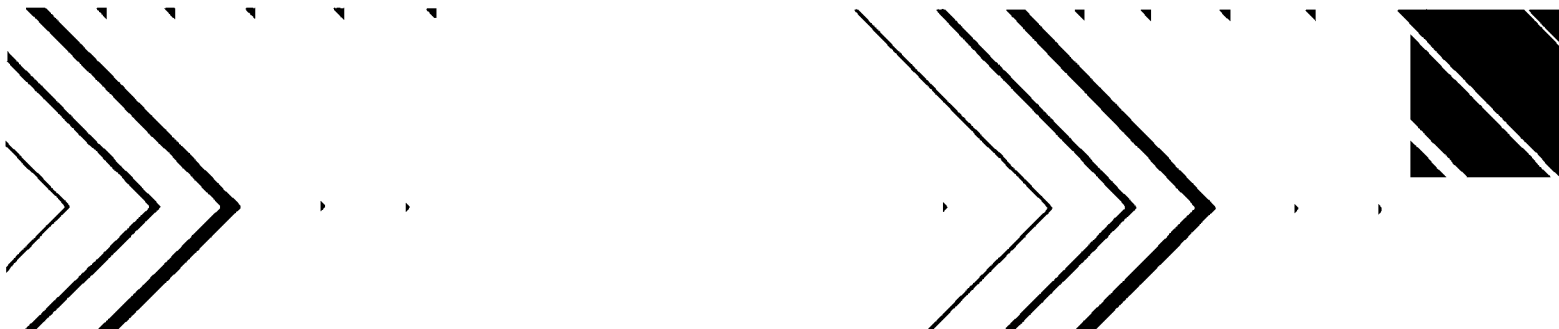




Evaluation of Technologies for In-Situ Cleanup of DNAPL Contaminated Sites



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EVALUATION OF TECHNOLOGIES FOR IN-SITU CLEANUP
OF DNAPL CONTAMINATED SITES

by

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FOREWORD

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This report provides a review and technical evaluation of in-situ technologies for remediation of DNAPL contamination occurring below the ground-water table. Various in-situ technologies are reviewed and are evaluated on the basis of their theoretical background, field implementation, level of demonstration and performance, waste, technical and site applicability/limitations, and cost and availability.

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ABSTRACT

Ground water contamination by non-aqueous phase liquids poses one of the greatest remedial challenges in the field of environmental engineering. Denser-than-water non-aqueous phase liquids (DNAPLs) are especially problematic due to their low water solubility, high density, and capillary forces arising from interfacial tension between the DNAPLs and water. As a result, conventional pump-and-treat technologies have met poor success in remediation of DNAPL contaminated aquifers. In fact, in certain situations, conventional pump-and-treat methods may actually extend existing contamination into previously uncontaminated areas. The problems associated with current pump-and-treat remedial approaches have served as the impetus to develop alternative technologies to accelerate in-situ DNAPL contamination remediation. This report provides a review and technical evaluation of in-situ technologies for remediation of DNAPL contamination occurring below the ground-water table. Various in-situ technologies are reviewed and are evaluated on the basis of their theoretical background, field implementation, level of demonstration and performance, waste, technical and site applicability/limitations, and cost and availability.

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SECTION 1.0

INTRODUCTION

1.1 OVERVIEW AND ORGANIZATION

Ground-water contamination by immiscible hydrocarbons, often referred to as non-aqueous phase liquids (NAPLs, or LNAPLs and DNAPLs denoting those lighter or denser than water, respectively), poses one of the greatest remedial challenges in the field of environmental engineering. DNAPLs are especially problematic due to their low water solubility, high density, and capillary forces arising from interfacial tension between the DNAPLs and water. As a result, conventional pump-and-treat technologies have met poor success in remediation of DNAPL contaminated aquifers [Wilson, 1992].

The objective of this report is to provide a comprehensive assessment of the current state-of-the-art of in-situ treatment technologies as they pertain to the treatment, mobilization, and recovery of DNAPLs from the subsurface. Focus is placed on attempting to identify in-situ technologies capable of addressing the remediation of DNAPLs situated below the water table; secondary importance is placed on contaminants dissolved in the aqueous phase. Several of the evaluated technologies were not originally developed for remediation of contaminated sites, much less DNAPLs. As a result, some of the technologies have not yet been demonstrated on DNAPLs, and owing to their developmental stage, have not been demonstrated in the field and below the water table. However, their applicability to remediation of DNAPLs is nonetheless considered in order to not rule them out prematurely. On the other hand, while the technology required to implement certain remedial approaches may be currently available, the expertise required for successful full-scale field application may be lacking. Also, some of the technologies have been fully demonstrated only in non-environmental applications and are just being adapted for environmental applications.

Aside from technology evaluation and selection, there are several factors controlling remedial options. Containment, recovery, and remediation options are usually dictated by site considerations, regulations, cost, extent of contamination, and presence of other waste types. The problem of mixed inorganic and organic wastes is a complicated one that has not been fully addressed here because this project was limited to DNAPLs. Nonetheless, site heterogeneity and regulatory approval are seen to be the most critical factors controlling remedial options. Extensive site heterogeneity can render all technologies ineffective, some more than others, and most technologies will require regulatory approval to implement. Albeit mentioned, regulatory acceptance and related issues are beyond the scope of this document.

In order to identify the various physical and technical barriers limiting DNAPL treatment, mobilization and recovery, the mechanisms responsible for DNAPL fate and transport are outlined in section 2.0. In-situ technologies are arranged alphabetically by major process type in Section 3.0 and are evaluated for their applicability to cleanup of DNAPL contaminated sites. The following aspects of each relevant in-situ technology were evaluated: theoretical background, field implementation, level of demonstration and performance, applicability/limitations, and cost and availability. Finally, the in-situ technologies are compared and contrasted on several different levels in section 4.0.

1.2 METHODOLOGY

This study was conducted between December, 1991, and May, 1993; and the major effort in this study was the review and compilation of information on in-situ DNAPL treatment technologies: no actual experiments were conducted. Approximately 400 references were compiled during this study. Much of this

information was collected from journal articles, conference proceedings, vendor and manufacturer fact sheets and literature, and federal, state, and local agency reports and publications. The authors also attended a number of conferences to obtain information as current as possible.

To supplement these sources of information, an "In-Situ DNAPL Remediation Technology Description Questionnaire," was developed in cooperation with EPA personnel at the Robert S. Kerr Environmental Research Laboratory. The questionnaires were sent to academic, federal and state, and institute and industry professionals working in the area of DNAPL cleanup. The first mailing of these questionnaires occurred in February, 1992. Positive responses were followed up with letters and personal contacts to the extent necessary for an adequate technology evaluation. As the project progressed, the correspondence was expanded as additional responses were solicited and received.

The technology descriptions of the relevant in-situ technologies were then prepared. The following aspects of each relevant in-situ technology were evaluated: theoretical background, field implementation, level of demonstration and performance, applicability/limitations, and cost and availability. Several technologies have been demonstrated at different stages of development or have been demonstrated numerous times. In such cases, an effort was made to evaluate the most current information and to select representative applications illustrating the more interesting or impressive capabilities of the technology. However, an exhaustive compilation of relevant case studies (as in the case of slurry wall construction) was beyond the scope of this effort. Thus, the technology descriptions are intended to provide a basic technical assessment of the technology and to identify its problem areas using basic principles.

1.3 LIMITATIONS OF THE REPORT

Due to the limited time frame of this project (18 months), the technology descriptions included within this report cannot be considered exhaustive nor are they intended to be. Several additional factors contribute to this fact: poor literature reporting; gaps due to unavailability of information; nature of proprietary research and/or confidential information; and stage of development of technology. Furthermore, the past performance of certain in-situ technologies which were originally designed for other applications and/or targeted waste groups is not directly transferable. Consequently, the anticipated performance of these technologies can be difficult to interpret within the context of DNAPL cleanup.

While this report can help identify potentially applicable in-situ technologies for cleanup of DNAPL contaminated sites, it is not intended to be the sole basis for selecting a technology for a particular DNAPL at a given site. Consequently, this report should serve as a complement to, not a substitute for, engineering judgement, analysis, and design. Potential in-situ technologies must be further evaluated by contacting technology developers (vendors, contractors, etc.,) and by performing bench-, and/or pilot-scale treatability tests as necessary under site-specific conditions. This is especially true for undemonstrated technologies and for technologies whose success depends heavily on the characteristics of the waste matrix.

