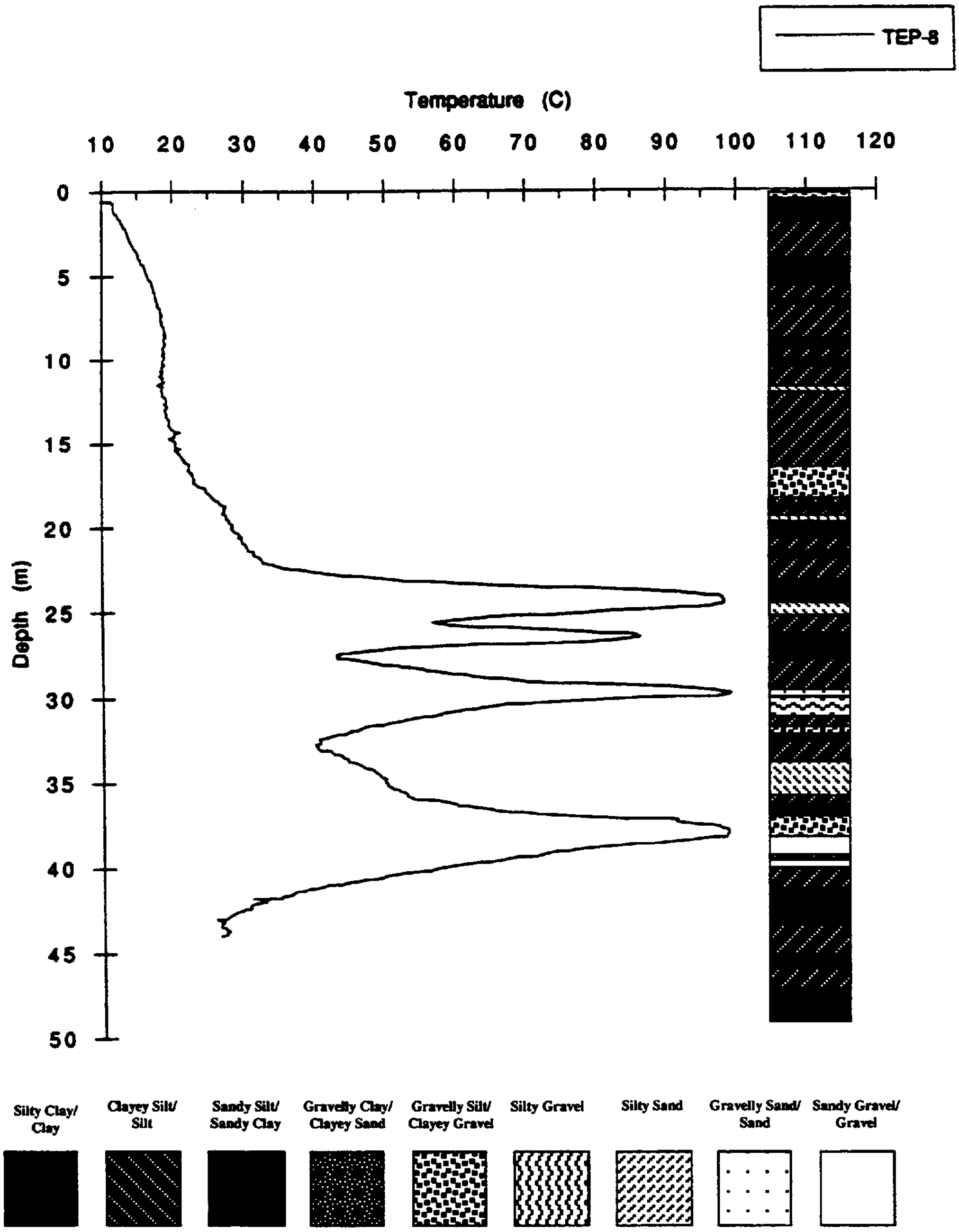

Figure G-5 Temperature log in an interior monitoring well (TEP-8) taken 21 days after the initiation of steam injection. Each peak shown corresponds to the flow of steam (or hot condensate) through the primary flow paths. The water table was originally at about 30 m.

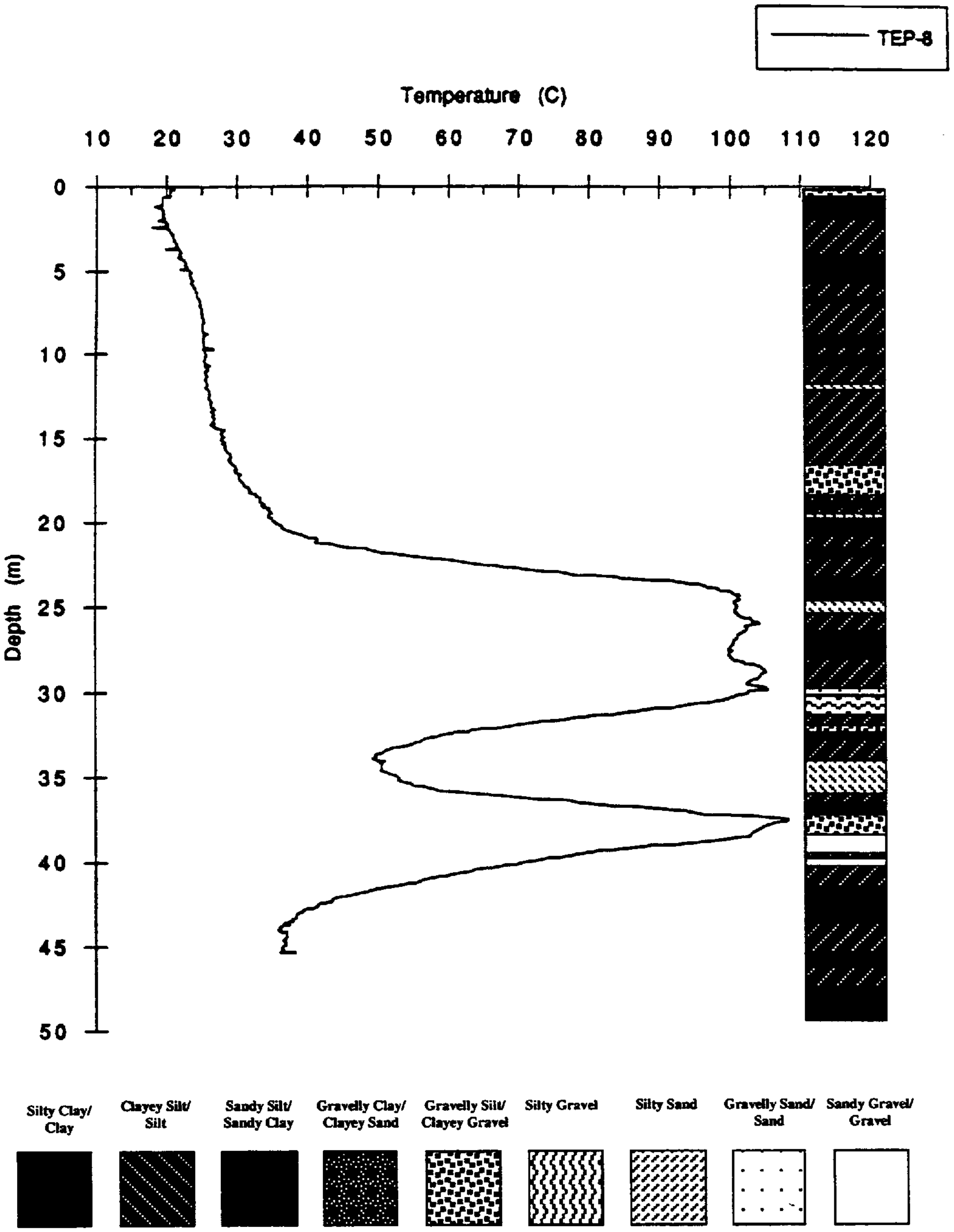

Figure G-6 Temperature log in TEP-8 taken 32 days after the initiation of steam injection. Heating by conduction allowed temperatures in thin (< 2 m) low permeability zones between layers containing steam to approach the steam temperature.

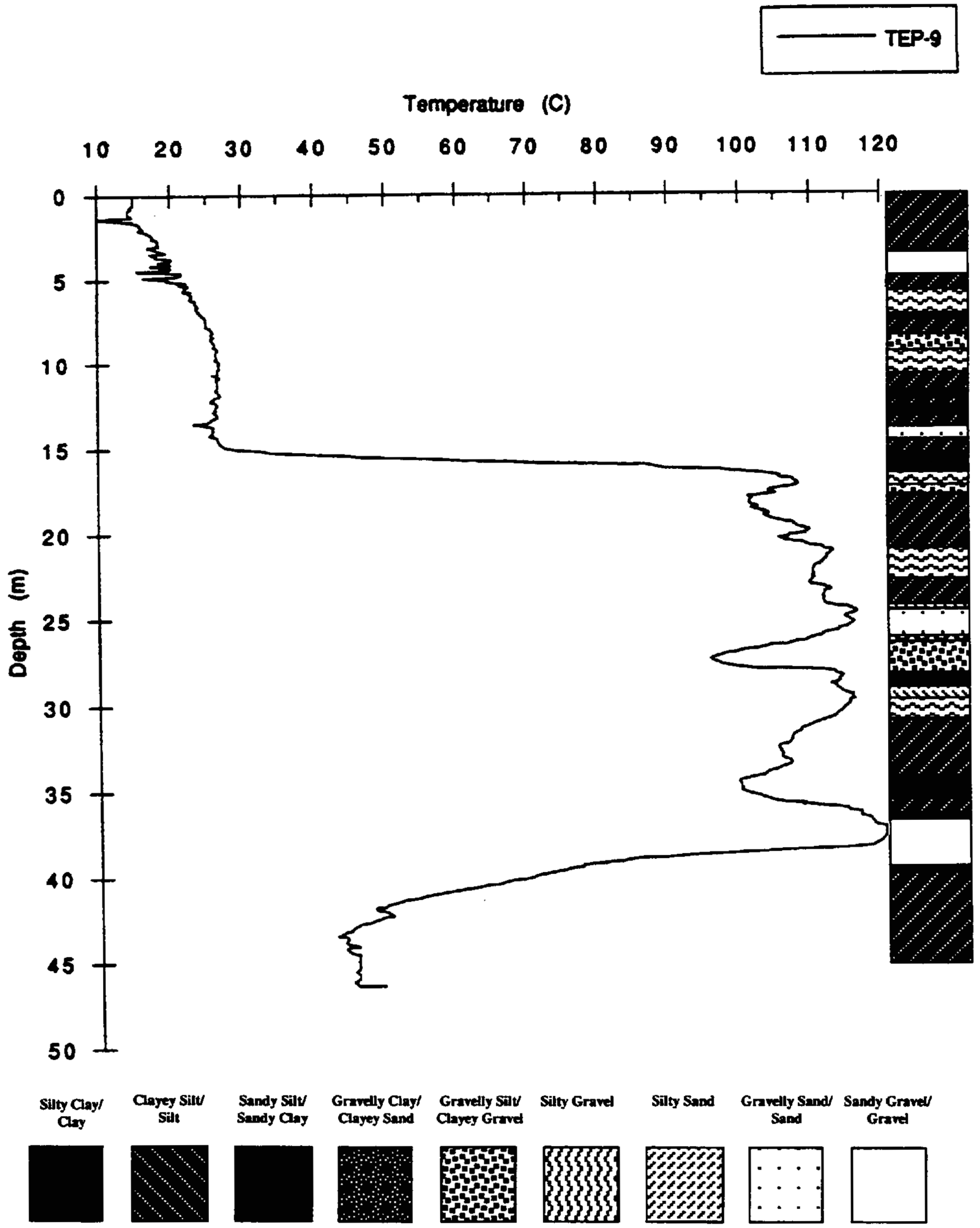

Figure G-7 Temperature log in an interior monitoring well taken 29 days after the initiation of steam injection. Relatively uniform heating of the target zone from 15 to 40 m was observed.

a thin sand layer not appearing on the geological logs.) Figure G-6 shows the temperature profile in the same well after an additional 12 days of steam injection. Comparison between figures G-5 and G-6 reveals that conduction effectively brings the low permeability layers up to steam temperature if the layer is contacted on top and on bottom by steam and if the thickness of the low permeability layer is sufficiently small. In this case a layer 2 m thick was heated to steam temperature by conduction in 12 days. Steam heating of the target zone was more uniform at other locations. Figure G-7 shows a temperature log of a location on the other side of the recovery wells from those of Figures G-4 and G-5. Here, relatively uniform heating of the zone between 15 m and 40 m was observed.

The recovery rates of gasoline in the various fluid phases as a function of time are shown in Figures G-8 to G-10. As illustrated in these figures, the highest rates of the gasoline recovery were observed in the gaseous phase, either in the air stream leaving the condenser or as liquid hydrocarbon in the condensate. The recovery rates of gasoline in solution and as a separate phase liquid from the extraction wells shown in Figure G-8 were increased due to steam injection. An increase in the gasoline solubility with temperature enhanced the recovery by ground water pumping. Also, the displacement of the liquid gasoline ahead of the steam zone allowed free product recovery just before steam break-through. 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.

The instantaneous recovery rates of gasoline as free product leaving the condenser (as illustrated in Figure G-9) were the highest of all fluid streams. The peak occurring at about 15 days corresponds to the time when steam was being recovered from the gravel zone below the water table. The values shown from 10 to 20 days were estimated from the actual steam condensation rates and the gasoline concentrations measured in the steam condensate from 20 to 30 days. The high rates observed from 23 days to the end of this reported period correspond to the time beyond steam break-through in the upper zone. Unlike the lower zone below the water table, steam and entrained hydrocarbon vapors can be continuously recovered from the unsaturated zone long after steam injection has been stopped. The rates of gasoline recovery from the condensate were also high at the end of the period of steam injection when only soil vapor extraction and ground water pumping were

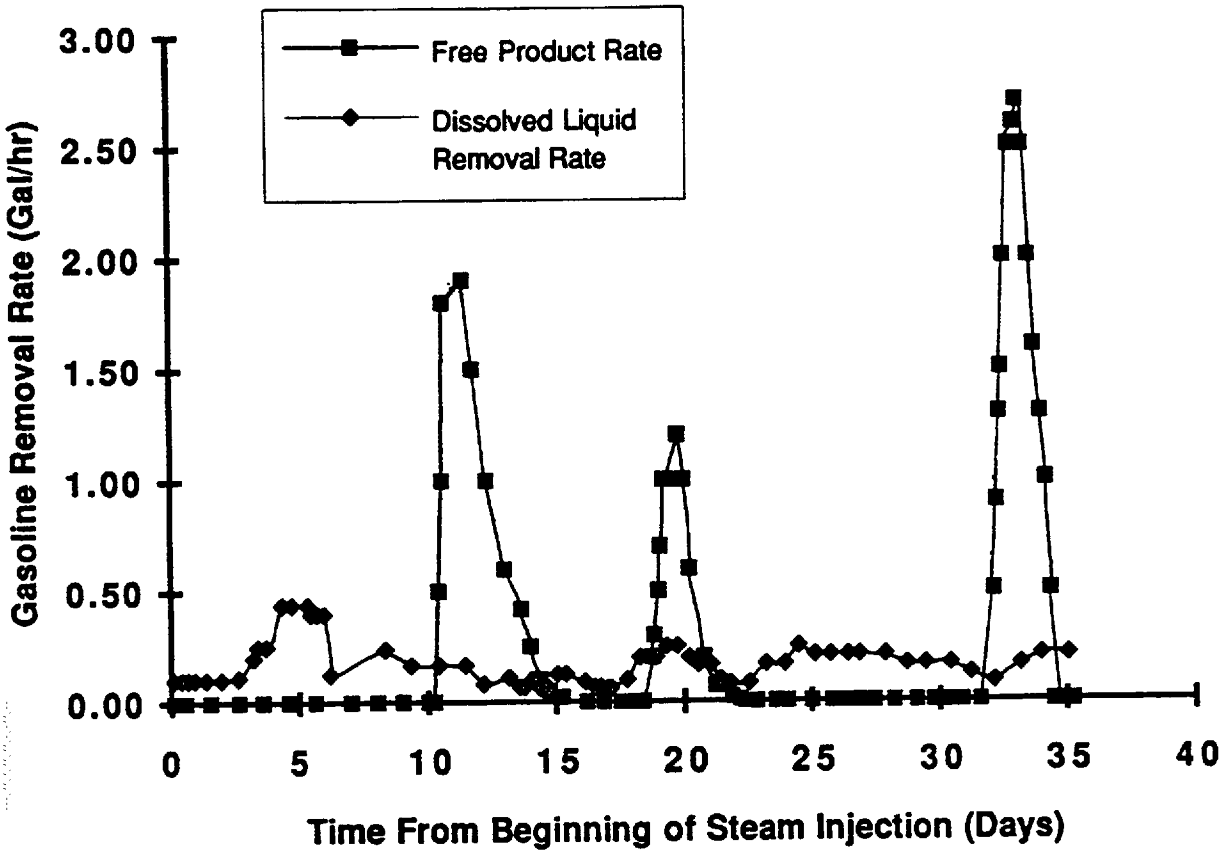

Figure G-8 Recovery rates of gasoline in solution and as a separate phase liquid from the extraction wells. An increase in the gasoline solubility with temperature enhanced the recovery by ground water pumping. The displacement of the liquid gasoline ahead of the steam zone allowed free product recovery just before steam break-through.

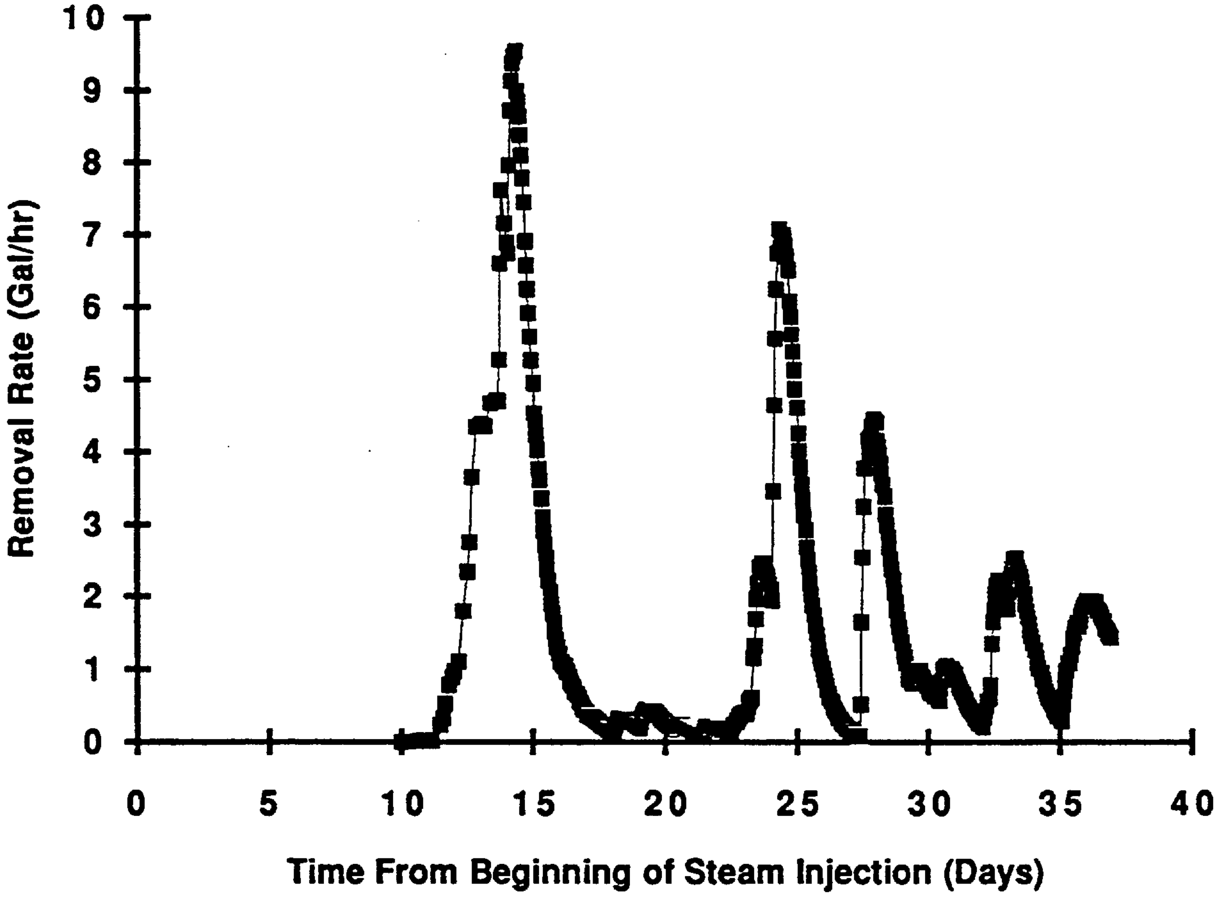

Figure G-9 Recovery rates of gasoline as free product leaving the condenser. The peak occurring at about 15 days corresponds to the time when steam was recovered from the gravel zone below the water table. The values shown from 10 to 20 days were estimated from the actual steam condensation rates and the gasoline concentrations measured in the steam condensate from 20 to 30 days.