SECTION 2.0

DNAPL FATE AND TRANSPORT PROCESSES

A dense non-aqueous phase liquid (DNAPL) is a sparingly soluble hydrocarbon having a specific gravity greater than that of water at a typical soil temperature, usually less than 20-25°C. The distribution of a DNAPL within the subsurface is the net result of coupled chemical and physical interactions between the DNAPL, pore water, pore gases, and porous media. The chemical properties of the NAPL and chemical equilibria relationships determine the partitioning of the compounds among the various phases, while the physical properties of the pore fluids and porous media determine the mobility of each fluid phase. A summary of the most important physical and chemical properties of DNAPLs found most commonly at Superfund sites is presented in Table 2.1.

As shown in Figure 2.1.1, four distinct phases, each consisting of many chemical species, can be present in the subsurface: the gas phase (in the vadose zone); the solid phase (rock, soil grains, soil organic matter); the aqueous (polar) phase; and the DNAPL (non-polar phase). The fluid phases may be mobile or immobile, and interphase partitioning is determined by such factors as the aqueous solubility limit, Henry's constant, octanol-water partitioning coefficient, and sorption coefficients.

It is impossible within the scope of this report to describe on a site specific basis every aspect of DNAPL transport in the unsaturated and saturated zones and the available modeling techniques. The aim here is to conceptually describe the basic physical and chemical processes to aid in the discussion of problems facing in-situ technologies (Section 2.7), and to aid in the evaluation of these technologies (Sections 3,4).

2.1 PHYSICS OF MULTIPHASE FLOW

While the actual DNAPL flow and distribution will be complex owing to soil heterogeneities, two major generalizations about the migration of DNAPL can be made. In order for the DNAPL to migrate as a separate phase in any direction, both the capillary pressure resisting DNAPL flow and the DNAPL retention capacity of the soil must be exceeded. For generality, portions of this discussion will be cast in terms of "NAPL" because the relationships apply equally to both LNAPLs and DNAPLs.

2.1.1 Darcy's Law and Capillary Forces

Gas or liquid phase flow is governed by Darcy's Law for multiphase flow which incorporates both capillary pressures and fluid properties and is written for each fluid phase (H₂O, NAPL, etc.) as [Freeze and Cherry, 1979; Muskat, 1982]:

$$v_i = \frac{-k k_{ri}}{\phi \mu_i} \left(\frac{\partial P_i}{\partial x} + \rho_i g \sin \theta \right) \quad (1)$$

Here, the subscript i denotes the fluid phase i; v_i is the interstitial velocity of fluid phase i; x denotes position; the fluid properties of viscosity and density are denoted by μ_i and ρ_i , respectively; parameters of the porous media are denoted by ϕ , k, and k_{ri} which are the porosity, permeability, and the relative permeability of fluid i to the porous media, respectively; P_i indicates the capillary pressure of fluid phase i; g denotes the acceleration due to gravity; and θ is the inclination of the porous media from the horizontal. Furthermore, in water saturated porous media, the capillary pressure, P_c , between the NAPL (n) and the

TABLE 2.1 MOST PREVALENT DNAPLS AT U.S. SUPERFUND SITES [adapted from USEPA, 1992a]

Compound	Density [1] (ρ)	Dynamic Viscosity[2] (μ)	Kinematic Viscosity[3] (ν)	Interfacial Tension[4]		Water Solub.[5] (log $C_{nw,sol}$)	Oct.-Water Part Coeff.[6] (log K_{ow})	Henry's Law Constant[7] (log K_H)	Vapor Pressure[8] (log P_a°)	Boiling Point[9] (b.p.)	Dielectric Constant[10] (ϵ)
				NAPL-Air (σ_{na})	NAPL-H ₂ O (σ_{nw})						
Non-halogenated Semi-volatiles											
Acenaphthene	1 2250 ^a					0.589 ^a		-2.921 ^a	-1 636 ^a	279 ^c	
Anthracene	1 2500 ^a			15 ^b		-1 125 ^a	4 45 ^c	-4 471 ^a	-4 967 ^a	340 ^c	
Benzo(a)Anthracene	1 1740 ^a					-1.854 ^a		-5 347 ^a	-8 936 ^a		
Chrysene	1 2740 ^a					-2 222 ^a		-4 921 ^a	-5 576 ^a	488 ^c	
m-Cresol	1 0380 ^a	21.0 ^a	20 ^a	41 7 ^b	31 3 ^b	4 371 ^a	1 96/2.01 ^c	-4 420 ^a	-0.815 ^a	203 ^b	11 8 ^{(13)d}
o-Cresol	1 0273 ^a			40.3 ^b	32 7 ^b	4.491 ^a		-4.328 ^a	-0.611 ^a	191 ^b	11 5 ^{(13)d}
p-Cresol	1.0347 ^a			41 8 ^b	31 2 ^b	4.38 ^a	1 92/1 94 ^c	-3 456 ^a	-0.967 ^a	202 ^b	9 9 ^{(20)d}
Dibenz(a,h)Anthracene	1 2520 ^a					-2.602 ^a		-7 135 ^a	-10 000 ^a	524 ^c	
2,4-Dimethylphenol	1.0360 ^a					3 792 ^a		-5.602 ^a	-1 009 ^a	211.5 ^c	
Fluorene	1 2030 ^a					0 279 ^a		-4 116 ^a	-3 176 ^a		
Fluoranthene	1 2520 ^a					-0 577 ^a		-5 187 ^a	-5 699 ^a	250 ^c	
2-Methyl Naphthalene	1 0058 ^a					1.405 ^a		-1.296 ^a	-1 167 ^a	242 ^c	
Phenol	1 0576 ^a		3 87 ^a	40 9 ^d		4 924 ^a	1 46 ^c	-6 108 ^a	-0 276 ^a	182 ^c	9 78 ^{(19)d}
Pyrene	1 2710 ^a					-0.8301 ^a		-4 921 ^a	-5 576 ^a	181.8 ^b	
Halogenated Semi-volatiles											
Aroclor 1242	1 3850 ^a					-0 347 ^a		-3 469 ^a	-3 391 ^a		
Aroclor 1254	1 5380 ^a					-1 921 ^a		-3 553 ^a	-4 113 ^a		
Aroclor 1260	1.4400 ^a					-2 569 ^a	4-7 ^f	-3 469 ^a	-4.393 ^a		
Chlordane	1 6 ^a	1 1040 ^a	0 69 ^a	25 ^b	50 ^b	-1 252 ^a		-3 658 ^a	-5 000 ^a		
1,2-Dichlorobenzene	1 3060 ^a	1 3020 ^a	0 997 ^a	37 ^b	40 ^b	2 000 ^a	3 38 ^b	-2 726 ^a	-0 018 ^a	180 ^b	9.93 ^{(11)d}
1,4-Dichlorobenzene	1 2475 ^a	1 2580 ^a	1 008 ^a			1 903 ^a	3 39 ^c	-2 801 ^a	-0 222 ^a	180 ^b	2 41 ^{(18)d}
2,3,4,6-Tetrachlorophenol	1 8390 ^a					3 00 ^a					

Compound	Density [1] (ρ)	Dynamic Viscosity[2] (μ)	Kinematic Viscosity[3] (ν)	Interfacial Tension[4]		Water Solub.[5] (log $C_{nw,sol}$)	Oct.-Water Part. Coeff.[6] (log K_{ow})	Henry's Law Constant[7] (log K_H)	Vapor Pressure[8] (log P_a)	Boiling Point[9] (b.p.)	Dielectric Constant[10] (ϵ)
				NAPL-Air (σ_{na})	NAPL-H ₂ O (σ_{nw})						
Halogenated Volatiles											
Chlorobenzene	1.1060 ^a	0.7560 ^a	0.683 ^a	33 ^b	37.41 ^b	2.69 ^a	2.84 ^b	-2.461 ^a	0.944 ^a	132 ^c	5.71 ^d
Chloroform	1.4850 ^a	0.5630 ^a	0.379 ^a	27.1 ^b	32.8 ^b	3.915 ^a	1.97 ^c	-2.426 ^a	2.204 ^a	61.2 ^b	4.81 ^d
1,1-Dichloroethane	1.1750 ^a	0.3770 ^a	0.321 ^a	24.75 ^b		3.744 ^a	1.78 ^a	-3.264 ^a	2.26 ^a	57.3 ^c	
1,2-Dichloroethane	1.2530 ^a	0.8400 ^a	0.67 ^a	32.2 ^b	30 ^{(13)b}	3.939 ^a		-2.959 ^a	1.804 ^a	83.5 ^c	
1,1-Dichloroethylene	1.2140 ^a	0.3300 ^a	0.27 ^a	24 ^{(11)b}	37 ^{(12)b}	2.602 ^a	1.48 ^a	-2.827 ^a	2.699 ^a	32 ^c	4.6 ^{(17)d}
Cis-1,2-Dichloroethylene	1.2480 ^a	0.4670 ^a	0.364 ^a	24 ^b	30 ^b	3.544 ^a	1.48 ^a	-2.125 ^a	2.301 ^a	60 ^b	9.2 ^{(13)d}
Trans 1,2-Dichloroethylene	1.2570 ^a	0.4040 ^a	0.321 ^a	24 ^b	30 ^b	3.799 ^a	1.48 ^a	-2.274 ^a	2.423 ^a	48 ^b	2.14 ^{(13)d}
1,2-Dichloropropane	1.1580 ^a	0.8400 ^a	0.72 ^a	29 ^b	37.9 ^{(12)b}	3.431 ^a		-2.444 ^a	1.597 ^a	96.8 ^c	
Ethylene Dibromide	2.1720 ^a	1.6760 ^a	0.79 ^a	38.75 ^b	36.54 ^b	3.531 ^a		-3.498 ^a	1.041 ^a	131 ^b	
Methylene Chloride	1.3250 ^a	0.4300 ^a	0.324 ^a	26.52 ^d		4.121 ^a		-2.59 ^a	2.544 ^a	39.8 ^b	9.08 ^d
1,1,2,2-Tetrachloroethane	1.6 ^a	1.7700 ^a	1.10 ^a	37.85 ^b		3.462 ^a		-3.301 ^a	0.69 ^a	146.4 ^c	
Tetrachloroethylene	1.6250 ^a	0.8900 ^a	0.54 ^a	31.3 ^b	44.4 ^{(13)b}	2.176 ^a	2.88 ^a	-1.644 ^a	1.146 ^a	121.2 ^b	
1,1,1-Trichloroethane	1.3250 ^a	0.8580 ^a	0.647 ^a	25.4 ^b	45 ^b	2.978 ^a	2.48 ^a	-2.389 ^a	2.000 ^a	71/81 ^c	
1,1,1,2-Trichloroethane	1.4436 ^a	0.1190 ^a	0.824 ^a	25.4 ^b	45 ^b	3.653 ^a		-2.932 ^a	1.274 ^a	113.7 ^c	
Trichloroethylene	1.4620 ^a	0.5700 ^a	0.390 ^a	29.3 ^b	34.5 ^{(13)b}	3.000 ^a	1.3	-2.050 ^a	1.769 ^a	87.2 ^b	3.4 ^{(17)d}
Miscellaneous											
Coal Tar	1.028 ^{(15)a}	18.98 ^{(15)a}								180 ^b	
Creosote	1.05 ^a	1.08 ^{(16)a}		15 ^b	20 ^b					180 ^b	

Properties indicated 20°C unless otherwise specified below. References: a, USEPA, 1990b; b, US Coast Guard, 1985; c, Verschueren, 1983; d, CRC Press, 1992; e, Sitar et al., 1987.

Notes

- [1] g/cc
 [2] centipoise (cp), $\mu_{\text{water}} = 1 \text{ cp (20°C)}$
 [3] centistokes (cs)
 [4] dynes/cm, $\sigma_{\text{water}} = 72.5 \text{ (20°C)}$
 [5] mg/l
 [6] units of $K_{ow} = \left(\frac{q_{\text{DNAPL}}}{LC_{10}C_{22}} \right) \left(\frac{q_{\text{DNAPL}}}{LH_2O} \right)$
 [7] units of K_H , atm·m³/mol
 [8] units of P_a , mm Hg
 [9] units of B.P., °C
 [10] dimensionless
 [11] 15°C
 [12] 22.5°C
 [13] 25°C
 [14] 30°C
 [15] 45°C
 [16] 15.5°C (varies with creosote mix)
 [17] 16°C
 [18] 50°C
 [19] 60°C
 [20] 58°C

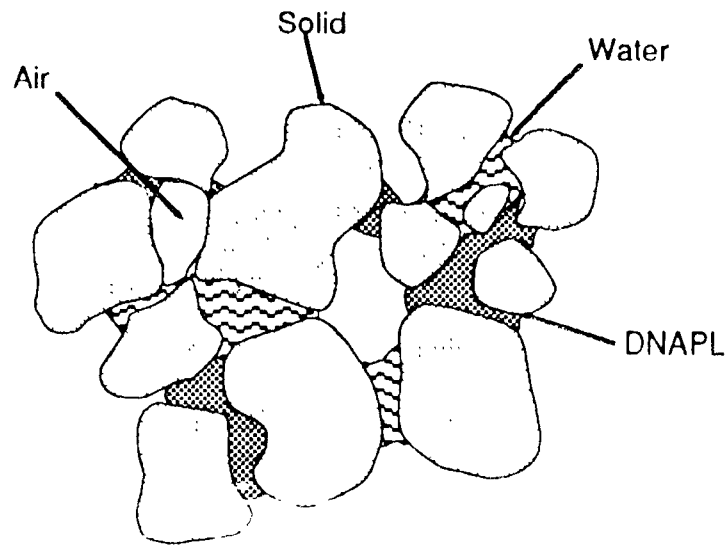


Figure 2.1.1 Schematic of a multiphase system consisting of DNAPL and air, water, and solid phases. [USEPA, 1992a].

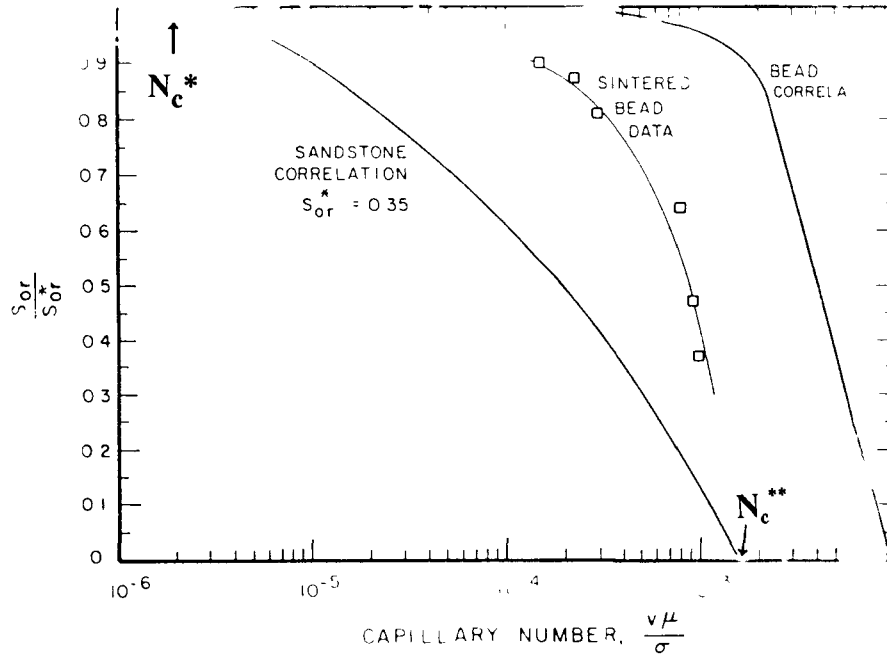


Figure 2.1.2 Mobilization of residual oil ganglia relating NAPL saturation ratio, S_{or}/S_{or}^* (initial/final NAPL S%), and the capillary number, N_c . N_c^* and N_c^{**} denote initial mobilization and 100% removal, respectively. [Morrow et al., 1985].

aqueous phase (w) can be expressed as [Muskat, 1982; Villaume, 1985; Hunt et al., 1988b]:

$$P_c = P_n - P_w = \frac{2\sigma_{nw} \cos\phi}{r_t} \quad (2)$$

where σ_{nw} is the NAPL-H₂O interfacial tension; ϕ is the contact angle (usually assumed to be zero when medium is water wet); and r_t is the mean pore throat radius.