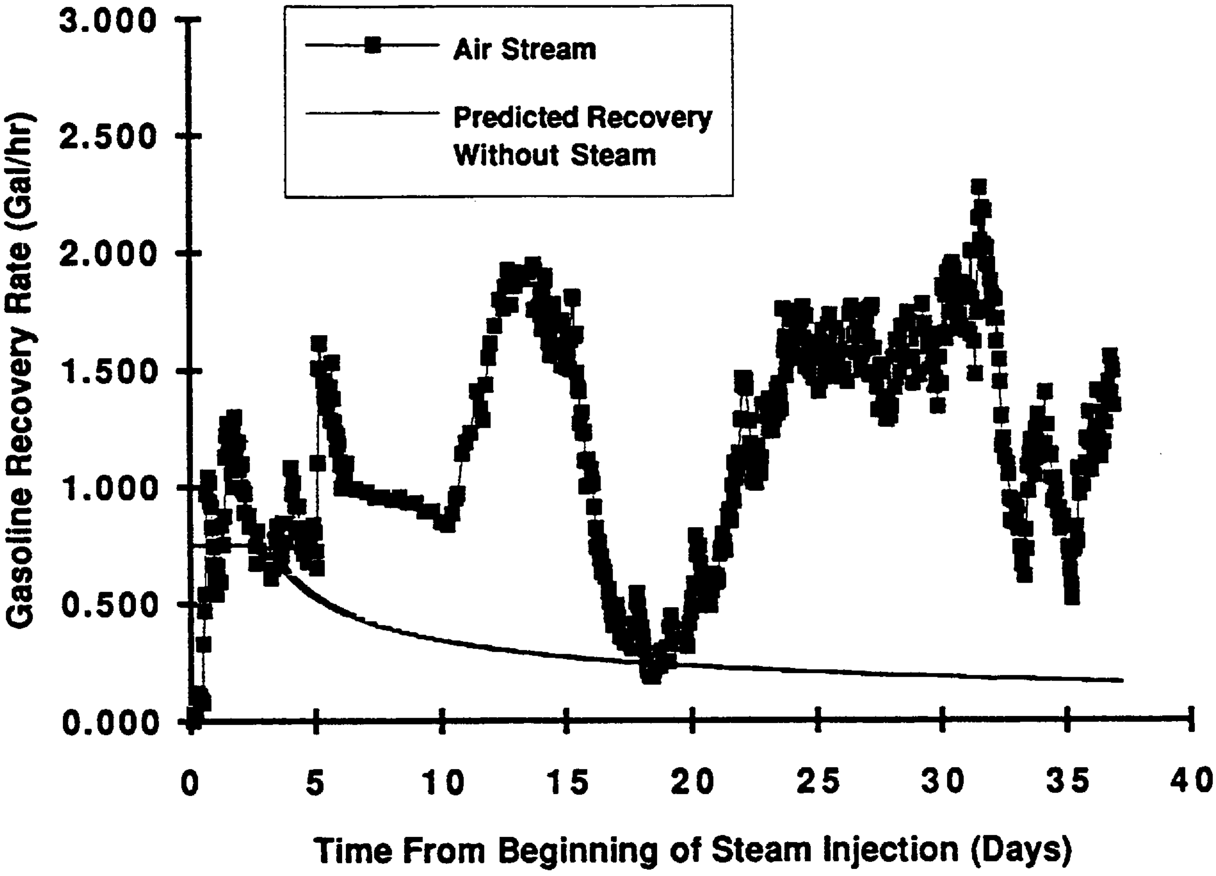

Figure G-10 Recovery rates of gasoline in the air stream as well as projected recovery if no steam were injected. Concentrations of gasoline vapor in the air leaving the condenser were at saturation values when separate phase gasoline was present in the condensate.

occurring. However, due to the air treatment rate limitations of the carbon system, high vapor phase pumping rates could not be maintained during that period.

Relatively high sustainable recovery rates were found in the air leaving the condenser when the steam condensate and condensed gasoline recovery rates were also high as shown in Figure G-10. This is due to the fact that the concentrations of gasoline vapor in the air leaving the condenser were near saturation values when separate-phase gasoline was present in the condensate. For comparison, the projected gasoline removal by vapor extraction alone without the enhancement of steam injection is also shown in this figure. These predictions assume an initial period of constant gasoline concentration at the initial measured values, followed by a period of concentration decline typical of diffusion-controlled evaporation with the same recovery rate as was measured on the 19th day. On the 19th day, the system was operating in a manner which would be characteristic of soil vapor extraction alone. As shown, significant increases in the air phase gasoline recovery are observed due to steam injection.

The cumulative gallons of gasoline recovered as a function of time are shown in Figure G-11. For comparison, the recovery expected by vapor extraction alone without steam injection is also shown. Steam injection increased the amount of gasoline recovered by a factor of 10 over that expected by vapor extraction alone after 30 days of electrical heating.

Soil gas and water pumping operations began again on May 24, 1993. The recovery rates of gasoline were found to be seven times higher than those observed at peak periods during the initial 35 days of operation. The increase is due in part to the installation of additional vapor treatment capacity. However, the hydrocarbon concentrations in the gas stream recovered from the vacuum wells were observed to be significantly higher after the 10 weeks of idle time. The increase in concentrations is presumed to be due to sufficient time for heat and mass transfer to occur over the length scales characteristic of the heterogeneities. On July 1, 1993, the injection of steam at LLNL was discontinued. An additional 5,500 gallons of gasoline was recovered during the second six-week period. Extraction operations continued at the site until the vapor hydrocarbon concentrations decreased significantly from the high levels observed as of July 1, 1993.

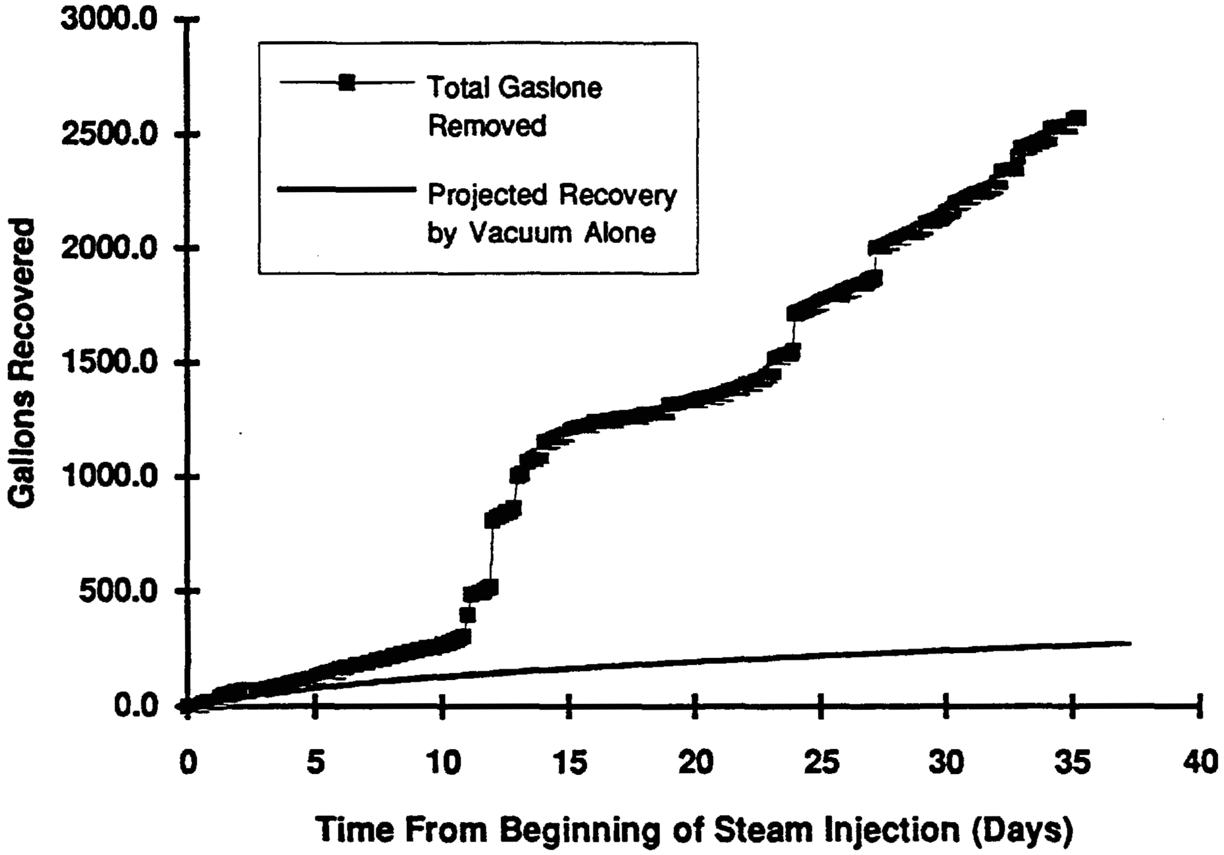

Figure G-11 Cumulative gallons of gasoline recovered as a function of time. For comparison, the recovery expected by vacuum extraction alone without steam injection is also shown. Steam injection increased the amount of gasoline recovered by a factor of 10 over that expected by vacuum extraction after 30 days of electrical heating.

Section 7

SUMMARY

Thermal technologies have demonstrated potential for petroleum product recovery from contaminated sites. The ability to increase the temperature of the subsurface can have dramatic effects on the recovery rates compared to ground water pumping or soil vapor extraction. The primary weakness in the use of these techniques is the difficulty in providing uniform heating at sufficient rates. Field experience is limited, so procedures have not been developed for routine application. Thus, comparative quantitative standards of performance have yet to be determined.

The implementation of thermal technologies in near-surface fractured low permeability material suffers from the same mass transfer limitations plaguing any in-situ technique. At this time the most promising approach appears to be coupling high pressure steam injection with hydraulic fracturing. While conceptually sound, this technique has never been tested. If shown to be successful in opening steam and fluid-flow paths through the fracture network however, it is viewed as offering the most reliable thermal approach in low permeability media.

Section 8

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SURFACTANT-ENHANCED SOIL FLUSHING IN LOW PERMEABILITY MEDIA

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ABSTRACT

The use of soil flushing, enhanced by the application of surfactants, is described and its capability to remove product in two types of low permeability settings evaluated. The paper includes a summary of the typical costs of surfactant flushing as well as case histories where it has been applied in porous media.

Section 1

DESCRIPTION OF THE TECHNOLOGY

1.1 OVERVIEW

Surfactants have the potential to enhance conventional 'pump-and-treat' techniques intended to remove organic contaminants from the subsurface. When the contaminants are present as a non-aqueous phase liquid (NAPL), surfactants can promote the NAPL's dissolution by increasing its components' solubilities in the flushing solution, or these surface-active additives can facilitate the NAPL's displacement via a reduction in interfacial tension. In addition, when hydrocarbons are sorbed to aquifer solids, surfactants can promote contaminant desorption by decreasing the solid/water partition coefficient. At lower concentrations, surfactants can also promote the release of soil colloids, which are very small particles that are larger than dissolved solutes but that remain suspended in water. These colloids may carry sorbed hydrocarbon contaminants.

There are some caveats, however. The most important is that successful surfactant flushing is limited to cases where the surfactant flush has access to the liquid or sorbed hydrocarbon contaminants. Other conditions for successful flushing include: (1) thick emulsions must not form at the NAPL-flush interface for they would impede NAPL solubilization and fluid propagation; (2) surfactant loss due to precipitation, sorption, or biodegradation must not be excessive; (3) there must not be excessive offsite migration of harmful surfactant or mobilized chemicals; (4) surfactants must not release so many colloidal particles that the porous medium becomes plugged; and (5) the surfactant should be recyclable. Laboratory experience indicates that many of these obstacles can be overcome when the site-specific geochemistry and surfactant behavior are well understood (Fountain *et al.*, 1991; Harwell *et al.*, 1992), although this has proved more difficult to demonstrate in the field. However, it must be reiterated that if the flushing solution lacks access to the contaminant due to hydraulic isolation, the technique will be of limited effectiveness.

1.1 SURFACTANT-ASSISTED DISSOLUTION

Of the mechanisms cited above, the dissolution mechanism has received the most attention in the literature for environmental applications. In contrast, reduced interfacial tension has been the primary goal for enhancing oil recovery in petroleum reservoirs. Surfactants promote dissolution due to their amphiphilic structure, meaning that the molecules contain a soluble and an insoluble segment. Above a threshold concentration (termed the critical micelle concentration, or CMC), micelles form from these amphiphilic molecules. This is a phenomenon unique to surfactants that involves the self-assembly of molecules into dynamic clusters called micelles, which are typically 3-4 nm in diameter (West and Harwell, 1992). Many organic compounds will partition into the insoluble or hydrophobic (oily) interior of these micelles. In the case of extremely hydrophobic contaminants, the apparent solubility can be dramatically increased with a surfactant additive. Solubility enhancement is dependent on the concentration of surfactant in the micellar form (X_m, mol/liter) and the partition coefficient of the chemical distributing between the surfactant and the aqueous phase (K_m, liters/mol):

$$S_{apparent} = S\,[1 + (X_m K_m)]$$

where $S_{apparent}$ is the contaminant's solubility (g/liter) in a micelle-containing solution, and S is the pure phase solubility of the compound in water (g/liter). For aromatic hydrocarbons and with a sodium dodecyl sulfate surfactant, K_m is approximately 15% of the K_{OW} (Jafvert *et al.,* 1991). Assuming a flushing solution containing 0.1 M sodium dodecyl sulfate (SDS) micelles (i.e., 2.6 weight percent), this implies that the apparent solubility of benzene, toluene, and C2-benzene would increase 3x, 8x, and about 20x, respectively. Therefore, the partitioning of a contaminant into micelles increases with decreasing contaminant solubility and the payoff for using surfactants increases dramatically for contaminants with low aqueous solubilities.

1.3 SURFACTANT-INDUCED DISPLACEMENT

The second mechanism of surfactant-induced NAPL removal is that of displacement, a mechanism that has the potential to displace a large portion of the NAPL ganglia (i.e. isolated irregular residual aggregates) with a single pore volume flush. Surfactant solutions bring about NAPL displacement by reducing the interfacial tension between the aqueous and non-aqueous phases, enabling the force of the flushing solution to move relatively large NAPL blobs. Over the last twenty years, specialty surfactant formulations have been developed which achieve ultra-low interfacial tensions (IFT) at the NAPL-flush interface (West *et al.,* 1992). These systems may also employ long-chain alcohols or co-solvents to enhance the performance of the surfactant. Such surfactant systems reduce the interfacial tension low enough that individual NAPL blobs are able to be displaced from relatively coarse materials like a medium grain sand.

When applied in the presence of NAPL or oil, these surfactant systems form microemulsions with the NAPL. Although such emulsions may promote subsurface removal of the NAPL, subsequent surface treatment may be impeded due to the difficulty of breaking the oil-in-water emulsion in above-ground facilities. Also, these systems are difficult to control because they are very sensitive to the salinity and temperature of the flushing water (Fountain *et al.,* 1991; West *et al.,* 1992). In instances where there is inconsistent groundwater quality, it may be quite difficult to design a surfactant system to do the job. An additional drawback of these ultra-low IFT surfactant systems is that they involve the injection of large quantities of chemicals (about 10% of the flush volume). One often noted 'side effect' of using surfactant flushing is that the practice may encourage undesired migration. For instance, the lowered surface tension can have the effect of allowing gravity to mobilize the denser-than-water NAPL downward (Fountain *et al.*, 1991).

1.4 SURFACTANT-INDUCED DESORPTION

Sorbed hydrocarbon contaminants can also be removed by surfactants. Just as surfactants can significantly increase the apparent solubility of hydrocarbons, they can also significantly increase a contaminant's partitioning to the aqueous phase from the solid phase. One can assess a surfactant's impact on flushing efficiency by examining the chemical's effect on the contaminant's retardation factor. For example, if one were flushing a 40 cm thick layer of silt exhibiting a fractional organic carbon content, f_{oc}, of 1% and porosity of 30% with water containing 0.5 M sodium dodecyl sulfate, the retardation factors calculated for benzene, toluene, and a representative C2-benzene would all be about 1.4 (as opposed to 5, 20, and 60, respectively, in the absence of the SDS). Note the increasingly dramatic impact of the surfactant for the more hydrophobic chemicals. With a retardation factor with the surfactant of nearly one, the chemicals would flow through the subsurface at approximately the same velocity as the flushing solution.

1.5 SURFACTANT-INDUCED COLLOID MOBILIZATION

Surfactants may also be able to promote the removal of contaminants by mobilizing colloids that contain sorbed hydrocarbons. For example, Ryan and Gschwend (1992) studied soil systems consisting of negatively charged silicates and clays and positively charged goethite (iron oxides) secondary deposits. They found that colloids were mobilized at very low concentrations (only about 0.002 weight percent) of an anionic surfactant (dodecanoic acid). Presumably, colloid release followed a surfactant-induced modification of the goethite's surface charge. Colloid mobilization affects the subsurface system in three important ways. First, it depletes the soil system of immobile colloidal phases (e.g., clays, iron oxides, humic substances) that may have served as sorption sites. Like the micellar-assisted transport, such colloidal phases may also increase the contaminants in the mobile phases. Finally, colloid mobilization may increase the permeability of the soil. Of course, when generating colloids, one needs to be careful that they do not plug the soil matrix.