Capillary pressures arise from the density differences in liquid properties, viscous forces caused by hydraulic gradients, and due to interfacial tension between the two liquid phases. The Bond and Capillary numbers are the ratios of buoyancy and viscous forces to interfacial forces in the vertical and horizontal directions, respectively, and are used to estimate the mobility of NAPLs [Wilson and Conrad, 1984]:

Bond number (N_B):

$$N_B = \frac{(\rho_{nw} - \rho_w) g k}{\sigma_{nw}} \quad (3)$$

Capillary number (N_C):

$$N_C = \frac{\mu_w v_w}{\sigma_{nw}} \quad (4)$$

where all the terms have been previously described. The relation between percent residual NAPL saturation and N_C (or N_B) for a variety of porous media and non-wetting hydrocarbons is illustrated in Figure 2.1.2. At low N_B s and N_C s, residual NAPL saturations (S_{or} s) have been observed to be independent of the NAPL composition but very sensitive to soil heterogeneity [Wilson et al., 1990]. Hunt et al. (1988b) have used these relationships and simple static force balance considerations to develop equations for the evaluation of the mobility of ganglia in terms of the mean pore throat diameter of the soil, d_t ($d_t = 2r_t$), and the interfacial tension, σ_{nw} :

Bond number (N_B):

$$\frac{(\rho_{nw} - \rho_w) g L_v d_t}{\sigma_{nw}} > 4 \quad (5)$$

Capillary number (N_C):

$$\frac{\mu_w v_w L_h d_t}{k \sigma_{nw}} > 4 \quad (6)$$

where L_v and L_h are the minimum lengths of ganglia for the NAPL mobilization to occur in the vertical and horizontal directions, respectively. When Equations 5 and 6 are not satisfied, i.e., L_v and L_h are less than the limiting lengths the NAPL ganglia become immobile or trapped. From equations 5 and 6, L_v and L_h are seen to be a function of liquid properties, pore throat size and pressure gradients. It can also be

inferred from these ratios that pore and macroscopic level soil heterogeneity (i.e., the actual distribution of the pore throat diameters) can greatly affect the in-situ flow path of the advancing NAPL. An example of an actual DNAPL distribution resulting from pore level soil heterogeneity is provided in Figure 2.1.3, while the effects of macroscopic (field scale) heterogeneities are detailed later in Section 2.5.



Figure 2.1.3 Random vertical migration of PCE in saturated bead pack (dia. 0.49 to 0.70 mm.) [Schwille, 1988].

During infiltration at the ground surface, the limiting value of N_B in the unsaturated and saturated zones is frequently exceeded in most soils, with the possible exception of silts and clays, and downward migration of the NAPL occurs. However, once emplaced, it is very difficult to mobilize the NAPL ganglia horizontally, because the requisite hydraulic gradients and flow velocities are large and unattainable [Wilson and Conrad, 1984; Sitar et al., 1987; Hunt et al., 1988b]. For example, in laboratory experiments, emplaced TCE and PCE ganglia could not be mobilized by horizontal flow velocities of up to 14 m/day [Schwille, 1988].

The ability of an injected fluid to displace the resident pore fluids from the porous media can be estimated using the mobility ratio, M . The mobility ratio, which neglects gravity and interfacial forces [Buckley-Leverett assumption], is often used to evaluate the potential success of a proposed fluid-fluid displacement. Using water flooding as an example, the mobility ratio is defined as the ratio of the velocity of the displacing fluid (water, w) to that of the resident pore fluids (i.e., NAPL or n):

$$M = \frac{v_w}{v_n} = \frac{\mu_n k_{rw}}{\mu_w k_{rn}} \quad (7)$$

A favorable displacement is usually indicated by $M \leq 1$ [Buckley and Leverett, 1942; Muskat, 1982]. This relationship is often referred to in soil washing applications, and its importance is discussed in section 3.5. The Gravity Number N_G , which is the ratio of gravity forces to viscous forces (N_B/N_C), provides an indication of the potential for gravity under-ride or over-ride during fluid displacement processes. N_G also provides a measure of the slope of the advancing displacing fluid saturation front in a homogeneous porous medium.

2.1.2 Saturation and Relative Permeability

The influence of fluid saturations on rate of migration of the advancing NAPL in both the unsaturated and saturated zones is accounted for by the relative permeability (Equation 1). Also, as the continuous NAPL advances in the vadose and water saturated zones, the soil retention capacity diminishes the volume of mobile NAPL, causing stranding and isolation of discontinuous ganglia within in the soil interstices.

Fluid saturation is defined as the ratio of the volume of the fluid in the pore space to the total pore volume. The saturations of primary interest are the irreducible water saturation (S_{ow}) and the residual NAPL saturation (S_{or} or S_r). These fluid saturations correspond to the capillary pressure at which the capillary pressure increases rapidly with negligible decreases in saturation [Corey, 1986]. Water flooding of sandstone cores has shown that S_{or} can be on the order of 27% to 43% for low Bond and Capillary numbers [Chatzis and Morrow, 1981]. The residual saturation definition is a matter of practical utility because the residual NAPL saturation is affected by numerous factors. (1) pore size distribution; (2) pore aspect ratio; (3) wettability; (4) soil texture; (5) clay fraction; (6) and the ambient Bond and Capillary numbers [Wilson and Conrad, 1984; Sitar et al., 1987; Wilson et al., 1990]. The latter of these factors has been observed to be the most important.

For example, laboratory studies employing glass beads showed that the typical range of S_{or} values for NAPLs was on the order of 16% to 18% at N_C values less than 7×10^{-6} , which is the range of typical ground-water conditions [Morrow and Songkran, 1981; Morrow and Chatzis, 1982; Chatzis et al., 1983]. However, in experiments in which the hydraulic gradient and thus the viscous forces were increased, complete NAPL displacement was observed at $N_C \geq 1 \times 10^{-3}$ [Wilson and Conrad, 1984]. This implies that any initial residual NAPL saturation (S_{or}^*) can be reduced to zero ($S_{or}^{**} = 0$) by elevating N_B and N_C , as shown in Figure 2.1.2. However, unless the chemical and physical properties of the NAPL and porous media are changed in some way, complete displacement of NAPL requires pressure increases beyond those realistically attainable under normal groundwater conditions [Sitar et al., 1987].

Residual NAPL saturation can be alternatively expressed as soil retention capacity or a retention factor, R , having the units of liters of NAPL per m^3 soil (l/m^3) [Schwille, 1967; de Pastrovich et al., 1979]:

$$R = S_{or} * n * 1000 \quad (8)$$

Table 2.2 presents experimentally determined values of residual saturations and retention factors of several hydrocarbons in a variety of soil types under saturated and unsaturated conditions [Mercer and Cohen, 1990]. The specific retention of NAPLs in unsaturated and saturated sandy soils has been shown to be on the order of 3 to 30 l/m^3 and 5 to 50 l/m^3 , respectively [Schwille, 1984; Wilson and Conrad, 1984; Mercer and Cohen, 1990]. In water-wet systems, vadose zone residual saturations are lower than residual saturations in the saturated zone for a variety of reasons: continuity of films during drainage; presence of non-wetting gas phase; larger buoyancy forces between NAPL and the gas phase compared to NAPL and water; lower interfacial tension between the NAPL and the gas phase [Wilson et al., 1990]. Retention is also affected by soil gradation (soil pore distribution). For example, under dry conditions, unsaturated fine

grained soils ($\sim S=55\%$) have been shown to retain more gasoline (multicomponent LNAPL) than coarse sands ($\sim S=14\%$) [Pfannkuch, 1983; Hoag and Marley, 1986].

The dependence of the relative permeability of water (k_{rw}) and NAPL (k_{rn}) on saturation in a binary fluid system is shown in Figure 2.1.4. The relative permeability can exhibit hysteresis and is a function of NAPL properties, soil type, fluid saturation and thus, capillary pressure. The k_{rw} and k_{rn} equal zero at S_{ow} and S_{or} , respectively. At any value above the irreducible water and residual NAPL saturations, the fluids are considered to flow simultaneously, albeit, not necessarily in the same pores [USEPA, 1992a]. Since the NAPL is the non-wetting fluid, it is likely to be flowing in the larger pore channels, and this partially explains why small increases in NAPL saturation in initially water-wet soils can result in very large decreases in the relative permeability of water [Schwille, 1988].

Ideally, relative permeability curves should be determined either experimentally or empirically fitted to existing data, or converted from existing capillary pressure-saturation curves. This requires great care because measurement methods and other experimental considerations such as testing techniques (steady vs. unsteady), saturation determination (in-situ vs. ex-situ), viscous fingering, capillary end effects, hysteresis, and scaling effects may affect two- and three-phase relative permeability estimations [Saraf and McCafferty, 1982; Honarpour et al., 1986]. As a result, the determination of site- and NAPL-specific relative permeability curves or capillary pressure-saturation curves is expensive, and often difficult, particularly in the case of three-phase relative permeabilities. While NAPL-water relative permeability data is certainly sufficient for estimating immiscible fluid flow in the saturated zone, three-phase (NAPL-H₂O-air) relative permeabilities are required for vadose zone transport analysis, and for analysis of situations when the gas phase is introduced into the saturated zone, such as in air sparging and steam injection.