1.6 UNDESIRABLE ASPECTS OF SURFACTANT BEHAVIOR

In addition to their desirable processes, surfactants may engage in other behaviors which compromise their overall effectiveness. For example, anionic surfactants may complex with ions in solution and subsequently precipitate, reducing the amount of effective surfactant molecules in solution and perhaps clogging the soil matrix (West *et al.*, 1992). A second problem is that surfactants may sorb to the soil matrix. The effect would be, not only to reduce the amount of effective surfactant concentration in solution, but also to increase the sorption of hydrocarbons onto the soil matrix (Vigon and Rubin, 1989; West *et al.*, 1992). Other possible fates include biological degradation (Gledhill *et al.*, 1991), utilizing oxygen that would otherwise be available for hydrocarbon bioremediation, and possibly the creation of by-products or intermediates that can be quite toxic (even if the surfactant itself is not; Giger *et al.*, 1984).

Section 2

GENERAL TECHNOLOGY CONSIDERATIONS

2.1 THE EFFECT OF HIGH SOIL WATER CONTENT

The effect of high soil water content on contaminant removal efficiency is not directly relevant for surfactant flushing because flushing will saturate the soil. A secondary consideration is that the soil moisture content may affect the location of the contaminant and thereby affect the efficiency of cleanup indirectly. Soil moisture will tend to be concentrated in the finer soil fraction, and the NAPL will tend to reside in the coarse fraction. If the soil moisture is very low, however, the NAPL will preferentially reside in the fines and be more difficult to remove.

2.2 ACCESSING UNDER BUILDINGS

Surfactant flushing for accessing under buildings and concrete pavement will generally require a horizontal flushing technique. In the case of saturated zone contamination, effective flushing may require that slurry walls and trenches be built to prevent offsite migration of the surfactant, though they would not be necessary if effective hydraulic control of the flushing solution can be maintained. Slurry walls would probably not be needed for vadose zone flushing; the key requirement is to design the system to adequately saturate the vadose zone and assure uniform coverage.

2.3 MAXIMUM DEPTH AND THE SIGNIFICANCE OF SOIL TYPE

There is no maximum depth beyond which surfactant flushing is infeasible. Since soils vary with respect to their surface charge, organic carbon content, mineralogy, and texture, the behavior of a given surfactant system will depend on the soil qualities and the groundwater qualities. The interrelationships between these variables are quite complex; the concerns relevant to surfactant usage are described as follows:

2.3.1 Surfactant Sorption

Surfactant sorption is a function of the surfactant properties (its ionic character and hydrophobicity) and soil qualities (e.g., surface charge and organic carbon content.) Since soil minerals are usually negatively charged (e.g., clays), anionic surfactants tend to sorb less than cationic ones. However, positively charged minerals like iron oxides, aluminum oxides, and calcium carbonates may result in some anionic surfactant sorption. Soils with significant organic carbon content tend to sorb more surfactant, regardless of the surfactant's charge.

2.3.2 Surfactant Precipitation

Soil mineralogy has an important impact on many aspects of groundwater quality. With regard to surfactant precipitation, the presence of specific cations that a mineral might release to solution can lead to surfactant salt precipitation. For example, calcite ($CaCO_3$) supports a level of solution Ca^{+2} which will likely precipitate anionic surfactants.

2.3.3 Soil Structure

As with other flushing techniques, surfactant flushing performs best in homogeneous, coarse soils. With low permeability soils, the deposit is much more difficult to flush. For example, when a lens of extremely low permeability is contaminated, hydrocarbon removal may be dependent on diffusion of the contaminant from the lens into the neighboring coarser zones, which is potentially a very time-consuming process. A similar argument applies to blocks of clay which have fractures throughout. In these instances, the openings through which most of the flow occurs may be easy to clean, but the matrix would not. A surfactant flush would offer little advantage towards remediating the matrix because the rate-determining step would be molecular diffusion through the low permeability soil.

2.4 PETROLEUM PRODUCTS OTHER THAN GASOLINE

As indicated earlier, surfactant flushing may become much more attractive when the products, such as crude oil, are highly hydrophobic, provided the primary mode of removal is dissolution or desorption. This is because the surfactant-based solubility enhancement of very hydrophobic hydrocarbons is much greater than the solubility enhancement of gasoline constituents. In a surfactant solution, highly hydrophobic hydrocarbons will concentrate in surfactant micelles and will, therefore, appear to have a greatly enhanced solubility. Gasoline components, in contrast, tend to be fairly soluble in unamended water and therefore exhibit a less dramatic solubility increase in a surfactant solution.

If the primary mode of contaminant removal is NAPL mobilization or displacement, then most petroleum products will be removed equally efficiently. There are some differences because interfacial tension varies from one petroleum product to another and because petroleum liquids exhibit a wide range of viscosity. When the viscosity of the petroleum product and the flushing fluid are significantly different, then there is potential for the flushing fluid to flow around the petroleum (assumed to be higher viscosity) rather than to displace it. This problem is regularly encountered by petroleum engineers who attempt to solve the problem by adding viscosity-enhancing polymers to the flushing fluid.

2.5 UNDESIRED REMOBILIZATION OF CONTAMINANT

By design, flushing operations mobilize contaminants in order to remove them from the subsurface. However, there is potential for undesired mobilization as well. For example, when the contaminant is a NAPL that is denser than water (i.e., a DNAPL), surfactants may reduce the interfacial tension sufficiently to cause the contaminant to migrate downward to the aquifer bottom or into low permeability layers where it will be even harder to recover. This consideration has lead some researchers (e.g., Fountain *et al.*, 1991) to attempt to remove DNAPL contaminants via the dissolution mechanism rather than via the mobilization mechanism. To that end, surfactants are chosen that maximize dissolution potential, while minimizing the reduction in interfacial tension.

Section 3

SURFACTANT-BASED REMEDIAL CAPABILITY IN NATURALLY-FRACTURED LOW PERMEABILITY SOILS

In the following discussion and calculations, surfactant flushing is examined for its ability to remove petroleum-derived hydrocarbons from subsurface pores that are hydraulically accessible. Surfactants are generally unable to remove contaminants from inaccessible locations, such as the interior cores of sand grains, or areas of relatively low hydraulic conductivity. In the former case, contaminants would move into a flushing solution only at rates which correspond to their diffusive release from the inaccessible sites. These 'access' issues are common to all techniques that attempt to flush contaminants.

Surfactant-containing solutions can be applied either vertically or horizontally. A vertical flush would be applicable to vadose zone contamination problems where the vertical conductivity is sufficient. Usually, the groundwater below the flushing zone would be extracted, serving to recover the flushate and prevent any offsite migration of the surfactant and the contaminant. Horizontal flushing would be applicable in the saturated zone, under buildings, or perhaps in horizontally stratified, low permeability soils. Horizontal flushing would require both injection wells and recovery wells. Impermeable walls might be built around the site in order to enhance flushing efficiency and to prevent offsite migration.

The following scenario is considered:

- An areally extensive clay that is 30-50 m thick
- The upper 2 m of the clay is highly weathered and cracked due to desiccation
- The fractures are primarily vertical with about 1-100 cm spacing
- The fractures have 10-40 um apertures
- The clay blocks between fractures are water-saturated (i.e., there are no continuous air pathways)
- Depth to the water table is 1-3 m
- The effective air-filled porosity is < 1%, the total porosity is 30%, and the natural organic content is 1%

Before estimating the effectiveness of surfactant flushing for this material, some relevant factors should be considered. First, because of the vertical fracturing and the high water table, it would be best to implement a vertical surfactant flush (Figure H-1). Flushate and product could be recovered in a combination of trenches and recovery wells. The recovery apparatus would be placed at the maximum depth of the fractures or just below the water table, whichever is higher. Because of the limited amount of horizontal fracturing, however, there is probably a fairly large amount of product in discontinuous fractures (i.e., fractures that are not part of a pathway from the surface to an extraction well or trench). Further, it is reasonable to expect a fair amount of surfactant would become trapped in the discontinuous fractures during the course of the flushing and thus would become effectively irretrievable. The overall treatability of the site will depend strongly on whether the recovery well locations or trenches could be designed in such a way that the majority of the fractures could be effectively flushed.

In order to estimate how quickly contaminants in such a scenario could be cleaned (Table H-1), we assume the following: (1) the contaminant has the properties of toluene, (2) the fracture width (b in Table H-1) is 20 um, (3) the fractureless blocks have a half-thickness (d in Table H-1) of 10 cm, (4) the length of the continuous pathways (L in Table H-1) is assumed to be 8 m, (5) the hydraulic gradient along the vertical path followed by the flush is assumed to be 1.0, and (6) the surfactant is 0.5 M sodium dodecyl sulfate (about 13% by weight, obviously a very concentrated flushate). Depending on where the contaminant "resides" in the deposit (Figure H-1), the characteristic times needed to remove it will vary; the following paragraphs explain how such time scales could be estimated.

It should also be noted that most of the commentary in this section should be viewed as speculative. There are no field data to verify or refute the behavior of a surfactant flushing solution in this geologic setting.

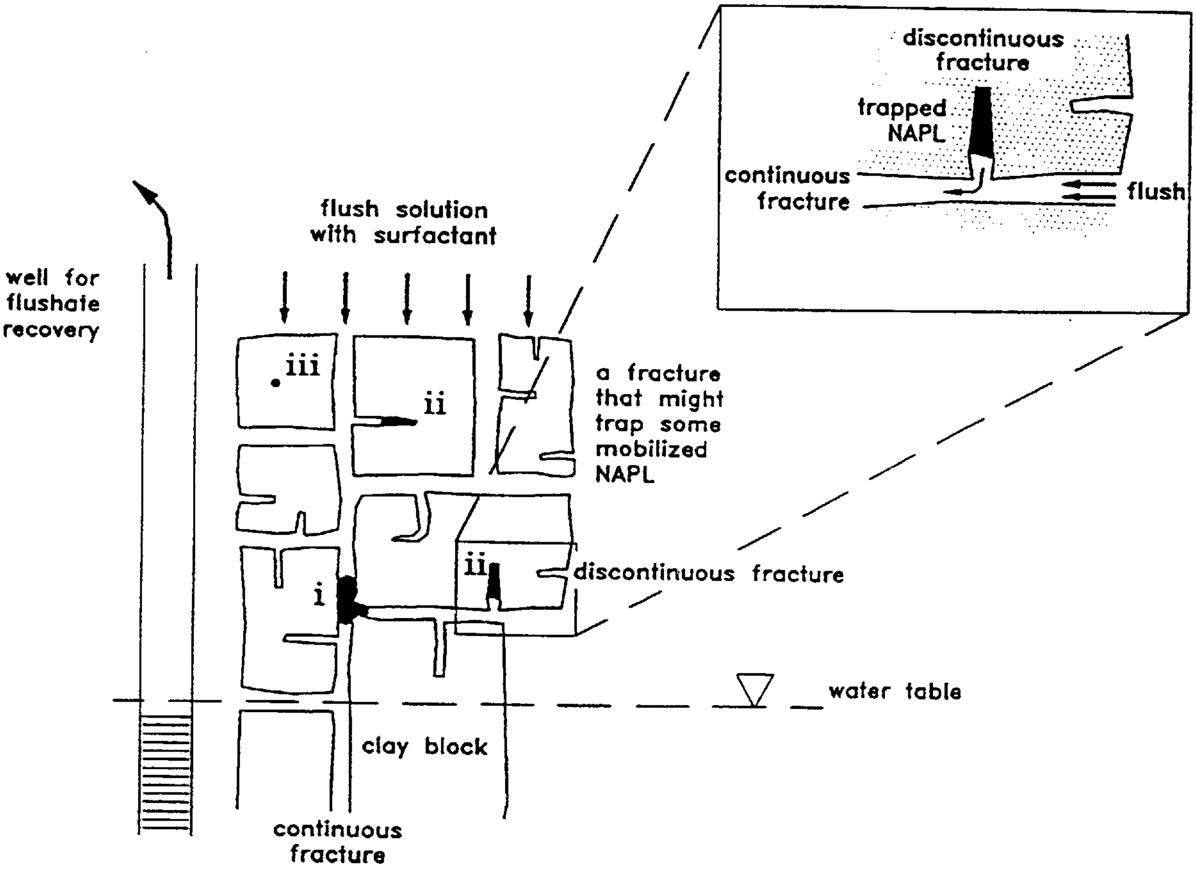

Figure H-1. Conceptualization of naturally-fractured tight soil which has been contaminated with a petroleum product. Contaminant locations include: (i) free product held in continuous fractures, (ii) free product trapped in discontinuous fractures which would be difficult to remove, and (iii) product that is both dissolved and sorbed within matrix material.

Contaminant Location	Assumptions	Time Calculation

(i) Free product in continuous fractures	The product is removed via the displacement mechanism. The rate of contaminant transport through the fractures is the same as the flow rate of water through the fractures.
	Removal of residual product on fracture walls can be estimated as in (v) below.
		Time = L / v,
		where v = flush velocity
		= $(pgb^2/12u)dh/dl$
		(Domenico and Schwartz, 1990).
		With: p = density = 10^3 kg/m^3;
		g = 9.8 m/s^2
		u = visc. = 10^{-3} Ns/m^2;
		b = fract. width = 20 um;
		dh/dl = 1.0; L = 8 m;
		Time = 7 hours

(ii) Free product in discontinuous fractures	(a) The rate limiting steps are assumed to be the diffusion of surfactant micelles from the continuous fractures to the NAPL and the return diffusion of the solubilized hydrocarbons back to the continuous fractures. (b) For "drainable" fractures removal time is governed by diffusion of surfactant monomers to the NAPL.	(a) Time = 2 x t_{diff}, where t_{diff} = the time of micelle diffusion = $d^2/D_{micelle}$ d(fract. length) = 10 cm; $D_{micelle} = 3 \times 10^{-6}$ cm^2/s Time = 2 years. (b) time = $d^2/D_{monomer}$ $D_{monomer} = 8 \times 10^{-6}$ cm^2/s. Time = 21 weeks
(iii) Dissolved & sorbed product in matrix blocks	Rate of contaminant removal is limited by SDS diffusion into the block, and subsequent diffusion of hydrocarbon in micelles back out of block.	Time = $2h^2/Deff$ where: h = block len. = 10 cm, Deff = $D_{micelle}$ x porosity^2 = 3×10^{-7} cm^2/s Time = 21 years
(iv) Product absorbed on organic soil material in blocks, this is most exposed sorbed fraction treated in (iii) above.	Sorbed contaminant is accessible to the surfactant flush in the continuous fractures, this reflects nearest 0.1 cm skin of block nearest to fractures.	Time = R x t_{flush} where R = retardation factor for desorption = 1.4 t_{flush} = 7 hours Time = 10 hours
(v) Residual product trapped in pore throats	The pore is accessible to the flushing solution. Contaminant removal is via the dissolution mechanism; here we assume 10% of air-filled porosity contains residuals.	Time = R x t_{flush} where R = retardation factor for dissolution; = 6.0 t_{flush} = 7 hours Time = 1.7 days

Table H-1: Calculation Scenarios for Massive Low Permeability Soils

3.1 SURFACTANT FLUSHING EFFECTIVENESS

3.1.1 Free Product Trapped in Continuous Fractures

These fractures, which form part of a pathway from the surface to the extraction well or trench, should be flushed within a couple of days for gasoline by means of the displacement mechanism. The dissolution mechanism would remove any residual product adhering to the sides of the fractures (Table H-1, case v). Note that the displaced product is in danger of becoming trapped in discontinuous fractures from which the product would be hard to recover. Therefore, it might be advisable to use a surfactant system that emphasizes dissolution even if this causes removal times to increase.

3.1.2 Free Product in Discontinuous Fractures

These fractures generally cannot be treated in a timely manner. Assuming the discontinuous fractures are accessible only by diffusion from the flushing solution, contaminant removal efficiency would be governed by diffusive transport of surfactant micelles from continuous fractures into discontinuous fractures and by diffusive mass transfer of solubilized hydrocarbons (i.e. micelles containing hydrocarbons) from the discontinuous fracture to the continuous fractures and the flowing surfactant solution. Removal time would vary for different soil geometries, but would be on the order of years (see Table H-1, case ii-a). However, if the discontinuous fracture happened to be located adjacent to a continuous fracture and oriented in such a way that the NAPL could drain into the continuous fracture, then it would stand a good chance of being cleaned much faster once the surfactant arrived (see Table H-1, case ii-b).

3.1.3 Dissolved Product Diffused into Matrix Blocks

Contaminants within the matrix, which would also be partially sorbed to the natural organic matter, would generally not be quickly removed by surfactants unless steps were taken to improve access to the interiors of the blocks. Note, this diffusive limitation would apply to any technique that does not modify the matrix. Assuming a block thickness of 20 cm, and an organic content of 1%, contaminant removal would have a characteristic time of decades (see Table H-1, case iii).

3.1.4 Product Absorbed in Organic Soil Material

This product could be readily removed by surfactant flushing provided the solution has access to the product and there are not significant kinetic limitations to desorption (as might be the case if the contaminant must travel by molecular diffusion to the bulk solution). Removal time would be less than a day (see Table H-1, case iv). As discussed previously, the surfactant would act to decrease the apparent soil-water partition coefficient by creating a third, organic pseudo-phase which would tend to travel with the flushing solution, although reduced relative permeability would slow migration.

3.1.5 Residual Product Trapped Within Pore Throats

This product could be effectively removed by the dissolution mechanism provided that the NAPL was accessible to the flushing solution and there were no significant mass transport limitations. Removal times would be on the order of a couple of days (see Table H-1, case v). If the residual product was trapped within the pore throat of a dead end pore, removal effectiveness would be quite limited as in the case of product trapped in discontinuous fractures.

3.1.6 Free Product Floating on the Water Table

This situation could be enhanced considerably by surfactant flushing provided there were continuous channels from the pooled product to the extraction wells or trenches. Surfactants could help by either lowering any capillary forces that may be impeding the product's flow to the recovery area or by solubilizing product and conducting it away. Hydrocarbon removal times would be approximately the removal time of free product in continuous fractures, but the precise time would depend on the viscosity of the NAPL. Note, it is conceivable that a significant amount of the pooled product would lack a continuous pathway to the extraction well and its removal would be quite limited as discussed above. By increasing the density of extraction wells and trenches, the amount of "continuous" pathways could be effectively increased.

3.2 COMPLEMENTARY OR IMPROVED TECHNOLOGIES

3.2.1 Pooled LNAPL

As noted above, pools of light non aqueous liquids (LNAPL) on the water table might be removed advantageously when surfactant flushing is done in conjunction with conventional direct product recovery techniques. One conventional technique for removing LNAPL in the vadose zone or pooled on the water table is to depress the water table (with either a trench or a well) and wait for the product to flow into the cone of depression. There, a second pump removes whatever product arrives. By combining this technique with the infiltration or injection of a surfactant that can significantly reduce the interfacial tension, the transport of the NAPL to the extraction well may be enhanced and some of the residual product may be removed as well. When the bulk of the product has been removed, less aggressive techniques such as biodegradation may be incorporated to treat the remaining constituents.

3.2.2 Low Permeability Zones

When aqueous phase contaminants are diffused into matrix blocks, it may be possible to enhance contaminant removal by chemically or mechanically treating the blocks to encourage colloid release. It would potentially both mobilize some contaminants that are sorbed to the colloids as well as increase permeability of the matrix. There is some evidence that ultrasonically-vibrated soil may release colloidal particles (Ryan, 1992). Also, there is evidence that some kinds of chemical treatment can be effective. For example, it has been shown that relatively low concentrations of surfactants (0.001 of the critical micelle concentration [CMC]), or changes in pH can effect colloid release (Ryan, 1992). However, it is questionable whether the surfactant could gain access to low permeability regions in a timely manner. A potentially promising alternative, which may be appropriate in certain soil systems, is to effect colloid release by changing the pH and dissolving secondary phases which hold and bond the colloids in place.