For these and other reasons, theoretical models have been developed to estimate three-phase relative permeability and capillary pressures from two-phase data [Stone, 1973; Parker et al., 1987; Delshad and Pope, 1989]. The two-phase relative permeabilities are often taken from Corey (1954) and the relative permeability to gas is only taken to be a function of total liquid saturation. Oil-water and gas-NAPL capillary pressures are assumed to be solely functions of water and gas saturations, respectively [Leverett, 1941; Parker et al., 1987].

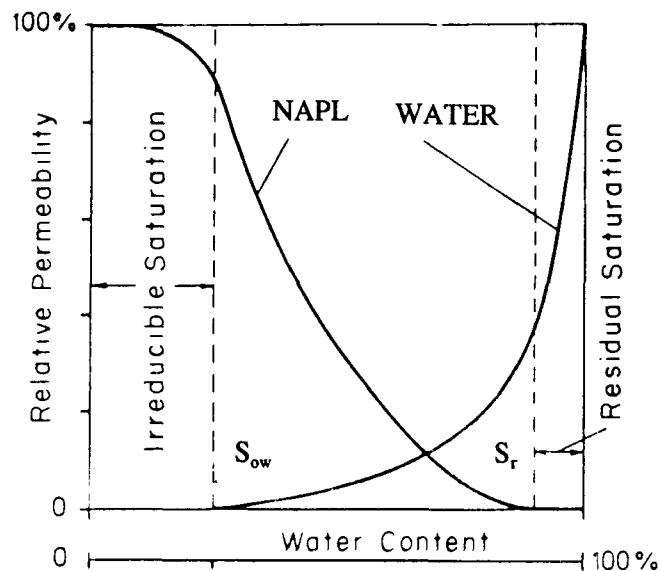


Figure 2.1.4 NAPL-water relative permeability curves in a porous medium [adapted from Schwille, 1988].

TABLE 2.2 TYPICAL SOIL RETENTION VALUES FOR ORGANIC LIQUIDS IN DIFFERENT SOIL TYPES [adapted from Mercer and Cohen, 1990]

NAPL	System	Soil	Residual Saturation (S_r) Retention factor, R ($1/m^3$)
DNAPL	vad.	sandy soils	$S_r > 0.01-0.10$ ⁽²⁾ $R > 3-30$ ⁽¹⁾
DNAPL	sat	sandy soils	$S_r > 0.02-0.15$ ⁽²⁾ $R > 5-50$ ⁽¹⁾
Tetrachloroethene	vad.	fracture with 0.2 mm aperture	$R = 0.5 \text{ m}^{-2}$ ⁽²⁾
Benzene	sat.	sand (92% sand, 5% silt, 3% clay)	$S_r = 0.24$ ⁽³⁾
Benzyl alcohol	sat.	sand (92% sand, 5% silt, 3% clay)	$S_r = 0.26$ ⁽³⁾
p-Cymene	sat	sand (92% sand, 5% silt, 3% clay)	$S_r = 0.16$ ⁽³⁾
o-Xylene	sat.	sand (92% sand, 5% silt, 3% clay)	$S_r = 0.19$ ⁽³⁾
Trichloroethene	vad.	medium sand	$S_r = 0.20$ ⁽⁴⁾
Trichloroethene	vad.	fine sand	$S_r = 0.19$ ⁽⁴⁾
Trichloroethene	vad.	fine sand	$S_r = 0.15-0.20$ ⁽⁴⁾
Trichloroethene	vad.	loamy sand	$S_r = 0.08$ ⁽⁵⁾
1,1,1-Trichloroethane	sat.	coarse Ottawa sand	$S_r = 0.15-0.40$ ⁽⁶⁾
Tetrachloroethene	sat.	coarse Ottawa sand	$S_r = 0.15-0.25$ ⁽⁶⁾

References:

1. Feenstra and Cherry (1988); 2. Schuille (1988); 3. Lenhard and Parker (1987); 4. Lin et al. (1982), 5. Cary et al. (1989), 6. Anderson (1988)

Delshad and Pope (1989) compared predicted versus experimental relative permeabilities using three sets of data and seven three-phase relative permeability models. All seven methods provided reasonably good fits to the experimental data and were seen to be dependent on the range of relative permeability modeled. Certain methods allow for more parameter adjustment than others, but this advantage can be offset by additional data requirements or assumptions. Despite these efforts, relative permeability data of DNAPLs of environmental concern remain sparse [Mercer and Cohen, 1990].

While experimental data can be reasonably approximated by the relative permeability models, recent visual experiments have shown that all aspects of DNAPL migration in a three-phase system cannot be fully captured using current analyses [Wilson et al., 1990]. For example, under imbibing conditions in a three-phase system, the sudden appearance of several discontinuous inter pore DNAPL ganglia in the downgradient direction could not be explained in relation to either stationary or slowly migrating continuous DNAPL. Closer inspection revealed that the formation of new DNAPL ganglia directly resulted from DNAPL film flow occurring at the air-water interface. Also, DNAPL film flow has been attributed to the propensity of the DNAPL to spread (see section 2.2.4) [Wilson et al., 1990]. Hence, DNAPLs may be mobile at low saturations, and phase continuity is not an essential prerequisite for appreciable DNAPL migration.

2.1.3 Other Factors Contributing to DNAPL Mobility

Factors other than capillary forces and retention capacity which contribute to the mobility of the DNAPL include: volume of contaminant release; area of infiltration of contaminant; and time period over

which the release occurred [de Pastrovich et al., 1979; Feenstra and Coburn, 1986; Pantazidou, 1991]. All of these factors relate to the soil volume contacted and thus contaminated by the DNAPL, the preponderance of a distinct separate phase, and the likely modes of transport.

DNAPL infiltration in the vadose zone can attain significant depths rapidly. In laboratory experiments using relatively homogeneous sands ($K \sim 1.2 \times 10^{-4}$ m/s, $n=50\%$), PCE traversed 100 cm of vadose zone at residual water saturation, ~ 40 cm of capillary fringe, and approximately 30 cm of the saturated zone in 4 hours, see Figure 2.1.5. In clean, water-saturated sands ($k \sim 10^{-6}$ cm²/s), the vertical migration of pure TCE and PCE has been observed to be 1 to 4 cm/s under a small DNAPL driving gradient [Schwille, 1988; Kueper and Frind, 1991a]. In other laboratory experiments using saturated sands, pure PCE moved around soil heterogeneities and penetrated up to depths of 35 cm in approximately 5.25 minutes [Kueper and Frind, 1991a,b]. In field experiments using the same DNAPL volume, the penetration depth was greater for the slower release and smaller application area [Poulsen and Kueper, 1992].

2.2 PHYSICAL AND CHEMICAL PROPERTIES OF NAPLS

Physical and chemical properties of hydrocarbons and their partitioning are influenced by the ambient pressure and temperature, and the type and quantity of other species in the system. For a single-component NAPL, the aqueous solubility and the NAPL properties at 20-25°C are appropriate for analysis and modeling purposes. In contrast, a multicomponent NAPL acquires properties reflecting the aggregated contribution of all hydrocarbons comprising it, and the former assumption is either completely inappropriate or only provides a first-order approximation. Hence, such values should be used judiciously, as discussed later.

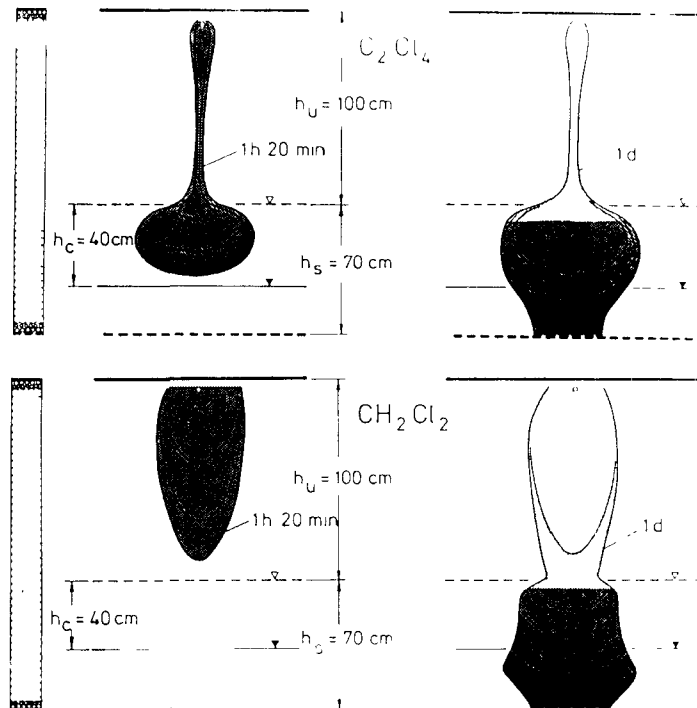


Figure 2.1.5 Infiltration of PCE (top) and DCM (bottom) in static glass trough experiments. Volume of DNAPL released: 10 liters. Elapsed time and heights of unsaturated (h_u), saturated (h_s) and capillary fringe (h_c) shown [Schwille, 1988].