Contaminant removal from impermeable zones could conceivably be achieved by first modifying the clay permeability and then flushing it. Some clays (e.g. smectite) are known to experience three orders of magnitude increase in permeability in the presence of certain organic chemicals (Sims *et al.*, 1983). However, such chemical treatments are suspect because the chemicals being injected (e.g., xylene, acetone) may be nearly as toxic as those being recovered. Further, such a treatment may be impractical time-wise since transport of these chemicals into the low permeability layers is diffusion-limited. For example, assuming an effective diffusivity of 3×10^{-6} cm^2/sec and an impermeable layer 10 cm thick, these chemicals would exhibit a characteristic time of about 2 years to diffuse into the layer (see Table H-1, case ii-a).

Section 4

SURFACTANT-BASED REMEDIAL CAPABILITY IN STRATIFIED LOW PERMEABILITY SOILS

The following scenario is considered:

- The soil is stratified with layers ranging from medium sand to silt
- The soil is relatively dry with continuous air pathways in both the silt and the sand
- The sand behaves like a porous media with regard to fluid flow
- There are some preferential pathways in the silt and in the sand
- The water table is located 3-4 m below the ground surface
- The effective air-filled porosity is 0.2; the total porosity is 0.3

In this scenario, it is probably best to infiltrate the flushing solution at the surface and recover the flushate at the water table with one or more extraction wells. Note, if there is concern that mobilized product might get trapped in low permeability layers, it may be useful to wet the soil initially with water because water-wet fines are very resistant to intrusion by NAPL. Impermeable walls could be built around the contaminant zone to help keep the vadose zone saturated and prevent offsite migration of surfactant and contaminant.

In order to assess how quickly contaminants in one location can be cleaned relative to those in another, it is assumed that: (1) the contaminant has the properties of toluene, (2) the aquifer (4 m thick) consists of alternating layers of medium sand (10 cm thick; conductivity: 10^{-2} cm/sec) and silt (1 cm thick; conductivity : 10^{-5} cm/sec), (3) the surfactant is 0.5 M sodium dodecyl sulfate, (4) the natural organic content is 0.1% and 1% for the sand and silt, respectively, and (5) the effective porosity for flushing is 0.3.

4.1 SURFACTANT FLUSHING EFFECTIVENESS

It is again noted that the following discussion is, for the most part, speculative, since there is little or no data available on actual field performance.

4.1.1 Free Product Trapped on Perched Low Permeability Lenses

This product may be removed relatively effectively with a surfactant flush (i.e. relative to water flushing) as long as the surfactant-laden flushate contacts the product to dissolve it. As it affects residual NAPL however, removal would be slow because of the lack of surface area of contact with the flush. Assuming removal occurs via the dissolution mechanism, removal times for the free product would be on the order of a few days for a 1 cm thick layer of product (Table H-2, case i). This estimate assumes that the average concentration of contaminant in the water flowing around the pool is 1% of the apparent solubility of the chemical and that vertical flushing is not affected by the existence of the pool. A more in-depth analysis of the fluid dynamics around the NAPL pool and NAPL blob size distribution would be necessary to determine the actual rate of NAPL dissolution Powers *et al.,* 1994).

4.1.2 Aqueous Phase Product Diffused into Continuous Low Permeability Layers

This product may be effectively treated with surfactant flushing provided that a significant portion of the flushing solution passes through the silt layer (hence the desirability of a vertical flush) and all the flush does not travel through the preferred pathways. The time of removal of aqueous phase product residing in the top layer of silt is about 20 days, assuming there is no major migration through preferred pathways (see Table H-2, case ii). If, on the other hand only 10% of flush goes through the silt layer, removal time may be on the order of 200 days.

4.1.3 Adsorbed Product on the Permeable Layers

Adsorbed product could be removed by surfactant flushing in about as much time as aqueous phase product (i.e. 20 days) provided it is accessible by the flushing solution and desorption is not kinetically-limited (see Table H-2, case iii).

4.1.4 Residual Product in the Permeable Layers

This product could be most effectively removed via the dissolution mechanism. If the product occupies about 6% of the bulk volume (as is assumed in Table H-2 using 30% porosity times 20% residual), then about 170 days would be required to dissolve and flush the product (see Table H-2, case iv).

Contaminant Location	Assumptions	Removal Time Calculation
(i) Free product on low permeability lenses	The principle removal mechanism is assumed to be dissolution. The average concentration of contaminant in the flush is assumed to be 1% of the enhanced solubility. It is assumed that the initial thickness of the pooled NAPL (i.e., toluene) is 1 cm or 0.8 g/cm^2.	Time = $m_{NAPL} / r_{dissolution}$ where $m_{NAPL} = 0.8$ g/cm^2 is the initial amount of NAPL present per cm^2 of horizontal area; $r_{dissolution} = 2 \times 10^{-6}$ g/cm^{2}s is the mass of contaminant removed based on the product of the flushate discharge, the enhanced toluene solubility, and the buildup to 1% of NAPL solubility in the discharge. Time = 5 days
(ii) Dissolved and sorbed product in the thick, low permeability layers	The principle removal mechanism is surfactant-enhanced desorption. Here we assume an organic content of 1%, and therefore a toluene soil-water partition coefficient of 2.5 mL/g.	Time = R_{desorb} L/v, where R_{desorb} = the retardation factor associated with desorption (= 1.4) L = 400 cm v = (dh/dl)(K/n) = 3.3×10^{-4} cm/s Time = 20 days
(iii) Adsorbed product on the permeable layers	The principle removal mechanism is surfactant-enhanced desorption	Included in (ii) above
(iv) Residual product in the permeable layers	The principle removal mechanism is surfactant-enhanced dissolution; here residual product is taken to fill 20% of the pore space.	Time = $R_{dissolution}$ L / v where $R_{dissolution} = 12$ L = 400 cm v = 3.3×10^{-4} cm/sec Time = 170 days
(v) Dissolved and sorbed phase in isolated lenses (2 cm thick) near the surface	Removal time is governed by diffusion from the silt lens and retarded advection through the whole vadose system.	Time = R_{lens} (d^2/D_{eff}) + R_{desorb} (L/ v), where Deff = 10-6 cm^2/sec, d = 5 cm, L = 4 m $R_{lens} = 1.4$ $R_{desorb} = 1.0$ v = 3.3×10^{-4} cm/sec Time = 419 days

Table H-2: Calculation Scenarios for Stratified Soils

4.1.5 Isolated Lenses

Contaminant recovery from isolated lenses would likely be slow relative to recovery from continuous lenses. With isolated lenses, there is more of a tendency for the flushing solution to flow around the lens, so there would be little advection of the flushing fluid through the lens. Contaminant removal time would be governed by molecular diffusion of contaminants from the lens to the permeable zone, in addition to advective transport time in the permeable zone. For a thin 1 cm lens, removal times would be slightly longer than a year (Table H-2, case v).

4.1.6 Free Product on the Water Table Adjacent to a High Permeability Layer

Removal of this product could be enhanced with a surfactant flush. Of course, even without a surfactant, much of the product could be removed by direct pumping provided there was a low resistance pathway from the product to the extraction well. A residual amount (i.e., the residual saturation) would remain, however. With a surfactant that reduces interfacial tension to approximately 0.001 dynes/cm, nearly all of the product could be drained or pushed to the extraction well where it could be removed directly. Removal time would likely be on the order of days, similar to Case i in Table H-2.

4.2 COMPLEMENTARY OR ALTERNATIVE TECHNOLOGIES

Some of the complementary technologies discussed in the previous section would also be applicable for flushing stratified soils. For instance, the strategy for mobilizing colloids in the fines would also be applicable here, assuming the fines cannot be flushed directly with water. One additional complementary technique to consider would be a surfactant system that also promotes biodegradation after the bulk of contamination has been removed.

Section 5

COST AND COMMERCIAL AVAILABILITY

A hypothetical site is remediated using conventional surfactant flushing techniques (i.e., the contaminants are dissolved in the surfactant flush). The site has dimensions: 100' x 100' x 15'. Its soil is a stratified, fine grain matrix contaminated with 1000 ppm gasoline. The following additional assumptions are made:

- The aquifer consists of alternating layers of medium sand (with hydraulic conductivity, $K = 10^{-2}$ cm/s), and layers of silt (with hydraulic conductivity, $K = 10^{-5}$ cm/s).
- The layers of silt account for 10% of the aquifer thickness.
- The organic carbon contents of the sand and silt are 0.1% and 1%, respectively.
- The effective porosity of both layers is 0.3. The bulk density is 1.8 g/ml.
- The water table is 15' below the ground surface
- The gasoline is assumed to behave like a single chemical, toluene.
- Contaminants are initially present as spatially distributed NAPL blobs at 1000 ppm throughout.
- The volume fraction of NAPL is 0.0021.

5.1 REMEDIATION PLAN

A vertical surfactant flush is proposed; the hydraulic conductivity of the silt layer should be sufficient so that transport times are acceptable. Vertical flow will be slow, but still faster than diffusive transport through these low conductivity lenses. The surfactant chosen is 0.125 M sodium dodecyl sulfate (about 4 weight percent) whose properties are as follows:

• Critical micelle concentration:	7 mM
• Molecular weight:	288 g/mole
• Surfactant concentration:	0.125 M = 3.6% weight fraction
• Cost:	\$0.1/liter solution (about \$1/lb surfactant, and possibly cheaper if purchased in bulk.)

The engineering calculations for surfactant flush are:

• Vertical flush velocity:	3.3×10^{-4} cm/sec
• Retardation factor in silt:	6.4
• Retardation factor in sand:	3.7
• Transport time of flushate in sand:	53.3 days
• Transport time of flushate in silt:	10.3 days
• Total time for contaminant removal:	64 days
• Total amount of solution injected:	5.1×10^6 liters
• Amount of flushate pumped:	10.2×10^6 liters

The estimated costs are as follows:

Pre and post-remediation soil sampling	=	\$ 25,000
Surfactant (if 80% recycle): (\$0.1/liter) (5.1×10^6 liters) (0.2)	=	\$102,000
Emulsification breakers:	=	\$ 50,000
Well construction: (\$100/ft)(30 ft) + \$7000 fixed	=	\$ 10,000
Flushate treatment (assuming air stripping and carbon)	=	\$ 50,000
Capital equipment (pumps, etc.)	=	\$ 30,000
Operating and maintenance costs	=	\$ 40,000
Design and engineering	=	\$ 50,000
Total Cost	=	\$357,000

5.2 COMMENTS

Because the retardation factor of liquid hydrocarbons in surfactant flushing is relatively constant for a wide range of contaminant hydrophobicities, the above calculations are valid for gasoline in general. The above analysis assumes ideal conditions with respect to geology and deviations from these assumptions could have a significant impact on the effectiveness of this flushing scheme. For example, the presence of preferential flow channels in the silt could extend the time required to flush the low permeability zones. In addition, it is possible that the low permeability layers have vertical conductivities significantly smaller than the ones used here, especially if they have an appreciable clay content. This would reduce the vertical flow velocity and prolong the time of treatment. The amount of flushing (i.e. the volume of flush needed) would not change however. Thirdly, it is possible that the low permeability layers are non-horizontal with the consequence that the flushing solution may migrate offsite on low permeability layers rather than flow toward the well. In this case, costly vertical barriers may be necessary.

5.3 COMMERCIAL AVAILABILITY

Much of the work on surfactants to date have been performed by oil companies or firms such as General Motors (Abdul *et al.*, 1992) who do not offer consulting services. There are only a few consulting companies that offer surfactant flush capabilities and these have little field data to demonstrate their capabilities. Clark *et al.* (1992) offers some insight into this topic.

Section 6

CASE HISTORIES

There have only been a few documented attempts to flush contaminants with surfactants, and many of these are only described in unpublished manuscripts. For example, Fountain (1992) has presented the results of a field test of surfactant flushing at Canadian Forces Base Borden in Ontario, Canada. The contaminated site was a hydraulically isolated cell with impermeable vertical walls on the sides and a clay bottom. The soil was reasonably conductive sand and the contaminant was a DNAPL, pentachlorophenol (PCP), of which a known amount was injected in order to gauge contaminant removal efficiency. The remediation scheme consisted of surfactant infiltration at the soil surface and recovery via a well near the clay bottom. Most of the PCP (> 90%) was removed within 14 pore volumes of flush, but a significant portion was left behind. Fountain hypothesized that the residual PCP had been hydraulically isolated from the flush. The PCP had apparently migrated to the aquitard where relatively little exposure to the surfactant flush occurred.

In another field study, Pitts *et al.*, (1993) and Sale *et al.*, (1989) describe a test in which waste wood-treating oil was spilled in a shallow alluvial aquifer. As part of a sequence of operations, these investigators reported that 1-2% by weight flushes with an ethoxylated nonylphenol and later by a dodecyl benzene sulfonate yielded about two-thirds of the spilled oil after about 8 pore volumes of flushing. It was also noted that only about 1% of the sulfonate surfactant was lost to the aquifer, although the surfactant emulsified the oil and there was difficulty in 'breaking' the emulsion at the surface.

Section 7

SUMMARY

The main strength of surfactants is that they have the ability to solubilize or displace extremely hydrophobic materials (like PCBs or automatic transmission fluid) that resist treatment by pump-and-treat or by air flushing technologies (soil vapor extraction or air sparging) that rely on volatility for removal. The main weakness of surfactant flushing is that it, like other flushing techniques, is only effective at removing chemicals to which it has access. In the early days of surfactant flushing, there was concern about surfactant precipitation and sorption; about whether surfactants could be recycled; and about their environmental impact. Most of these issues are now reasonably understood, although the technology is still considered emerging.

Surfactant usage for remediation has been largely confined to relatively homogeneous conductive soil where this approach has been reasonably successful (e.g., Abdul *et al.*, 1991). In more heterogeneous soils, surfactant effectiveness is reduced, but it may be feasible to a point. The usefulness of surfactants, specifically in low permeability applications, is limited because of the accessibility issue as discussed above. In the case of the specific stratified soil scenario considered in this study, surfactants could still play a role because they could be advected through the higher permeability layers. In the case of massive clay settings where contaminants have diffused into the clay blocks, surfactants - like other flushing technologies - would be largely ineffective unless the permeability of the blocks could be modified.

Section 8

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MIXED REGION VAPOR STRIPPING AND CHEMICAL OXIDATION FOR IN-SITU TREATMENT OF NAPLS IN LOW PERMEABILITY MEDIA

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ABSTRACT

The use of in-situ soil mixing is described and its capability to remove product using both physical and chemical mechanisms in two types of low permeability settings is evaluated. The paper includes a summary of the typical costs of soil mixing as well as case histories where it has been applied in low permeability media.

Section 1

DESCRIPTION OF THE TECHNOLOGY

Fine-textured soils and sediments contaminated by organic solvents and petroleum hydrocarbons present a significant environmental restoration challenge. Despite the overall low permeability of a fine-textured deposit, migration of non-aqueous phase liquids (NAPLs) into and throughout subsurface regions can occur over years to decades as contaminants in the non-aqueous, aqueous, and vapor phases move along a variety of pathways (e.g. fractures, macropores, micropores). Diffusion can occur from the fractures and macropores into the matrix of fine-textured media. As a result of this transport process, removal of contaminants from the deposit and delivery of treatment agents into and throughout the deposit are often hindered, making rapid and extensive remediation difficult. While in-situ processes such as bioremediation and soil vapor extraction can function at sites with permeable sands (e.g., $K_{sat} > 10^{-3}$ cm/s), they are normally ineffective in silt and clay soils and sediments. 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 as the delivery system for fluids or reagents which remove or treat the contaminants. Adapted largely from construction drilling technologies, soil mixing has evolved as an approach for enabling remediation of contaminated sites by various in-situ treatment processes. As applied for in-situ treatment of NAPLs in low permeability media, soil mixing can be used to accomplish several objectives including disruption of fracture systems, homogenization of heterogeneous regions, and delivery and distribution of treatment agents. 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 I-1).

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 poly-chlorinated biphenyl (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). In 1992 a U. S. Department of Energy (DOE) demonstration was completed at a trichloroethylene (TCE) contaminated site in Ohio where three 10-ft diameter by 15-ft deep columns were treated (Siegrist et al., 1993). In both these demonstrations, the short-term immobilization of the target organics was substantial, although long-term stability was not evaluated. In recent years, soil mixing has been developed further to facilitate in-situ treatment by other physicochemical processes including vapor stripping and chemical oxidation (West et al., 1993a; West et al., 1993b; Gates and Siegrist, 1993a; Gates and Siegrist, 1993b; Siegrist et al., 1993). Modeling, experimentation, and field demonstrations have indicated high treatment potential in low permeability media contaminated with NAPLs.

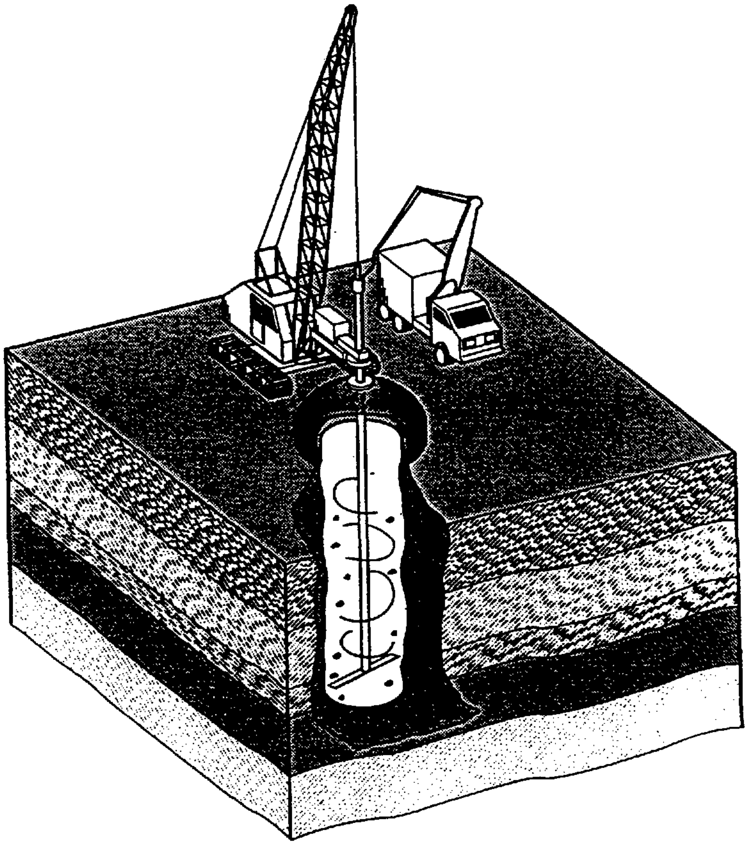

Figure I-1: Illustration of soil mixing of low permeability media to facilitate in-situ treatment in a subsurface soil reactor concept. (Note: treatment agents are delivered through the mixing blade(s) with any emissions captured in the hood covering the mixed region.)

Mixed region treatment 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 NAPL-contaminated low permeability media is attractive since it offers perhaps the only way to rapidly and extensively disperse treatment agents and concomitantly remove/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.

Section 2

MIXED REGION VAPOR STRIPPING

2.1 DESCRIPTION OF MRVS TECHNOLOGY

Mixed region vapor stripping (MRVS) involves injection of compressed gases at high volumetric flow rates (e.g., 1 soil reactor volume per min.) to volatilize and advectively remove organics from the subsurface. The removed organics are either released to the atmosphere or captured in a shroud or hood and managed by a variety of offgas treatment techniques (e.g. carbon adsorption, catalytic oxidation). Soil mixing technology can include various auger designs while gas injection can be accomplished through orifices along the auger blade(s) or out the bottom end of a mixing shaft. Removal efficiency is generally dependent on contaminant/media properties (e.g., pore size and continuity, water content, sorption) and injected gas properties (e.g., flow rate, energy content) (Gierke et al., 1992; West et al., 1993a; West et al., 1993b).

2.2 GENERAL MRVS TECHNOLOGY CONSIDERATIONS

2.2.1 Effect of High Soil Water Content on Contaminant Removal Efficiency

The effect of water content on the efficiency of MRVS has not been clearly defined. Removal of volatile organics during MRVS occurs by diffusion wherein volatiles migrate through matrix micropores (normally water-filled) and inter-aggregate macropores (either water- or air-filled), followed by advection, in which volatiles must be in contact with the gas phase which is moving through the continuous air-filled macropores. Since diffusion through air occurs at a much higher rate than diffusion through water, increasing water content will likely retard diffusive and possibly advective transport processes, thereby reducing the rate of removal. However, increasing water contents toward saturation can enhance mixing efficiency and possibly heat transfer, both of which could provide removal efficiency benefits. Under saturated conditions, MRVS becomes a mixed region air sparging process. The efficiency of MRVS is probably less sensitive to water content than conventional soil vapor extraction (SVE), due to physical disruption and homogenization associated with the mixing process and the high gas flow rates.

The MRVS process has been employed on at least one occasion for treatment of saturated soils below the water table (Siegrist et al., 1993). Removal of TCE from the saturated zone of a silt/clay deposit was high (>85%), but somewhat lower than removal from the overlying unsaturated zone (>95%). However, the relative effect of water content could not be evaluated as the TCE concentrations varied with depth and the treatment time per unit volume of media also varied.

2.2.2 Accessing Under Buildings and Concrete Pavement

MRVS 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 MRVS does not adversely affect the stability of the structures (e.g. by disturbing building foundations). However, since current mixing technologies employ near-vertical penetration, MRVS treatment under surface obstructions could entail considerable disruption of surface features. To overcome this, implementation of MRVS enabled by directional drilling or auguring equipment is needed. However, any treatment process implemented in this manner would require further developments in offgas capture and treatment techniques. In addition to potential surface physical disruption, the effects of media volume expansion on surface structures needs to be considered (see Section 2.2.3).

2.2.3 Maximum Depth for which Technology is Appropriate and Soil Types

The equipment utilized for soil mixing has been adapted from the construction industry where caisson drilling has occurred to depths well over 100 ft. MRVS 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., density, water content, air permeability), and the power and geometry of the mixing equipment (e.g., maximum torque, mixing blade features). Higher air injection pressures may also 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 MRVS to 15 ft depth 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.

2.2.4 Remediation of Petroleum Products Other Than Gasoline

MRVS was found to be effective for removing volatile organics such as TCE (vapor pressure (v.p.) = 8 kPa; Henry's constant (H) = 0.9 kPa–m^3/mol at 20°C) and 1,1,1-trichloroethane (TCA) (v.p. = 13.2 kPa; H=2.8 kPa–m^3/mol) from soils with a total organic carbon (TOC) content ranging from 0.01–0.1% by wt. (West et al., 1993a). It is expected to be equally efficient on gasoline contaminants since the predominant BTEX compounds in gasoline have similar vapor pressures, Henry's constants, and aqueous phase partition coefficients (a property of the contaminant/soil system that may be estimated from the solubility of the compound and TOC of the soil). Desired properties of the contaminants include high vapor pressure, high Henry's constant, and low aqueous phase partition coefficients. The effectiveness in volatilizing heavier components, [e.g., n-octane (v.p. = 2.6 kPa; H = 300 kPa-m^3/mol) and dodecane (v.p. = 0.015 kPa; H = 750 kPa-m^3/mol)] needs to be investigated. These compounds have very low vapor pressures but higher Henry's constants (due to lower aqueous solubility).

2.2.5 Removal Time by SVE and Biodegradability of Heavier Components

MRVS treatment time is a function of several factors, including (1) the chemical properties of the target contaminants (i.e., v.p. and H), (2) the partitioning behavior within the contaminant/media system (Kd), (3) the physical properties of mixed soil/media (e.g., aggregate size and surface area), (4) the volume of soil to be treated, (5) the air flow rate and energy content, and (6) the required removal efficiency.

Laboratory and field tests of MRVS have shown that from 400 to 700 unit volumes of air (ambient temperature) per unit volume of soil (a.k.a. reactor volume, or r.v.)

were required to reduce TCE concentrations in clay soils by at least 80% (West et al., 1993a; Siegrist et al., 1993). The treatment time for ambient air MRVS of a given volume can be roughly estimated for a prescribed airflow rate. For example, for a treatment volume of 460 cu ft (~6 ft diameter, 20 ft depth) and an air flow rate of 1500 cfm, an estimated treatment time is obtained as follows:

$$treatment\,time = 400\,r.v. \times \frac{460\,cu.ft.}{1500\,cfm} = 123\,\mathrm{min} \qquad [1]$$

This estimation procedure is thought to be valid for contaminants with vapor pressures similar to TCE , and for contaminant/soil systems that exhibit partitioning behavior similar to that of the TCE/soil system at the DOE Portsmouth site (Kd ~0.1 mL/g). For petroleum products (e.g. gasoline, diesel) and other soil systems, laboratory tests and/or modeling coupled with laboratory measurement will be necessary to estimate required reactor volumes.

MRVS may enable secondary treatment through biological degradation in much the same manner that bioventing can occur during conventional soil vapor extraction. This possibility was considered through during a MRVS demonstration at a land treatment site in Ohio (Siegrist et al., 1993). Comparisons of microbial activity before and after treatment revealed increases in total bacterial populations (e.g., 1000x) although the significance of this remains under investigation.

2.3 REMEDIAL CAPABILITY OF MRVS IN NATURALLY-FRACTURED MASSIVE LOW PERMEABILITY SOILS

The following scenario is considered:

- An areally extensive clay that is 30-50 m thick
- The upper 2 m of the clay is highly weathered and cracked due to desiccation
- The fractures occur with about 1-100 cm spacing, and they are primarily vertical
- The fractures have 10-40 um apertures
- The clay blocks between fractures are water-saturated (i.e., there are no continuous air pathways)
- Depth to the water table is 1-3 m
- The effective air-filled porosity is < 1%, the total porosity is 30%, and the natural organic content is 1%

2.3.1 Removal of: (1) Free Product Trapped in Continuous Fractures; (2) Free Product Trapped in Discontinuous Fractures; (3) Aqueous Phase Product Diffused into Matrix Blocks; (4) Product Adsorbed on Organic Soil Material; (5) Residual Product Trapped Within Pore Throats; (6) Free Product Floating on the Water Table

Based on existing experience, MRVS should be effective in removing all volatile contaminants from the upper 20-30 ft (7-10 m) of a massively-fractured low permeability site. Given the characteristics of the scenario (i.e., massive clay with only the upper 6.5 ft (2 m) weathered and the water table at 3-10 ft (1-3 m depth)), efficient treatment within this depth region should address the bulk of the contamination. This is fortunate, since mixing diameter 6-10 ft (2-3 m) soil columns to depths >30 ft (10 m) has not known to been implemented for MRVS treatment. Difficulties that may be encountered at greater depths could include: (1) excessive power requirements for the equipment to mix soils (e.g. augers) under significant overburden pressures, (2) excessive volume expansion that will be more substantial when mixing deeper soil columns, and (3) higher injection air pressures that may be required to maintain air flow rates in deep columns.

Since the original structure of the deposit would be substantially disrupted during MRVS, the original distribution of contaminants within the fractures/blocks of the clay deposit is not expected to significantly influence treatment effectiveness. NAPLs will be more easily volatilized than aqueous phase contaminants since the vapor pressure of a pure phase is always higher than its vapor pressure in solution. Therefore, mass removal may be more rapid for NAPLs as compared to aqueous phase solutions.

2.3.2 Complementary Technologies in This Type of Setting

Coupling MRVS approaches with horizontal fracturing could provide benefits by reducing the number of vertical mixed regions and utilizing them as "chimneys" within the deposit. Providing thermophysical enhancements such as soil heating could enhance removal rates in some settings. Incorporating secondary treatment processes could also provide benefits. For example, passive volatilization and/or bioremediation enhancements could be employed following MRVS. It is also conceivable that vegetative restoration techniques could be beneficially implemented following a MRVS process. Finally, fluid and particulate streams could deliver a variety of treatment agents to the subsurface during and following MRVS (e.g. zero-valence metals, sorbents). These agents could effect treatment for prolonged periods following the actual mixed region treatment operation.

2.4 REMEDIAL CAPABILITY OF MRVS IN STRATIFIED LOW PERMEABILITY SOILS

The following scenario is considered:

- The soil is stratified with layers ranging from medium sand to silt
- The soil is relatively dry with continuous air pathways in both the silt and the sand
- The sand behaves like a porous media with regard to fluid flow
- There are some preferential pathways in the silt and in the sand
- The water table is located 3-4 m below the ground surface
- The effective air-filled porosity is 0.2; the total porosity is 0.3

2.4.1 Removal of: (1) Free Product Trapped on Perched Low Permeability Lenses; (2) Aqueous Phase Product Diffused into Continuous Low Permeability Layers; (3) Adsorbed Product on Both Permeable and Low Permeability Layers; (4) Residual Product in Both Permeable and Low Permeability Layers; (5) Free Product on the Water Table Adjacent to the High Permeability Layer; (6) Contaminant Recovery from Low Permeability Isolated Lenses Rather than Continuous Layers

MRVS is applicable to this scenario for the same reasons stated above for the low permeability massive deposit (see Section 2.3). However, MRVS could also be utilized to perforate the low permeability interbedded deposits, thereby providing continuity between high permeability regions above and below each low permeability layer. In either a perforated or complete treatment approach, the MRVS strategy may be more effective than conventional soil vapor extraction, since MRVS will more effectively remove contaminants trapped in the low permeability lenses. The relatively dry conditions and high air-filled porosity will generally benefit a MRVS process. As in the previous scenario, NAPLs are expected to volatilize more easily than aqueous phase products and MRVS should be effective in removing NAPLs from both the permeable and low permeability layers.

2.4.2 Complementary Technologies in This Type of Setting

As described for the massive deposit scenario, several technologies could be utilized to provide enhanced treatment. Thermophysical enhancements such as soil heating within the low permeability deposits could enhance removal rates in some settings. Incorporating secondary treatment processes could also provide benefits. For example, passive volatilization and/or bioremediation enhancements could be implemented following MRVS. It is also conceivable that vegetative restoration techniques could be beneficially implemented following the MRVS process. Finally, fluid and particulate streams could deliver a variety of treatment agents to the subsurface during and following MRVS (e.g. zero-valence metals, sorbents).

2.5 COST AND COMMERCIAL AVAILABILITY OF MRVS

The cost and commercial availability of the MRVS technology can be illustrated considering a hypothetical site, 100 ft by 100 ft by 15 ft deep (~5550 yd^3). This site is characterized by stratified fine-grained media contaminated with gasoline that is diffused into the low permeability matrix blocks at a concentration of 1000 ppm.

2.5.1 Cost to Remediate Down to 200 ppm Level

Based on a limited amount of full-scale data with chlorinated solvents like TCE, the estimated cost for MRVS (ambient or heated air) to achieve an 80% removal efficiency is approximately \$100-150/yd^3 These data are projected based on a treatment cost of \$200/yd^3 for 90% removal of TCE as determined during a full-scale field demonstration at a secured DOE site where higher costs are normally encountered (Siegrist et al., 1993). This assumes that offgas treatment constraints are nominal.

2.5.2 Estimated Time to Remediate

Based on limited full-scale data, the estimated treatment time for the site is 30 to 60 days based on a processing rate of 100-200 yd^3/day (Siegrist et al., 1993).

2.5.3 Extent to which Technology is Commercially Available

MRVS is a commercially available technology although its application for in-situ treatment of NAPLs in low permeability media is limited. One of the first commercial vendors of in-situ mixing and hot air/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. 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). This system includes a crane-mounted vertical auger system designed to mix the subsurface using 6- to 14-ft diameter augers. During the in-situ mixing process, treatment agents are injected through a vertical hollow shaft and out into the soil through orifices in horizontal soil mixing blades. 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. However, these authors are not aware of any application of these systems with MRVS at a NAPL-contaminated site.

2.6 FIELD EXPERIENCES WITH MRVS

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 VOC's 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. Steam is injected at 450-475°F and 380 psi, and the soil temperature reaches 160-175°F. Waste streams produced by the Detoxifier™ system include offgas that is contained by the shroud and routed through a scrubber for particulate removal, and through activated carbon for organic removal. The offgas 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./day 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 MRVS of NAPLs in low permeability media has been under study at 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). Modeling, laboratory experimentation, and full-scale field demonstration 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.

MRVS processes employing ambient air and hot air were first evaluated in a pilot-scale apparatus using a number of undisturbed 8 in. diameter by 24 in. long cores from the site (West et al., 1993a; West et al., 1993b). To enable additional experimental runs, 8 in. diameter by 9 in. long cores were packed with clay soil from the X-231B site and spiked to yield soil TCE concentrations of 1 to 5 ppm. Results of this work revealed that offgas VOC concentrations rose rapidly and then declined during in-situ mixing and air injection. Removal efficiencies were variable, but ranged up to 95% for the clay soils with initial VOC concentrations in the ppm range. Hot air injection enabled somewhat higher removal efficiencies (a few percent) as compared to ambient air during the same treatment time period.

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 MRVS with ambient and heated air. Three, 10-ft diam. soil columns were treated using hot air stripping (i.e. ~130°C) to a depth of 15 ft while one column was treated to a depth of 22 ft. An additional three, 10-ft diam. 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 auger moving continuously up and down during a total treatment time of ~225 min. 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. The treatment performance achieved with hot air injection into the mixed region was substantial (e.g. Figure I-2). Concentrations of VOC's in the offgas from the system rose immediately after air injection. The offgas concentrations then slowly declined during mixing up and down in the upper 7-ft zone. Upon penetration to 15-ft depth, the VOC concentrations exhibited a similar response, but typically lower in magnitude.

Mass removal curves deduced from offgas hydrocarbon concentrations suggested that removal of VOCs from the hot air soil columns continued throughout the entire treatment interval. 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. Preliminary 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 also appeared to be ~88%, somewhat lower than that achieved during treatment of the 15-ft depth zone. The reasons for this lower efficiency are currently unknown although it could have been due to several factors, including higher concentrations of pre-treatment soil VOC's, 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. These data agreed with modeling predictions that treatment efficiency of heated air MRVS would only be modestly higher than that of ambient air MRVS due to the low TOC of the soil and high volatility of TCE. Processing rates and costs determined in the demonstration were ~200 yd^3/day and ~\$200/yd^3 (Siegrist et al., 1993).

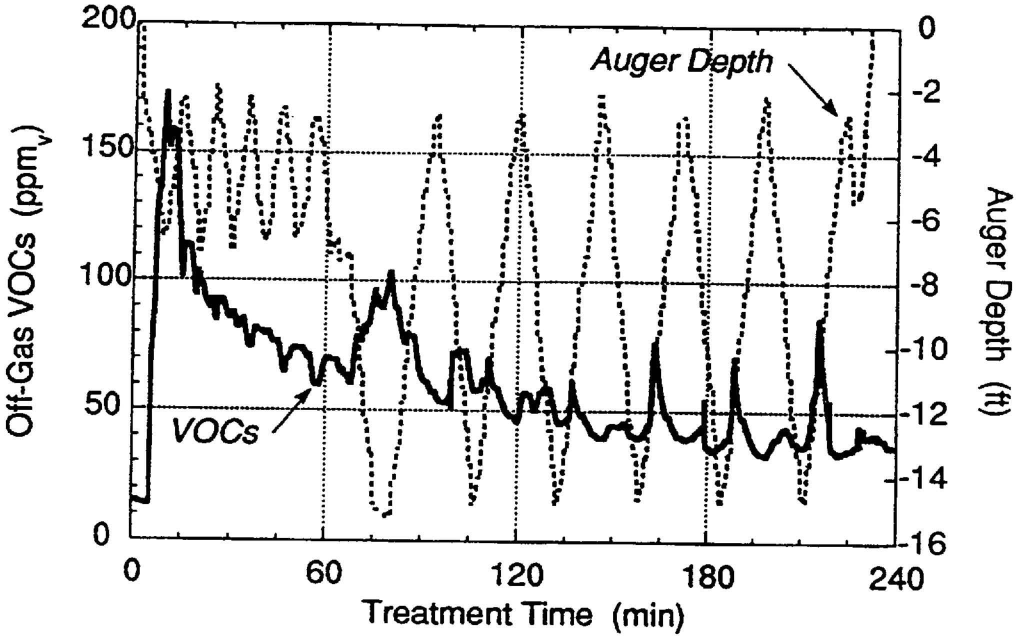

Figure I-2: Treatment operation and offgas VOC concentrations for a 10-ft. diameter by 15-ft. deep soil column treated by MRVS with 130°C hot air (Siegrist et al., 1993).

2.7 SUMMARY OF MRVS

2.7.1 Overall Strengths and Weaknesses of This Technology

The strengths of MRVS include the inherent benefits of mixing a low permeability deposit as well as:

(1) enhanced mass transfer in low permeability deposits where conventional vapor extraction is infeasible,
(2) shorter treatment times when compared to conventional vapor extraction due to reductions of matrix pore path lengths and greatly increased air flow rates,
(3) amenability to process monitoring and control, and
(4) feasibility of coupling different treatment processes (e.g., vapor stripping with chemical oxidation).

The weaknesses of MRVS technology include:

(1) may be unsuitable for areally extensive contaminated sites,
(2) may be unsuitable for media with subsurface utilities and obstructions, or media underlying structures whose stability will be undermined by soil mixing,

(3) may be unsuitable for deeper contamination (e.g., >100 ft.), and
(4) treatment costs of $100-$300/yd^3 may be higher than competing technologies in some settings.

2.7.2 Needed Breakthroughs Before Technology can be Routinely Applied

Further laboratory- and field-scale tests of MRVS for some NAPLs (e.g. gasoline and diesel fuel) in low permeability media are required. The benefits of the complementary technologies described in Sections 2.3 and 2.4 require further research and development. Equipment modifications are needed to enable subsurface access at surface obstructed sites (e.g., articulated mixing arms) and to treat smaller, shallower sites (e.g., smaller scale equipment).