The physical properties of a multicomponent NAPL mass located in the subsurface also evolve over time. The more soluble, volatile, and biodegradable components of the NAPL mass can be more rapidly depleted with time, leaving the more viscous, sorptive, and less volatile components behind [Geller, 1990; Hunt et al., 1988a; Mercer and Cohen, 1990; Sitar et al., 1992]. As a result, the characteristic properties such as viscosity, density, and interfacial tension of the NAPL mass are likely to change.

2.2.1 Aqueous Solubility

The aqueous solubility limit, $C_{iw, sol}$, refers to the maximum dissolved concentration of that compound in pure water. Sparingly soluble hydrocarbons have aqueous solubilities on the order of less than 10 mg/l. When such hydrocarbons are present at quantities exceeding the solubility limit, a second liquid phase forms consisting of nearly pure hydrocarbon with trace quantities of water. This phase is commonly referred to as the "NAPL" or as the "immiscible" or "separate" phase. The $C_{iw, sol}$ is an expression of the chemical equilibrium in the water-NAPL binary liquid system, and its exact value may be influenced by hydrocarbon molecular structure, degree of halogenation, polarity, pH, temperature, and pressure.

Rather than existing as a single continuous phase in porous media, the NAPL is more likely to exist predominantly as discontinuous droplets, or "ganglia," which are very difficult to locate in the subsurface. Once emplaced, single- or multicomponent NAPL ganglia slowly dissolve into the adjacent pore water, serving as long-term sources of contamination. The concentration of each hydrocarbon in the aqueous phase then depends on its solubility limit, its mole fraction in the NAPL, and on mass transfer limitations [Sitar et al., 1987, 1992].

2.2.2 Density

Fluid density, defined as the mass per unit volume, is a useful parameter for estimating the potential for the downward migration of an NAPL in the subsurface. An analogous term, specific gravity (SG) is often used to describe fluid density. The NAPL specific gravity (SG_i) is the ratio of NAPL density to that of water. An NAPL with an SG less than unity is termed an "LNAPL" (lighter-than-water NAPL) or a "floaters" because the LNAPL normally resides at or above the water table in the subsurface. However, LNAPL ganglia can be also trapped below a fluctuating water table, as discussed later.

Generally, the greater the hydrocarbon molecular weight and degree of halogenation (Cl^- , Br^- substitutions, etc.), the denser the NAPL will be, as can be seen in Table 2.1. The downward vertical mobility of DNAPL increases with increasing molecular weight and density. Density differences as small as ~1% influence fluid movement in the subsurface, and most DNAPLs possess densities 10-50% greater than water [Mackay et al., 1985]. Density is often a strong function of temperature, and a DNAPL may be effectively changed to an LNAPL by increasing temperature.

2.2.3 Interfacial Tension

Interfacial tension develops at the phase (solid, polar liquid, non-polar liquid, gas) boundaries and refers to the surface energy that develops at the physical interfaces between immiscible phases, such as the air-water interface or between polar and non-polar liquids (e.g., water-DNAPL). Interfacial tension has the units of force per unit length and it is a measure of the deformability of the interfacial contact. In general, the water-NAPL interfacial tension increases with the degree of halogenation (see Table 2.1); it decreases with increasing temperature and it is affected by pH, and gases and surfactants [Mercer and Cohen, 1990].

Interfacial tension is a controlling factor in the prediction of ganglia mobilization under a variety of conditions. The inference made from Equation (2) is that increasing interfacial tension results in a greater degree of emplacement and lesser DNAPL mobility. Ganglia mobilization can be facilitated by reducing or eliminating the interfacial tension through addition of surfactants and hydrophilic cosolvents, and by increasing the temperature.

2.2.4 Wettability and Spreading

Wettability refers to the preferential spreading of one fluid over the solid surfaces in a multiphase system. In porous media, the wetting fluid has the tendency to spread and occupy the smaller pore spaces and channels, and flow of the non-wetting fluids is generally limited to the larger pore flow channels [Schwille, 1988; Mercer and Cohen, 1990]. Wettability is a function of the interfacial tension and it is normally indexed to the contact angle between two immiscible fluid phases at the solid surface as shown in Figure 2.2.1. The contact angle is determined from Young's Equation [Adamson, 1982]:

$$\cos\phi = \frac{\sigma_{ns} - \sigma_{ws}}{\sigma_{nw}} \quad (9)$$

where ϕ is the contact angle, and σ_{ns} and σ_{ws} are the NAPL-solid and water-solid interfacial tensions, respectively. Porous media systems are usually described as: water wet if $\phi \leq 70^\circ$, NAPL-wet if $\phi \geq 110^\circ$, and neutral if $\phi = 70^\circ$ - 110° [Anderson, 1986a]. Others use $\phi \leq 90^\circ$ and $\phi \geq 90^\circ$ to define water-wet and NAPL-wet systems, respectively [Wardlaw, 1982; Villaume, 1985]. In most natural porous media systems, preferential wettability decreases in the order of H_2O , NAPL and air, unless the medium has been previously contacted by the NAPL. Wettability is affected by mineralogy, presence of organic matter, presence of surfactants, NAPL composition, pore water chemistry, and saturation history [Mercer and Cohen, 1990]. Some crystalline compounds such as dolomite, graphite, limestone, sulfides, sulfur, talc, and talc-like silicates, may be preferentially NAPL-wet [Craig, 1971; Anderson, 1986a]. Table 2.3 presents the contact angles of several DNAPL's in natural soils [Arthur D. Little, Inc., 1981]. Contact angles studies have shown that NAPL wettability increases with time [Craig, 1971]. Hysteresis between the contact angles of advancing NAPL in initially water-wet medium and of receding NAPL from NAPL-contaminated medium is a well known phenomenon [Villaume, 1985; Morrow, 1990]. Differences on the order of 5 to 10 degrees are common. An extensive review of the various factors influencing wettability, its measurement, and its effect on capillary pressures, relative permeability, residual saturation and NAPL recovery is presented in Anderson (1986a,b,c; and 1987a,b,c).



Figure 2.2.1 Relationship between contact angle (ϕ) and wettability [Mercer and Cohen, 1990].

TABLE 2.3 EXPERIMENTALLY MEASURED CONTACT ANGLES OF DNAPLS IN DIFFERENT SOIL TYPES [adapted from Arthur D. Little, Inc., 1981].

DNAPL	Substrate	Medium	ϕ (°)
Tetrachloroethene	clay	APL	23-48
Tetrachloroethene	clay	air	153-168
1,2,4-Trichlorobenzene	clay	APL	28-38
1,2,4-Trichlorobenzene	clay	air	153
Hexachlorobutadiene	clay	water	32-48
Hexachlorocyclopentadiene	clay	water	32-41
2,6-Dichlorotoluene	clay	water	30-38
4-Chlorobenzotrifluoride	clay	water	30-52
Carbon tetrachloride	clay	water	27-31
Chlorobenzene	clay	water	27-34
Chloroform	clay	water	29-31
S-Area DNAPL	clay	APL	21-54
S-Area DNAPL	clay	water	20-37
S-Area DNAPL	clay	air	170-171
S-Area DNAPL	fine sand and silt	water	30-40
S-Area DNAPL	clayey till (30-40% clay)	water	20-37
S-Area DNAPL	Ottawa fine to coarse sand	water	33-50
Tetrachloroethene	Ottawa fine to coarse sand	water	33-45
Tetrachloroethene	Lockport Dolomite	water	16-21
Tetrachloroethene	Lockport Dolomite	air	171
S-Area DNAPL	Lockport Dolomite	water	16-19
S-Area DNAPL	Lockport Dolomite	air	164-169
S-Area DNAPL	NAPL-contaminated fine sand	APL	45-105
S-Area DNAPL	soils with vegetative matter	water	50-122
S-Area DNAPL	paper	water	31
S-Area DNAPL	wood	water	34-37
S-Area DNAPL	cotton cloth	water	31-33
S-Area DNAPL	stainless steel	water	131-154
S-Area DNAPL	clay	water (SA)	25-54
S-Area DNAPL with solvents	clay	water	15-45

Adsorbed S-Area (New York, USA) chemicals were detected on some of the clay samples. APL refers to aqueous phase liquids (water containing dissolved chemicals). SA refers to surface-active agents (Tide® and Alconox®) which were added to the water. S-Area DNAPL is comprised primarily of tetrachlorobenzene, trichlorobenzenes, tetrachloroethene, hexachlorocyclopentadiene, and octachlorocyclopentene.