Section 3

MIXED REGION CHEMICAL OXIDATION

3.1 DESCRIPTION OF MRP TECHNOLOGY

As an alternative to MRVS, chemical oxidation processes involving a variety of liquid (e.g. peroxides, permanganates) or gaseous oxidants (e.g. ozone) can be coupled with soil mixing technologies for in-situ treatment of NAPL-contaminated low permeability 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 soil iron (both ferrous and ferric) in a variety of competing reactions (Tyre et al., 1991):

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

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

$$OH\cdot + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad [4]$$

$$HO_2\cdot + Fe^{3+} \rightarrow O_2 + H^+ + Fe^{2+} \quad [5]$$

$$H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot \quad [6]$$

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

$$RH + OH\cdot \rightarrow R\cdot + H_2O \qquad [7]$$

$$R\cdot + Fe^{3+} \rightarrow Fe^{2+} + \text{products} \qquad [8]$$

where R·= organic radicals. This reaction of hydrogen peroxide with iron to yield free radicals is commonly referred to as *Fenton's Process.*

Mixed region peroxidation (MRP) involves injection of solutions of hydrogen peroxide (and potentially additives) into and throughout a contaminated region during soil mixing. Treatment efficiency appears to be principally a function of media properties (e.g. natural soil organic matter content, pH), H_2O_2 concentration and mass loading rate, and H_2O_2 delivery and distribution. 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 and sufficient fluid volume to disperse the oxidant without slurrifying the soil system and yielding free water (e.g., Gates and Siegrist, 1993a). To enhance distribution of oxidant throughout the mixed region, hydrogen peroxide solution can be injected into an air stream (e.g. 300 cfm) 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 offgas organics are captured in a shroud or hood covering the ground surface and managed as required by a variety of offgas 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).

3.2 GENERAL MRP TECHNOLOGY CONSIDERATIONS

3.2.1 Effect of High Soil Water Content on Contaminant Removal Efficiency

High soil water content should not adversely affect MRP treatment efficiency. In fact, it may enhance MRP by increasing the amount of soluble contaminant to be treated and increasing the efficiency of mixing and distribution of peroxide solution throughout the region of interest.

3.2.2 Accessing Under Buildings and Concrete Pavement

The problems with accessing under surface obstructions outlined in Section 2.2.2 for MRVS also apply to MRP. Beyond these considerations, in-situ MRP should not be adversely affected by overlying structures or pavements, providing moderate increases in soil/sediment water content do not alter structural integrity. Potentially applicable to MRP, some mixing equipment is available that has the capability to mix and extract soil from underneath a building using directional mixing techniques and forming an in-situ slurry from the contaminated soil.

3.2.3 Maximum Depth for which Technology is Appropriate and Soil Types

As described in Section 2.2.3, the equipment utilized for soil mixing has been adapted from the construction industry where drilling has occurred to depths well over 100 ft. MRP of silt/clay soils to 15 ft 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 a peroxide solution should reduce power requirements for mixing as compared to MRVS. Regarding the peroxidation treatment process itself, process efficiency should not be negatively affected by increasing depth. However, monitoring of process effectiveness may be more difficult at lower depths.

Mixing of deeper and denser soil regions (e.g. >20 ft) may also increase absolute volume expansion (i.e. more soil will be lifted above the original ground surface). The volume expansion observed during MRP to 15 ft depth in a dense silt/clay deposit was observed to be ~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).

3.2.4 Remediation of Petroleum Products Other Than Gasoline

Peroxidation in aqueous matrices has been shown to be an effective treatment technique for a variety of organic contaminants (Table I-1). It has also been shown to degrade certain chlorinated solvents and petroleum hydrocarbons in soil systems (e.g., Tyre et al., 1991; Gates and Siegrist, 1993a; Gates and Siegrist, 1993b). Its effectiveness on heavier petroleum fractions in soil has not been demonstrated extensively nor has there been extensive experience with in-situ applications for NAPLs in low permeability media.

Contaminant	Matrix	Reference
Tetrachloroethylene	silica sand	Leung et al., 1992
	water	Bellamy et al., 1991
Trichloroethylene	silica sand	Gurol and Rivikumar, 1991
	water	Bellamy et al., 1991
	silt and clay soil	Gates and Siegrist, 1993a
	silt loam soil	Hurst et al., 1993
Carbon tetrachloride	water	Bellamy et al., 1991
Trans-1,2-dichloroethylene	water	Bellamy et al., 1991
Pentachlorophenol	silica sand	Gurol and Rivikumar, 1991
	natural soil	Watts et al., 1990; Tyre et al., 1991
2,4-dichlorophenol	water	Bowers et al., 1989
Dinitro-ortho-cresol	water	Bowers et al., 1989
Formaldehyde	water	Murphy et al., 1989
Trifluralin	natural soil	Tyre et al., 1991
Hexadecane	natural soil	Tyre et al., 1991
Dieldrin	natural soil	Tyre et al., 1991
Motor oil and diesel fuel	naturally contaminated soil	Watts, 1992
Octachloro-dibenzo-p-dioxin	natural soil	Watts et al., 1991

Table I-1: Compounds successfully treated by chemical oxidation using hydrogen peroxide.

3.2.5 Removal Time by SVE and Biodegradability of Heavier Components

The treatment time is believed to be controlled by delivery and distribution of the hydrogen peroxide 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). During a field demonstration in a silt/clay deposit, treatment efficiencies of 70% were achieved for TCE-contaminated clay soils during 75 min. of MRP in 10-ft diameter by 15-ft deep columns (Siegrist et al., 1993). There is potential for secondary bioremediation to occur. For example, MRP may partially degrade refractory or inhibitory compounds to the extent that they become amenable to biotreatment which should be enhanced by oxygen released during peroxide decomposition.

3.3 REMEDIAL CAPABILITY OF MRP IN NATURALLY-FRACTURED MASSIVE LOW PERMEABILITY SOILS

The following scenario is considered:

- An areally extensive clay that is 30-50 m thick
- The upper 2 m of the clay is highly weathered and cracked due to desiccation
- The fractures occur with about 1-100 cm spacing, and they are primarily vertical
- The fractures have 10-40 um apertures
- The clay blocks between fractures are water-saturated (i.e., there are no continuous air pathways)
- Depth to the water table is 1-3 m
- The effective air-filled porosity is < 1%, the total porosity is 30%, and the natural organic content is 1%

3.3.1 Removal of: (1) Free Product Trapped in Continuous Fractures; (2) Free Product Trapped in Discontinuous Fractures; (3) Aqueous Phase Product Diffused into Matrix Blocks; (4) Product Adsorbed on Organic Soil Material; (5) Residual Product Trapped Within Pore Throats; (6) Free Product Floating on the Water Table

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 the NAPLs should occur, whether they are present as residual product or as dissolved product diffused into the matrix blocks. This will potentially mitigate any adverse affects associated with the described heterogeneities. Oxidation of various types and concentrations of organic compounds including soil organic matter have been demonstrated (Table I-1). The extent of degradation is a function of peroxide 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.

3.3.2 Complementary Technologies in This Type of Setting

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. MRP may partially degrade refractory or inhibitory compounds to the extent that they become amenable to biotreatment which should be enhanced by oxygen released during peroxide decomposition. Processes that are dependent on contaminants being in free or aqueous state could benefit from MRP due to its anticipated soil organic matter degradation capabilities. Providing thermophysical enhancements, such as soil heating, could enhance degradation rates in some settings. Finally, coupling MRP approaches with horizontal fracturing could provide benefits by distributing oxidants into zones beyond the boundaries of the mixed region itself.

3.4 REMEDIAL CAPABILITY OF MRP IN STRATIFIED LOW PERMEABILITY SOILS

The following scenario is considered:

- The soil is stratified with layers ranging from medium sand to silt
- The soil is relatively dry with continuous air pathways in both the silt and the sand
- The sand behaves like a porous media with regard to fluid flow
- There are some preferential pathways in the silt and in the sand
- The water table is located 3-4 m below the ground surface
- The effective air-filled porosity is 0.2; the total porosity is 0.3

3.4.1 Removal of: (1) Free Product Trapped on Perched Low Permeability Lenses; (2) Aqueous Phase Product Diffused into Continuous Low Permeability Layers; (3) Adsorbed Product on Both Permeable and Low Permeability Layers; (4) Residual Product in Both Permeable and Low Permeability Layers; (5) Free Product on the Water Table Adjacent to the High Permeability Layer; (6) Contaminant Recovery from Low Permeability Isolated Lenses Rather than Continuous Layers

MRP is applicable to this scenario for the same reasons stated above for the massive deposit (see Section 3.3). 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 the NAPLs should occur, whether they are present as residual product or diffused into matrix blocks.

3.4.2 Complementary Technologies in This Type of Setting

As described for the massive deposit scenario (see Section 3.3) several technologies could be utilized to provide enhanced treatment. Thermophysical enhancements, such as soil heating, within the low permeability deposits could enhance degradation rates in some settings. Incorporating secondary treatment processes could also provide benefits. For example, passive volatilization and/or bioremediation enhancements could be used following MRP. In this scenario, hydrogen peroxide might also be injected in such as way as to flow through the permeability layers and over and into the low permeability layers/lenses. In this way, treatment might be achieved beyond the mixed region boundaries.

3.5 COST AND COMMERCIAL AVAILABILITY OF MRP

The cost and commercial availability of the in-situ MRP technology can be illustrated for a hypothetical site, 100 ft by 100 ft by 15 ft deep (~5550 yd^3). This site is characterized by stratified fine-grained media contaminated with gasoline that is diffused into the low permeability matrix blocks at a concentration of 1000 ppm.

3.5.1 Cost to Remediate Down to 200 ppm Level

Based on a limited amount of full-scale data for MRP with chlorinated solvents like TCE, the cost for 80% removal efficiency is estimated at approximately \$100-\$150/yd^3 These data are projected based on a treatment cost of \$200/yd^3 for 70% removal of TCE as determined during a full-scale field demonstration at a secured DOE site (Siegrist et al., 1993). This assumes that offgas treatment constraints are nominal. These costs are not significantly different than those associated with MRVS, since major costs are associated with mobilization/demobilization and operation of the mixing equipment (Siegrist et al., 1993). Coupling chemical oxidation with secondary processes might reduce the treatment costs.

3.5.2 Estimated Time to Remediate

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 100-200 yd^3/d (Siegrist et al., 1993).

3.5.3 Extent to which Technology is Commercially Available

As described in Section 2.5.3, soil mixing technology is commercially available. Adaptation to enable MRP should be readily accomplished.

3.6 FIELD EXPERIENCES WITH MRP

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. One field process involves placing contaminated soil into a hopper and mixing it under vacuum while hydrogen peroxide is added. The offgas is passed through carbon filters to remove VOC's. Approximately one hundred sites containing TCE and other VOC's have reportedly been treated by this latter method with VOC levels reduced below 1 mg/kg at typical processing rates of 100 yd^3/day (Khan, 1990).

Other 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 between 200 and > 2000 mg/kg were effectively treated to less than 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 MRP has been studied at Oak Ridge National Laboratory as part of a program on in-situ oxidation of contaminated soil, including various oxidants, contaminant/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 Plant in Ohio, an evaluation was made of chemical oxidation coupled with soil mixing. MRP of VOCs was first studied in bench- and pilot-scale apparatus using clay soil material from the DOE site (Figure I-3). Initial experiments were conducted with clean clay soil contaminated with an aqueous solution of TCE (~1-35 mg/l). 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. 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 MRP was completed in Spring 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 used for testing MRVS processes (see Section 2.6). The MRP treatment operation was conducted for approximately 60-75 min. During injection of a peroxide mist into the mixed soil region, concentrations of VOC's in the offgas from the system initially rose, but to a much lower concentration than during MRVS, and then slowly declined. The treatment performance achieved as a result of 75 min. of operation with the MRP process to 15-ft depth appeared to average ~70%. The apparent VOC treatment efficiency with peroxidation was below that achieved with ambient and heated air MRVS processes. This could have been due to several factors; the dependency of in-situ peroxidation on intimate mixing and reagent contact is probably most important.

3.7 SUMMARY OF MRP

3.7.1 Overall Strengths and Weaknesses of This Technology

The strengths of MRP of NAPLs in low permeability media include the inherent benefits of mixing as well as:

(1) rapid treatment time,
(2) high destruction efficiency for VOC's and petroleum hydrocarbons,
(3) innocuous by-products, and
(4) availability and low cost of hydrogen peroxide as an oxidant.

The weaknesses of the MRP technology include:

(1) process is most suitable for acidic soils (pH<~6),
(2) degradation efficiency has not been evaluated extensively for gasoline or heavier petroleum products in low permeability media, and
(3) treatment costs of \$100-\$300/yd^3 may be higher than competing technologies in some settings.

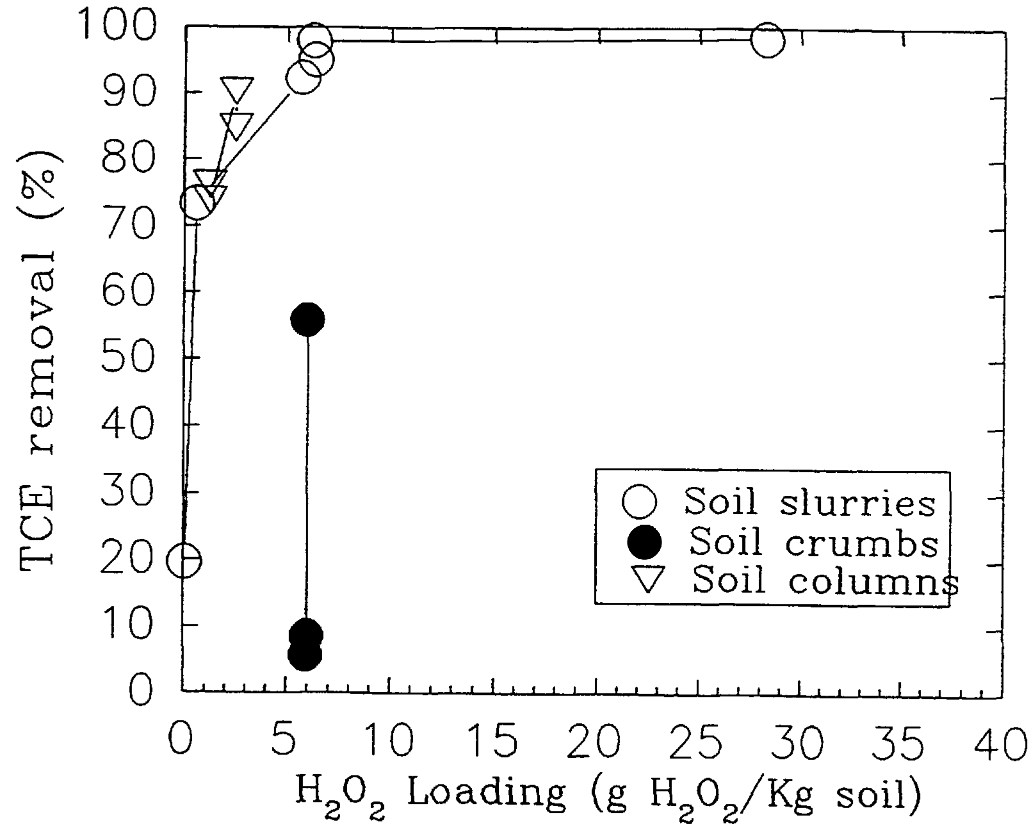

Figure I-3: TCE removal from a silty clay soil in bench- and pilot-scale experiments (Gates and Siegrist, 1993a).

3.7.2 Needed Breakthroughs Before Technology Can Be Routinely Applied

Laboratory- and field-scale tests of MRP for some NAPLs (e.g. gasoline and diesel fuel) in low permeability media are required. Parameters to be evaluated under a range of conditions include: peroxide concentration and mass loading, iron amendment requirements, optimum pH, peroxide delivery efficiency, repeated peroxide additions, reaction time, and temperature. The benefits of the complementary technologies described in Sections 3.3 and 3.4 also require further research and development. Finally, equipment modifications are needed to enable subsurface access at surface-obstructed sites (e.g., articulated mixing arms) and to treat smaller, shallower sites (e.g. smaller scale equipment).

Section 4

CONCLUSIONS

Coupling of soil mixing with treatment processes like vapor stripping and chemical oxidation offers the potential of providing a rapid and effective in-situ remediation technology for organic compounds in soil and sediments. This mixed region strategy is 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 NAPL-contaminated low permeability media is very attractive since it offers perhaps the only way to rapidly and extensively disperse treatment agents and concomitantly remove/degrade contaminants in such settings. Much of the complexity and cost of a mixed region treatment process (either MRVS or MRP) is associated with mobilization/demobilization and operation of the soil mixing and delivery system. The costs associated with the treatment agents themselves (e.g., ambient air, heated air, hydrogen peroxide) are relatively minor. Offgas treatment costs can represent minor or moderate costs, depending on the level of contaminants and treatment required.

The state-of-knowledge and -practice is such that firm guidelines cannot be given regarding selection of one mixed region treatment process over another (e.g., MRVS vs. MRP) or the optimum conditions for implementation in a given setting. However, some remarks can be made concerning the relative advantages and disadvantages of MRVS versus MRP. MRVS has the advantage of providing high treatment efficiencies while being relatively simpler and easier to implement. Chemical solutions are not involved in MRVS and thus, chemical handling equipment is not required, injection permits are unnecessary, and health and safety hazards are less. Moreover, since MRVS physically removes NAPL contaminants from the subsurface, on-line process monitoring and control is feasible. Finally, since no liquids are introduced, there is no potential for contaminant leaching.

In contrast, MRP has the advantage of more rapid treatment of not only volatile, but also semi-volatile organics. The addition of hydrogen peroxide yields oxygen thereby enhancing potential biodegradation of original or partially oxidized organics. MRP may also enhance mixing efficiency and reduce mixing energy requirements. Finally, MRP may reduce the potential for post-treatment leaching of untreated contaminants (e.g., heavy metals) by reducing matrix and bulk deposit permeability as a result of increasing water content and site recompaction.

Given a MRVS process, benefits from the use of heated air or steam rather than ambient air will depend on the contaminant properties (i.e. concentration and solubility) and media properties (i.e. sorption and heat transfer). Benefits gained by injecting heated air are measurable and probably warranted for contaminant/media systems with relatively higher sorptive properties (e.g. Kd > 0.1 mL/g). Injection of steam is more uncertain as it may result in saturation and water flooding prior to system drying and vapor stripping of NAPLs.

There is potential for coupling MRVS, MRP, and other complementary technologies (e.g. fracturing systems and oxidation, bioremediation, and other treatment processes). For example, MRVS could be employed to remove the accessible volatile fractions followed by MRP to facilitate degradation of the remaining less volatile or entrapped organics.

In summary, modeling, experimentation, and field demonstration efforts have provided considerable insight into the principals and processes of MRVS and MRP technologies. Nevertheless, there is need for further research and demonstration to fully understand the potential and limitation of these and related mixed region technologies, and to optimize their implementation for NAPLs in low permeability media and other contaminated site conditions.

Section 5

ACKNOWLEDGMENTS

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MODELING ISSUES ASSOCIATED WITH FRACTURED MEDIA

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ABSTRACT

This paper describes the modeling issues associated with predicting the behavior of LNAPL's in fine-grained soils. It specifically considers the use of models for predicting the performance of soil vapor extraction (SVE) technologies in this media. At the present time, it is felt that screening level models alone are appropriate for this analysis and therefore only these models are included in the discussion.

Section 1
INTRODUCTION

Research on modeling flow and contaminant transport in fractured media has been conducted since the early 60's (Barenblatt et al., 1960). The interest in this problem was initially limited to groundwater flow, and at that time various dual porosity models were developed. In the early 80's the research focus shifted to contaminant transport problems, mostly due to the plans for storage of radioactive wastes in deep rock formations. Most research efforts have been concerned with solute transport in the aqueous phase. Two modeling approaches were used: (1) analytical models of solute transport in geometrically simple fractures, and (2) numerical models of transport in complex fracture systems, including randomly distributed fractures.

The second approach simulates media that are closer to reality. However, for most practical subsurface contamination problems, the details of fracture spatial distribution and geometry are not known, even in the stochastic sense. The problem is further complicated by the fact that the distribution and composition of contaminants in the subsurface are typically not well determined. For these reasons it is felt that modeling of soil vapor extraction in fractured media should be treated as a screening, not a predictive, tool. In such a screening model a number of simplifying assumptions concerned with the fracture and matrix geometry as well as contaminant distribution can be introduced. It is understood that the modeling results should be used to analyze the overall feasibility of vapor extraction for a given site, and not for performance prediction. It is emphasized, however, that the screening function of the models is very important. In site-specific situations the screening models may be very helpful in deciding whether SVE technology is effective for mitigating the site.

In the next two sections the major physico-chemical processes that need to be taken into account in the modeling effort will be discussed. Some simple models that can be used to analyze the problem will also be explained. This information should be useful to modelers intending to develop computer codes that could be used to analyze vapor extraction in layered or fractured formations and to engineers who plan and evaluate such modeling efforts.

Section 2
MAJOR PROCESSES

The problem of concern is vacuum or vapor extraction of hydrocarbons from a fractured vadose zone. Figure J-1 illustrates the fractured media concept, including the relationship of the fractures and the matrix blocks which provide low and high resistivity to air flow, respectively. It is assumed that the fractures are void of water but the soil matrix is water-saturated. The soil matrix is treated as a hydrophilic medium, meaning it is attracted to water. Under such conditions any separate-phase hydrocarbons will be stored in the fractures, and will not enter the soil matrix. The last assumption can be violated if the oil-water capillary pressure is greater than the oil entry pressure.

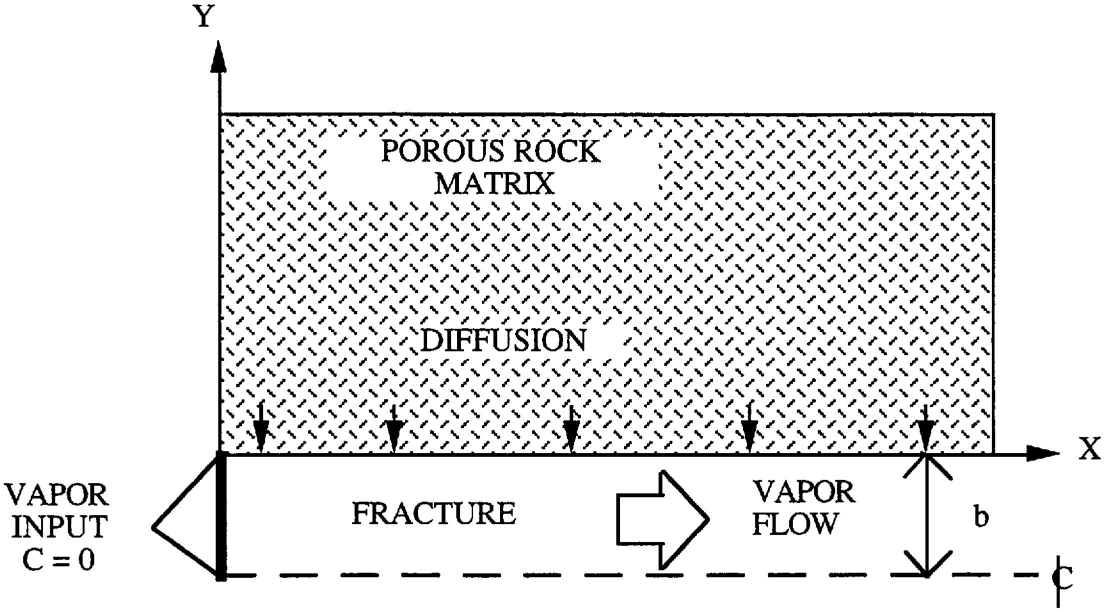

Figure J-1. Schematic representation of Scenario 1. (b = half of the fracture aperture)

Regarding the distribution of hydrocarbons, four scenarios are considered: (1) all hydrocarbons are dissolved in the aqueous phase in soil the soil matrix blocks; (2) residual hydrocarbons are distributed in fractures above the water table, partially saturating the fractures with hydrocarbons present in both the separate and dissolved phases while allowing vapor flow; (3) hydrocarbons in fractures form a 'pancake' on the water table; and (4) hydrocarbons are stored in the vadose zone in a low permeability layer overlain by a high permeability layer.

For these scenarios, the following processes need to be considered in the screening models:

Hydrocarbon - vapor partitioning. This takes place in fractures (Scenario 2) or at the interface between hydrocarbon pancake and soil vapor (Scenarios 3 and 4). The phenomenon can be modeled using the ideal gas law that linearly relates the vapor concentration of a given compound to its mole fraction in the hydrocarbon mixture.

Hydrocarbon - water partitioning. This occurs at fracture walls when a separate-phase hydrocarbon is present in the fractures. The modeling approach is to use Raoult's law. This is a linear law which relates the aqueous concentration of a given compound to its mole fraction in the hydrocarbon mixture, i.e. the equilibrium aqueous concentration is equal to the product of the compound's solubility and its mole fraction in the hydrocarbon mixture (Johnson et al., 1990, equation 25).

Hydrocarbon - soil partitioning. This occurs in the soil matrix between the aqueous phase of the contaminant and the organic carbon in the soil. The modeling approach is to use linear reversible equilibrium.

Water - vapor partitioning. This phenomenon occurs after the separate hydrocarbon is removed from the fractures. The modeling approach is to use Henry's law. This law is a linear relationship between the aqueous and vapor concentrations of a given compound.

Vapor flow. The flow takes place in fractures and is calculated using the cubic law, i.e. flow is proportional to the fracture aperture cubed. For a simple fracture geometry the flow can be estimated analytically; complex fracture systems may require numerical simulations.

Hydrocarbon diffusion in the vapor phase. This occurs above the pancake (Scenario 3) or a low permeability layer (Scenario 4). The modeling approach is to use Fick's law which describes the flux of contaminants as being linearly proportional to the concentration gradient. A molecular vapor diffusion coefficient is the constant of proportionality.

Hydrocarbon diffusion in the aqueous phase. This occurs in the soil matrix. The modeling approach is to use Fick's law with the aqueous diffusion coefficient for a given compound.

Hydrocarbon dispersion in the vapor phase. This occurs in fractures due to a non-uniform velocity distribution. The modeling approach is again to use Fick's law.

Water table upconing. This phenomenon occurs due to reduced vapor pressure above the water table, which in turn is caused by an SVE trench or well(s). The water table rise is approximately equal to the pressure reduction (vacuum), expressed in inches of water. This phenomenon has to be considered for all the scenarios to ensure that the contaminated zone is not flooded by water, thus preventing efficient vacuum extraction.

Section 3
SCREENING MODELS

Most models developed to simulate transport in fractured systems assume that the transport process will take place in one phase. In the case of vapor extraction, the transport occurs in two (aqueous and vapor) phases. However, when linear partitioning between the phases is assumed, the one-phase models can be modified to be used for the two-phase problem. Also, the models typically assume that a dissolved contaminant enters a clean fractured media. This situation can be reversed to simulate SVE conditions by using the superposition principle. In the next section the available models that can be used to simulate hydrocarbon vapor extraction for the four scenarios will be described. Most emphasis will be placed on Scenario 1 (all dissolved phase hydrocarbons in the matrix blocks), which is felt to be most common.

3.1 SCENARIO 1

In this scenario clean vapor enters the contaminated fractured zone on one side (possibly via passive vapor wells or trenches) and is removed on the other side by a vacuum trench or well(s). It is assumed that initially the contaminant is uniformly dissolved in the aqueous phase present in the soil matrix. As the vapor travels through the fracture system, the contaminant is partitioned between the aqueous and vapor phases (Figure J-1). Theoretically, the higher the vapor flow rate through the fractures, the higher the contaminant removal rate. This is related to the fact that for the higher vapor flow rates, the vapor concentration in the fractures is lower, thus enhancing the diffusion of contaminant out of the soil matrix (Figure J-2). However, as the vapor flow rate increases, the process becomes limited by the aqueous phase diffusion of the contaminant.

There are several models that can be used to simulate this problem. The general guideline for choosing one of them for a site-specific analysis is that the geometry of the fractures should correspond as closely as possible to the fracture scheme assumed in the model.

The simplest model is the one developed by Grisak and Pickens (1981). This model neglects dispersion in the vapor phase, which is felt should not have a significant impact on the results of SVE analysis. The model was developed for a single fracture.

Tang et al. (1981) developed a general transient solution for a single fracture (Figure J-3). In their model they included the dispersion in the vapor phase.

In this case the soil matrix block is assumed to extend to infinity in the direction perpendicular to the planar fracture. The solution was developed for an infinite fracture, but it can be used for finite length fractures with a small loss of accuracy. This solution can be used to analyze, for example, vapor extraction via a large single fracture created by hydrofracturing.

Sudicky and Frind (1982) derived a transient solution for a system of parallel infinite fractures (Figure J-4). The dispersion in the vapor phase is included in the solution. Again, the solution can be used to analyze vapor extraction in a system of finite-length fractures, particularly if the magnitude of dispersion in fractures is insignificant compared to the advection mechanism.

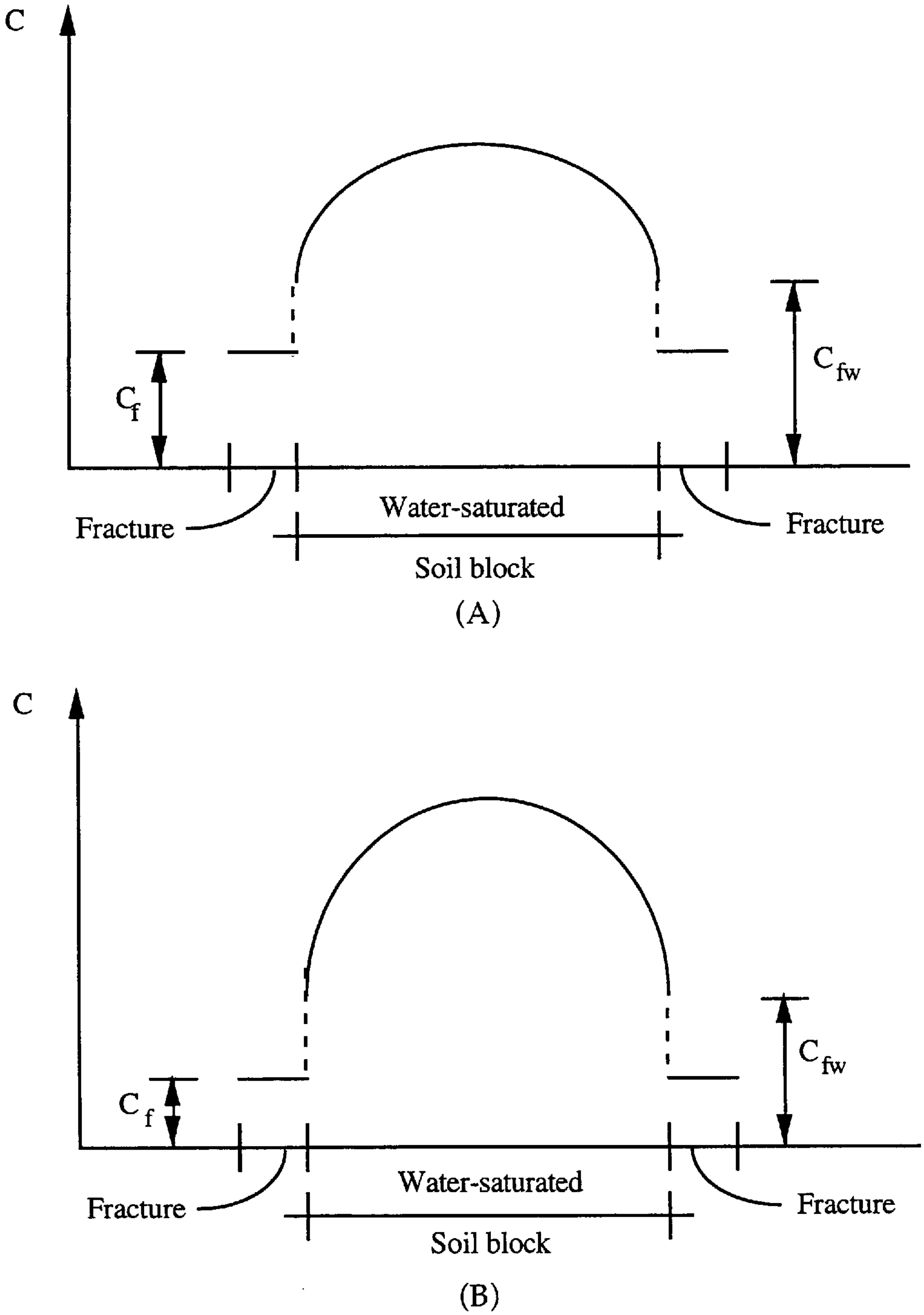

Figure J-2. Concentration profile in soil matrix block: (A) low vapor flux, and (B) high vapor flux. (C_f = concentration in the vapor phase at the fracture-matrix interface, C_{fw} = concentration in the aqueous phase at the fracture-matrix interface)

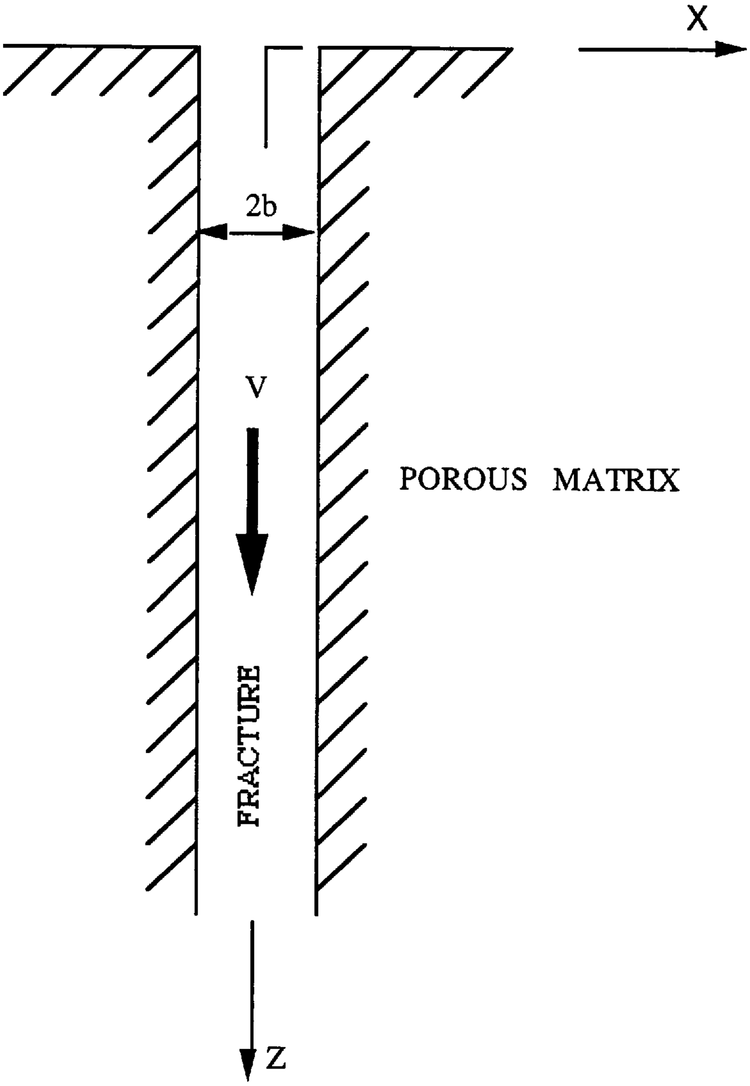

Figure J-3. Venting in a single fracture. (2b = fracture aperture, V = vapor velocity)

Dykhuizen (1992) presents a solution for diffusive transport out of perpendicular matrix blocks into a system of parallel fracture-channels (Figure J-5). Flow occurs in the fractures, but they are not uniform and are assumed to 'pinch out' in places. In the figure, this is simulated by assuming that flow occurs only in the 'active' channels which are uniformly spaced along the fracture plane. The solution assumes that the concentration in the fractures is constant. This solution can be used to simulate vapor extraction at high vapor flow rates. In this case the vapor concentration can be assumed to be close to zero, and thus the mitigation process is limited by aqueous diffusion.

Rasmuson (1984) presents a complex transient solution to one-dimensional transport in fractures and radial diffusion in spherical soil blocks. The solution is obtained in the form of an infinite integral. It is felt that this solution is too complex for screening purposes.

3.2 SCENARIO 2

In this scenario, the separate-phase hydrocarbon partially fills some fractures, without totally obstructing the vapor flow through those fractures. The modeling approach for this scenario consists of two components: (1) separate-phase hydrocarbon removal, and (2) removal of the hydrocarbon dissolved in the aqueous phase. The second component is the same as for Scenario 1. The separate-phase hydrocarbon removal involves vapor flow in fractures and oil-vapor partitioning, and can be simulated using a lumped-parameter model developed by Johnson et al. (1990). Using this approach, the vapor flow rate through the contaminated zone can be calculated using the cubic law, taking into account the partial saturation of fractures. Then the removal rate can be estimated as a product of the flow rate and the contaminant equilibrium concentration. The latter is estimated using the ideal gas law. After a given compound is essentially removed from the separate phase, the second model component is used to analyze the removal of the compound from the aqueous phase.