Usually, the spreading of NAPLs is not prevalent in the saturated zone because the soil is typically water-wet. However, since transport in the subsurface occurs in both the vadose and saturated zones and the vadose zone is a three-phase system (NAPL-water-gas), NAPL spreading and migration in the vadose zone will almost certainly contribute to the degree of contamination occurring in the saturated zone. The spreading behavior of a NAPL in the water-NAPL-gas system can be estimated from its spreading coefficient, Σ [Adamson, 1982; Wilson et al., 1990]:

$$\Sigma = \sigma_{aw} - (\sigma_{ow} + \sigma_{ao}) \quad (10)$$

where σ_{aw} , σ_{ow} and σ_{ao} are the air-water, NAPL-water and NAPL-air interfacial tensions, respectively. Negative spreading coefficients indicate the tendency of the NAPL to "bead" at the air-water interface. On the other hand, positive Σ indicates the potential for the formation of an organic liquid film at the air-water interface [Wilson et al., 1990]. Laboratory studies using porous media have indicated that these films, because of their continuity, allow the DNAPL to migrate even though DNAPL ganglia may appear discontinuous and isolated [Wilson et al., 1990]. Hence DNAPL films can potentially lead to the net migration of the DNAPL in the downgradient direction. Other implications of film flow have yet to be assessed, such as the effect of films on mass transfer processes in the subsurface.

2.2.5 Viscosity

The absolute, or dynamic viscosity of a fluid is defined as its resistance to flow. In general, absolute viscosity increases with increasing molecular complexity, molecular size and polarity, but decreases with increasing temperature and degree of halogenation. The kinematic viscosity is one of the better indicators of NAPL mobility since it incorporates both viscous and density effects. The infiltration rates of NAPLs with low kinematic viscosities are expected to exceed those with high kinematic viscosities [Schwille, 1984; Pantazidou, 1991; Pantazidou and Sitar, 1992]. For example, it has been shown that certain LNAPLs and DNAPLs comprised of polynuclear aromatics are 2-10 times less mobile than water, while DNAPLs comprised of aliphatics are 1.5-3.0 times more mobile than water in porous media [Schwille, 1981, 1988]. However, Figure 2.1.5 shows that in identical DNAPL releases of PCE ($\nu = 0.54 \text{ mm}^2/\text{s}$) and DCM (dichloromethane, $\nu = 0.32 \text{ mm}^2/\text{s}$), the PCE not only migrated faster, but it also remained confined to a zone with a smaller radius; and thus, the quantity of PCE retained by the soil was smaller. Schwille attributed the slower penetration and spreading of DCM to possible vaporization of DCM owing to its high vapor pressure; but more plausible explanations include that for the same soil, the Bond Number, N_B , of PCE is greater than that of DCM, and that some heterogeneity may have existed in the DCM column.

2.2.6 Vapor Pressure and Henry's Law Constant

The vapor pressure is the pressure exerted by the vapor when it is in equilibrium with its pure solid or liquid phase at a specified temperature (usually 20°C). The vapor pressure of a hydrocarbon represents an "air solubility limit" expressed as pressure, not concentration, and is therefore analogous to the aqueous solubility limit. Vapor pressure, and thus volatility, generally increase with increasing hydrocarbon aliphaticity and degree of halogenation. The Henry's Law Constant (K_H) is an air/water partitioning constant which is defined as the ratio of the hydrocarbon vapor pressure (atm) to its molar aqueous solubility limit (mole/m^3) at a reference temperature of 20°C or 25°C.

Hydrocarbons are usually classified as "volatile" if their vapor pressures at 20°C are greater than 1 mm Hg ($1.31 \times 10^{-3} \text{ atm}$), and as "semi-volatile" if their vapor pressures are between 10^{-10} mm Hg to 1 mm Hg (1.31×10^{-13} to $1.31 \times 10^{-3} \text{ atm}$) [USEPA, 1992a]. Hydrocarbons with vapor pressures greater than 0.5 mm Hg can be expected to significantly volatilize from leaking underground storage tanks (USTs) [Bennedsen et al., 1985], while hydrocarbons with vapor pressures less than 10^{-7} mm Hg are not expected to significantly volatilize [Dragun, 1988].

In subsurface applications, these rule-of-thumb conventions based on vapor pressure are useful indicators in cases in which pure products are in contact with the gaseous phase in the vadose zone. For NAPL ganglia emplaced below the water table or for a dissolved hydrocarbon plume, the hydrocarbon volatility is more dependent on its aqueous concentration because the NAPL is no longer in direct contact

with the vadose zone. In this situation, it is much more realistic to evaluate hydrocarbon volatility on the basis of Henry's constant, K_H . Hydrocarbons having K_H greater than 10^{-5} atm m³/mole can be successfully air stripped from ground water [Nirmalakhandan et al., 1987; Speece et al., 1987], or in-situ air-sparged from porous media [Brown et al., 1991]

2.2.7 Octanol-Water Partitioning Coefficient (K_{ow})

The octanol-water partitioning coefficient (K_{ow}) is used to estimate the hydrophobicity and sorptive tendencies of hydrocarbons. Octanol is used to simulate an immiscible organic phase such as soil organic matter (section 2.3.4). Most often, K_{ow} is used to correlate hydrocarbon sorption in aquifer media. The K_{ow} is the ratio of the hydrocarbon concentration in the octanol ($C_{10H_{22}}$) phase to the aqueous phase:

$$C_{iw} = (K_{ow})^{-1} C_{io} \quad (11)$$

where C_{iw} (g hydrocarbon/l H₂O) and C_{io} (g hydrocarbon/l C₁₀H₂₂) are the hydrocarbon concentrations in the water and octanol phases, respectively. For convenience, K_{ow} is often reported in logarithmic form ($\log K_{ow}$) because representative values of K_{ow} for the class of immiscible hydrocarbons which are of environmental concern span several orders of magnitude (Table 2.1). Negative $\log K_{ow}$ values indicate hydrophilicity, that is, preference for the aqueous phase. Conversely, positive $\log K_{ow}$ value indicate hydrophobicity and the hydrocarbon's preference to form separate phases, sorb strongly to solids, or potentially volatilize.

2.2.8 Boiling Point

The boiling point (b.p.) is the temperature at which the vapor pressure of the liquid equals the pressure of gases above the liquid, causing bubbles of vapor to form throughout the liquid. This temperature varies with pressure, and the normal boiling point is given at a reference pressure of 1 atm. The boiling point provides a measure of the volatility of the fluid; low boiling point (b.p.<100°C) and high boiling point (b.p.>100°C) liquids are classified according to the normal boiling point of water (100°C). This convention is used as a benchmark for comparisons, such as required energy input and mass transfer between the contaminant and water, when considering stripping and thermal process applications.

2.2.9 Dielectric Constant

The dielectric constant (ϵ) is the ratio of the permittivity of a medium to that of a vacuum, and is a reflection of the ability of the medium to interact electrostatically and conduct an electrical current. A fluid with a low dielectric constant (most sparingly soluble hydrocarbons) does not respond well to an applied electric field: it acts as an insulator. Behavior of this type is important when considering the interactions of clayey soils and pore fluids which contain hydrocarbons. Because hydrocarbons do not align themselves in the electrostatic field (diffuse double layer) generated by the surface charge of the clay particles, the diffuse double layer effectively shrinks allowing interparticle interactions to occur. These particle interactions lead to clay flocculation and increase hydraulic conductivity. Certain technologies (see sections 3.3, 3.7.3) make use of the differences between dielectric constants of NAPLs ($\epsilon < 10$) and water ($\epsilon \sim 80$) to aid in detection and/or cleanup.

2.3 PHYSICAL PROPERTIES OF SUBSURFACE SYSTEMS

Darcy's Law for multiphase flow and the capillary pressure expression (Equations 1 and 2) indicate which parameters govern the mobility of the DNAPL. These parameters are: porosity, permeability, relative permeability, and mean pore throat diameter.

2.3.1 Porosity

The porosity, ϕ , of the aquifer media is defined as the dimensionless ratio of the pore volume to the total bulk volume of aquifer media. Fluid flow, however, may only occur in a portion of the total pore space, since preferential flow may occur through macropores, cracks and other features, and flow will not occur in dead end pores [Anderson et al., 1985a,b; Bowders, 1985; Connor et al., 1989]. Hence, in the case of fissured clays, for example, the effective porosity may be considerably smaller than the total porosity.