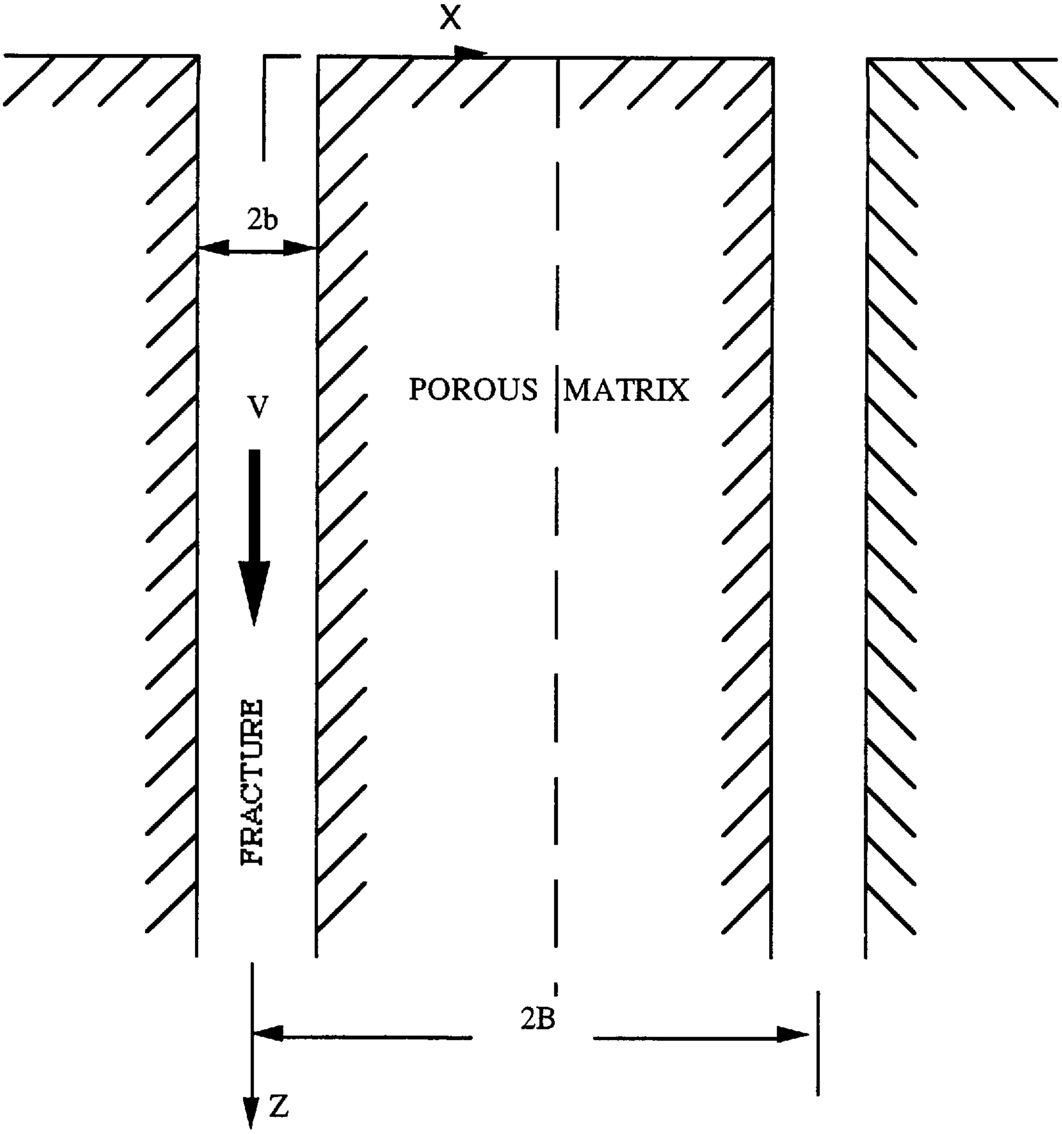

Figure J-4. Venting in parallel fractures. (2b = fracture aperture, V = vapor velocity, 2B = average distance between fractures)

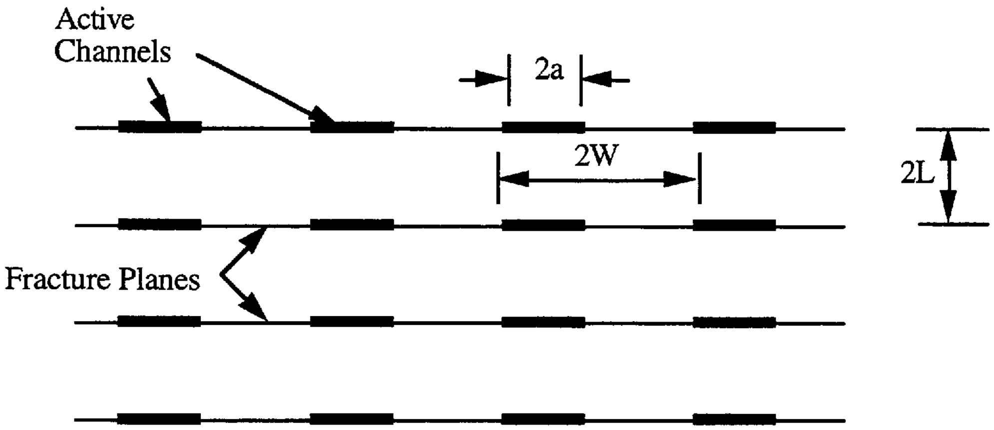

Figure J-5. A system of channels. In this schematic: 2a = average width of active channels in the fracture plane (note that flow occurs through these channels only into the paper), 2W = average distance between active channels, and 2L = average distance between fracture planes

3.3 SCENARIO 3

In this case there are three processes that need to be considered in the model: (1) partitioning of hydrocarbons between the oil "table" and the vapor phase, (2) vertical diffusive transport of hydrocarbons in the vapor phase, and (3) horizontal advective transport of hydrocarbons in the vapor phase into a vapor extraction trench or well (Figures J-6a, J-6b and J-7). These processes can be simulated in each fracture (Figure J-8) using the boundary layer approach (Johnson et al., 1990).

The approach assumes that the vapor concentration at the hydrocarbon-vapor interface can be estimated using the ideal gas law. It also assumes that the general form of the concentration distribution within the boundary layer can be approximated using a simple polynomial function. This function has to satisfy in this case three boundary conditions: (1) the vapor concentration at

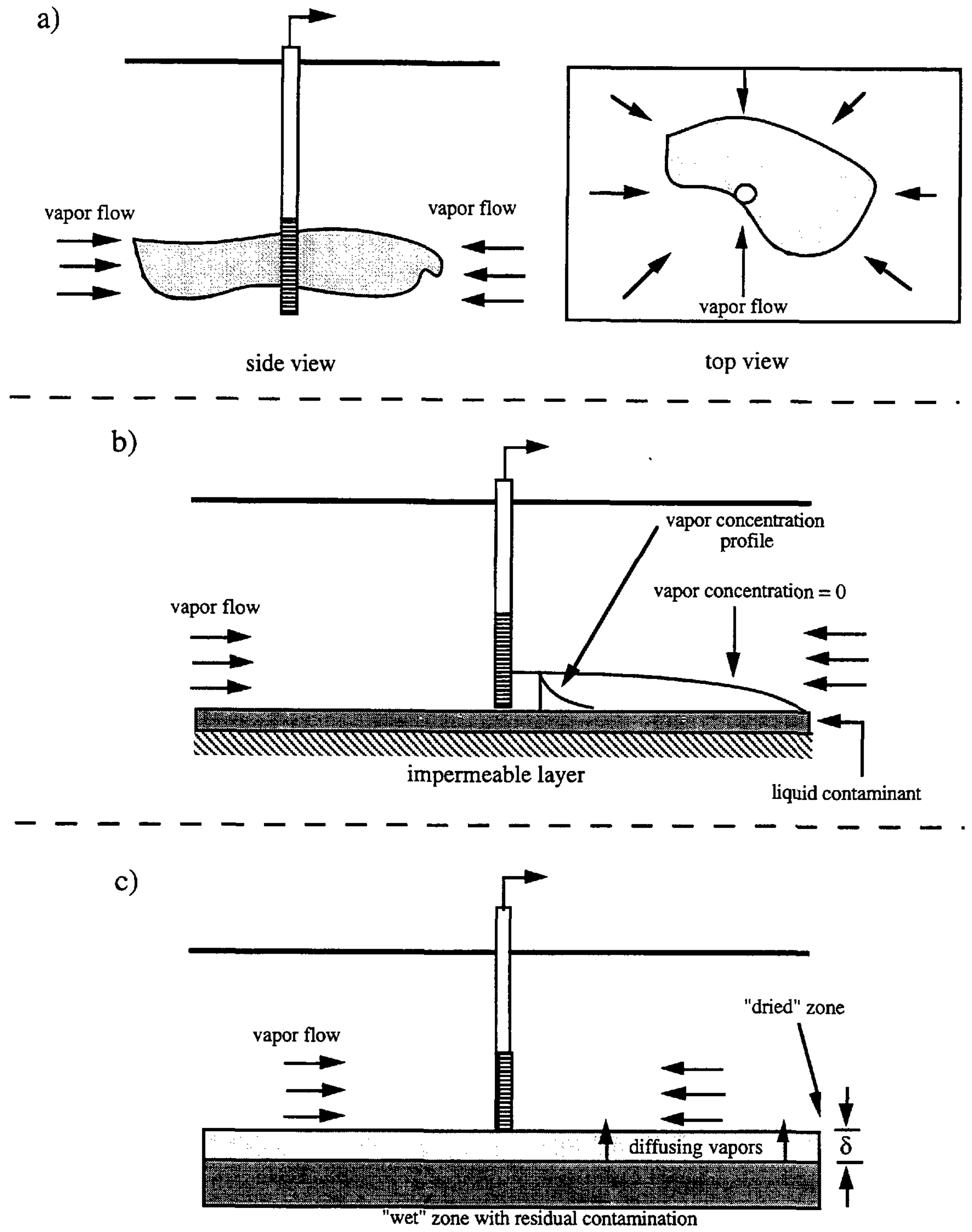

Figure J-6. Scenarios for removal rate estimates (δ = thickness of dried out zone)
Note: These figures are taken from Johnson et al., 1991.

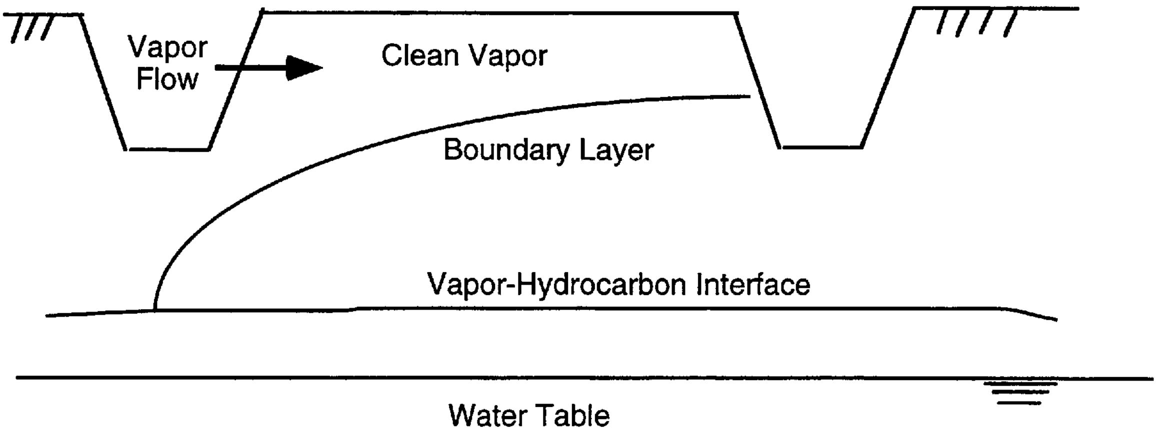

Figure J-7. Venting of pancake

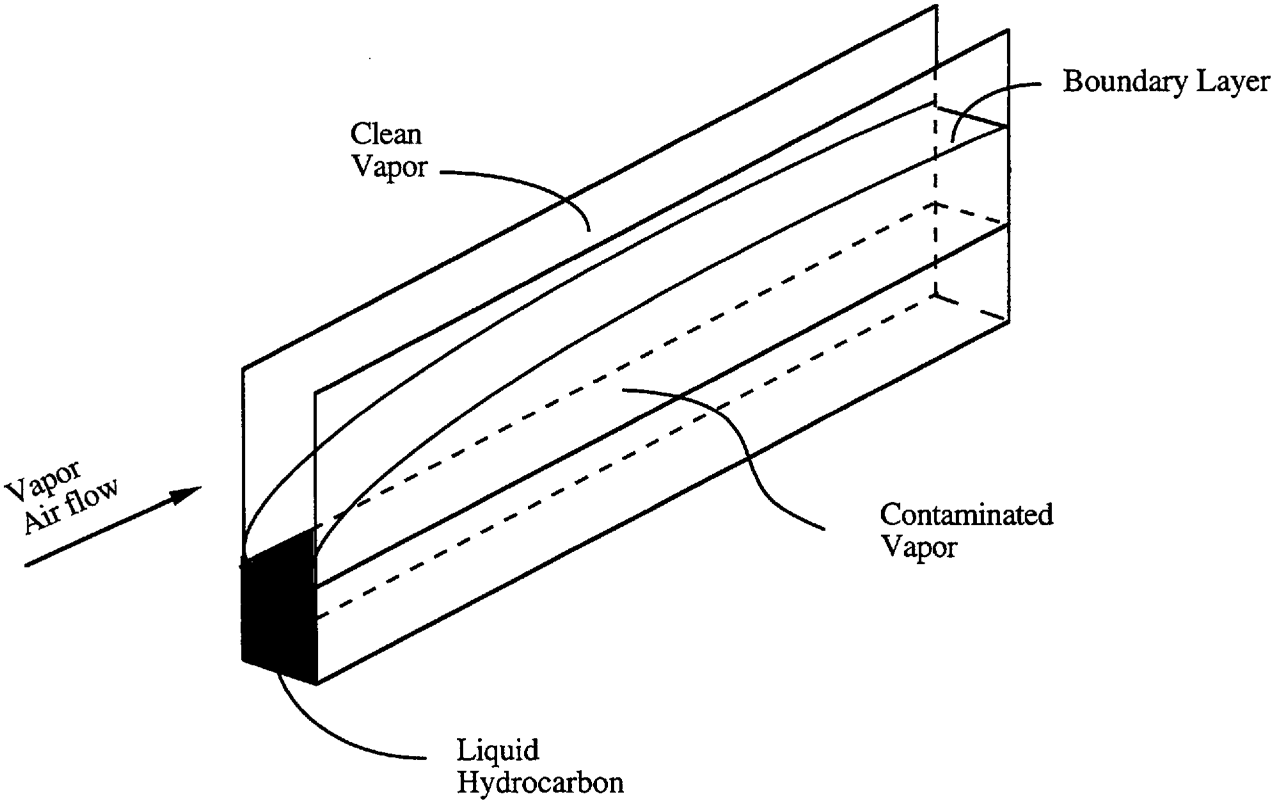

Figure J-8. Boundary layer in a single fracture the hydrocarbon-vapor interface is known and constant along the fracture, (2) at the upper vertical limit of the boundary layer the concentration is equal to zero, and (3) at the upper vertical limit of the boundary layer the vertical component of the concentration gradient is equal to zero (Figure J-9). Using this approach, the removal rate of any compound from the hydrocarbon mixture can be estimated. This information can then be used to update the composition of the hydrocarbon mixture via mass balance. For the sake of simplicity this approach neglects any transport processes within the pancake.

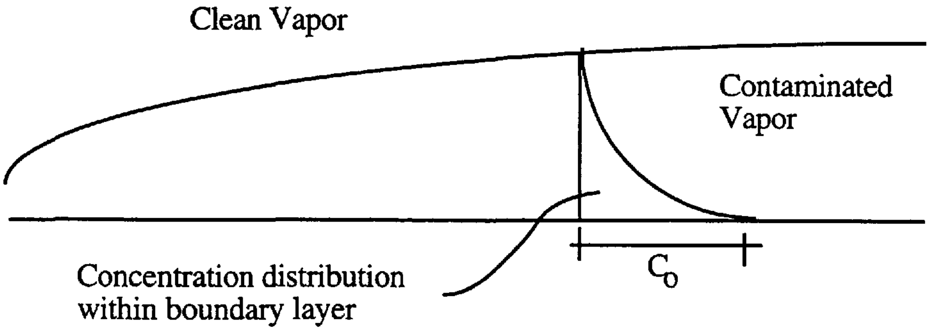

Figure J-9. Concentration distribution within a boundary layer.
C_O = equilibrium concentration

3.4 SCENARIO 4

Figure J-6c depicts the situation in which vapor flows primarily past, rather than through the contaminated soil zone, such as might be the case for a contaminated clay layer surrounded by sandy soils. In this case vapor phase diffusion through the clay to the flowing vapor limits the removal rate. The maximum removal rate in this case occurs when the vapor flow is fast enough to maintain a very low vapor concentration at the permeable/impermeable soil interface. At any time t, a contaminant-free "dried out" zone of low permeability will exist with a thickness δ. An estimate of the removal rate R_{est} from a contaminated zone will be proportional to the estimated equilibrium vapor concentration (ideal gas law), C_{est} and the effective porous media vapor diffusion coefficient, D, and inversely proportional to thickness δ. With time $\delta(t)$ will grow larger. In the case of a single component system the dry zone thickness can be calculated from the mass balance equation (Johnson et al., 1991, Equation 11). The solution to the mass balance equation yields the equation that predicts the change of "dried out" zone thickness with time (Johnson et al., 1991, Equation 12). This equation can be used to estimate the time it takes to vapor extract hydrocarbons out of the low permeability layer by the diffusion process.

Section 4

DATA NEEDS

In this section the most important data that are needed to perform vapor extraction feasibility analysis will be described. It is assumed that standard chemical data, such as molecular diffusion coefficients, vapor pressures, etc., are available for the compounds of interest.

4.1 CONTAMINANT DATA

4.1.1 <u>Hydrocarbon composition</u>

This is used to estimate the equilibrium vapor concentrations if separate-phase product is present (Scenarios 2, 3, and 4). This information may be obtained by a complete chemical analysis of a hydrocarbon mixture sample, using one of the following methods:

EPA 8240, 8020, 8010	- volatile organic chemicals (VOC)
EPA 8270	- semi-volatile organic chemicals
EPA Modified 8015	- total petroleum hydrocarbons (TPH, reported as either gasoline range or diesel range organics)

For complex contamination mixtures, such as gasoline, diesel fuel, and solvent mixtures, it is not practical or necessary to identify and quantify each compound present. In such cases it is recommended that a "boiling point" distribution be measured for a representative sample of the residual contamination (Johnson et al., 1991).

4.1.2 Hydrocarbon distribution in the solid phase

This data is essential. SVE efficiency will be quite different, depending on which of the four scenarios is applicable. This data can be obtained by collecting soil samples and analyzing them for TPH, which can include gas chromatographic (GC) methods like GRO (gasoline range organics) and DRO (diesel range organics) in addition to Method 418.1. Costs can be minimized and more data obtained by utilizing field screening tools, such as hand-held vapor meters or portable field GC's. These instruments can be used to measure both residual soil contamination levels and soil gas vapors above contaminated soils.

4.1.3 Hydrocarbon concentrations in the aqueous phase

This is the initial condition for Scenario 1 and the second phase of Scenario 2. The information can be obtained using the following methods to analyze formation water samples:

EPA 8240, 8020, 8010	- volatile organic chemicals (VOC)
EPA 8270	- semi-volatile organic chemicals

4.2 SUBSURFACE DATA

4.2.1 Fracture distribution, aperture, and connectivity

This data is required to estimate the flow rate through the contaminated zone (Scenarios 1, 2, and 3) and to determine the typical soil matrix block geometry at a site (Scenarios 1 and 2). It can be obtained by analyzing drilling cuttings, analyzing surface fracture distribution of exploratory trenches, and by analyzing results of in-situ tracer tests (either in the vapor phase in the vadose zone or in the aqueous phase in the saturated zone). With the tracer tests, an average aperture diameter is assumed and the measured flow is used to back-calculate an average fracture spacing, using the cubic law.

4.2.2 Retardation coefficients for the aqueous phase diffusion

These parameters are required to estimate the cleanup time for the soil matrix blocks (Scenario 1 and the second phase of Scenario 2). The principal parameter is the fraction of organic carbon in the soil, which can be obtained by a TOC (total organic carbon) analysis.

4.2.3 Soil layering

This information is required to analyze efficiency of vapor extraction for Scenario 4. It can be generated by analyzing drilling logs or with tools such as cone penetrometers.

Section 5
SUMMARY

Four hydrocarbon contamination scenarios have been described according to the major physico-chemical processes affecting the feasibility of remediating them by soil vapor extraction. Several simple models that can be used as screening tools to evaluate SVE efficiency in fractured media have also been evaluated. These models are not developed to the point where they can be relied upon to give quantitative predictions of the performance of soil vapor extraction systems. However, for sites where the fracture-matrix dimensions and contaminant distributions are consistent throughout a site, and where there are little or no large scale heterogeneities, these screening models should be able to give an indication of whether SVE is viable in terms of the approximate time frame for cleanup.

Section 6
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