Even in soils without macroscopic discontinuities, the gradation and spatial distribution of pore and pore-throat sizes directly affect the distribution of capillary pressures and, thus, DNAPL flow and emplacement [Wilson and Conrad, 1984; Sitar et al., 1987]. Emplacement is thought to occur by two mechanisms: snap-off and by-passing [Mohanty et al., 1980; Chatzis et al., 1983]. Both mechanisms are observed in varying proportions depending on the characteristics of the porous media. Snap-off, that is, the formation of discrete intrapore ganglia, is favored when the aspect ratio of the pore body to the pore throat is large. Low aspect ratios and heterogeneities usually promote by-passing, that is, the formation of large clusters or interpore ganglia [Chatzis et al., 1983; Wilson and Conrad, 1984]. Since the measurement of the actual pore and pore throat size distribution is difficult at best, empirical relationships have been developed to obtain an estimate of the average pore throat size from the mean soil grain diameter [Villaume, 1985].

2.3.2 Permeability

The permeability, k , of natural soils, sediments, and rocks spans approximately 13 orders of magnitude [Freeze and Cherry, 1979]. The factors that affect the permeability of the soil include the soil porosity and gradation, the spatial distribution of the soil grains and pore throat sizes, and the scales over which they vary. Permeability is related to soil gradation through the square of the mean soil grain diameter and a constant of proportionality which incorporates such factors as particle shape, packing, and the shape of the gradation curve [Hubbert, 1940]. Macroscopically, the changes in grain size and gradation are manifested as stratigraphy and soil heterogeneity, two of the most important factors affecting the mobility and the distribution of the DNAPL.

Of particular importance is the presence of clay minerals, their activity, and the proportion of the clay fraction in the media. Permeability decreases with increasing clay fraction, and permeabilities of pure and compacted clays can range from 10^{-11} to 10^{-15} cm^2 [Freeze and Cherry, 1979]. Therefore, NAPL migration is not likely to occur in aquitards, and liners have been commonly thought to serve as adequate barriers against DNAPL migration. However, hydrocarbons can traverse clayey aquitards via diffusion, and NAPLs can migrate through new or pre-existing fissures [Mitchell and Madsen, 1987; Feenstra and Cherry, 1988]. These modes of transport are most important in the vicinity of "pools" and "lenses" of DNAPL.

Pools of DNAPL tend to accumulate in the depressions along relatively impermeable layers such as clayey aquitards. Large diffusive fluxes resulting from simple Fickian diffusion of concentrated and mobile contaminants across a competent, impermeable clay soil ($k < 5 \times 10^{-13}$ cm^2) have been observed [Johnson et al., 1989]. Thus, diffusion into clayey aquitards and more permeable fine grained soil layers should be expected.

At locations where the DNAPL pool intersects pre-existing cracks and discontinuities in clayey aquitards or fissured clays (or fractured rock), penetration of DNAPL into these macroscopic features has been documented. The ability of a DNAPL to penetrate into fractures depends on the DNAPL driving gradient, the DNAPL-water interfacial tension, and aperture of the fissure [Kueper and McWhorter, 1991; Middleton et al., 1992]. Modeling studies indicate that a pool thicknesses on the order of 0.1 to 1.0 meters

may be sufficient to permit the flow of PCE into fissures with apertures of 10 μm to 50 μm , if the top of the pool exists under imbibition conditions [Kueper and McWhorter, 1991].

2.3.3 Clay-Pore Fluid Interactions

Due to the surface charge and large specific surface of clay particles, clayey soils are susceptible to changes in pore water chemistry. Studies have revealed that concentrated organic compounds can influence the ability of clayey soils to act as barriers against organic chemical transport by causing hydraulic conductivity changes of up to several orders of magnitude [Acar et al., 1985a,b; Anderson et al., 1985a,b; Bowders, 1985; Fernandez and Quigley, 1985; Mitchell and Madsen, 1987]. Good summaries of the performance of clay soils [Daniel et al., 1985; Mitchell and Madsen, 1987] and clay liners [Mitchell and Jaber, 1990] with respect to contaminant and clay type, testing conditions, and testing apparatus are available.

Clay-organic compound interactions such as sorption, intercalation, and cation exchange may result in clay fabric changes, cracking, and shrinking [Mitchell and Madsen, 1987]. For example, clay swelling in pore throats of granular (sandy) soils can also lead to DNAPL trapping by the bypassing mechanism (sections 2.1.2, 2.3.1). Sorption of polar organic compounds (alcohols, ketones) and ionizable hydrocarbons such as phenols [Lee et al., 1990], quinoline [Zachara et al., 1987, 1988], and nitrogen heterocyclic compounds [Zachara et al., 1987] has been observed to be a function of porewater pH conditions and their acidity constants (pK_a 's). Hydrocarbon sorption to chemically altered clay soils has also been observed [Estes et al., 1988]. However, most dense sparingly soluble hydrocarbons are both nonionizable and often non-polar, so their sorption onto clays is small compared to their partitioning into soil organic matter. Of primary concern is desiccation of clays that generally results from differences in dielectric constants (ϵ) between pore fluids composed of sparingly soluble hydrocarbons ($\epsilon < 10$) and water ($\epsilon = 80.4$). As a result, flow of non-polar hydrocarbons has been observed in interconnected cracks and macropores [Anderson et al., 1985a,b; Bowders, 1985].

More importantly, the migration of hydrocarbons through clayey soils may be enhanced in the presence of polar and hydrophilic organic compounds. Experiments in which a water saturated clay was sequentially permeated with water, ethanol, and benzene (in that order), revealed that the hydraulic conductivity of the clay could be increased by approximately four orders of magnitude [Fernandez and Quigley, 1985]. Since water and ethanol are completely miscible, ethanol displaced most (75% wt.) of the water from the clay minipores and macropores. Benzene, which is completely miscible with ethanol, was then used to displace the ethanol. Approximately half (50% wt.) of the ethanol was displaced, and approximately 30% (wt.) benzene composed the total pore fluid. In separate experiments in which no ethanol was used, benzene displacement of water resulted in only 8% (wt.) residual benzene in the total pore fluid. Hence, the net effect of ethanol was to quadruple the residual saturation of benzene in the clay. Similar trends were observed in sequential permeation experiments using ethanol and xylene and cyclohexane [Fernandez and Quigley, 1985]. Since the dielectric constants of carbon tetrachloride ($\epsilon = 2.2$) and TCE ($\epsilon = 3.4$) are comparable to that of benzene ($\epsilon = 2.2$), analogous behavior appears likely, especially, if density effects are also taken into consideration.

2.3.4 Organic Matter

The portion of a sediment or soil that consists of organic detritus (waste material such as dead microorganisms, slimes, plant fibres, etc.) is referred to as the natural organic matter. The fraction of organic matter (f_{oc}) is important with respect to hydrocarbon partitioning and sorption within the soil matrix. Karickhoff (1984) provides a detailed review of sorption in aquatic systems, and this work contains many useful references.

The sorption isotherms of hydrophobic organic compounds to natural sediments have been shown to be linear, if their dissolved concentration is less than 10^{-5} M, or less than half of their solubility limit, whichever is lower [Karickhoff, et al., 1979]. Experimental observations encompassing a wide variety of soils indicate that this partitioning is directly related to the f_{oc} , and the octanol-water partitioning coefficient, K_{ow} [Karickhoff et al., 1979, Chiou et al., 1983]. For hydrocarbons having solubilities between 0.5-1800 mg/l and for soil particles < 50 μ m, sorption was observed to be reversible, independent of grain size, and there was no competitive adsorption between multiple contaminants. An empirical relationship developed by Karickhoff et al. [1979] is stated as:

$$K_d = 0.6 f_{oc} K_{ow} \quad (12)$$

where K_d is the distribution coefficient of the compound between the aqueous and soil phases and has the units of (g hydrocarbon/g soil)/(g hydrocarbon/l H_2O), and f_{oc} is generally taken to be the portion of the organic matter occurring in the soil fines. The K_d , like the K_{ow} , is an equilibrium constant that provides a reasonable estimate (within a factor of 2) of partitioning of the compound into the soil phase. In addition to equation (12), the Brunauer, Emmett and Teller (BET), Langmuir, and Freundlich isotherms can also be used to estimate contaminant sorption [see Karickhoff, 1984]

2.4 MULTICOMPONENT MULTIPHASE EQUILIBRIA

From a practical standpoint, it is of interest to predict how hydrophobic compounds will partition in a complex subsurface environment, and to what extent in-situ technologies will affect partitioning. Generally, two classes of equilibria problems are of interest: (1) the case when only sparingly soluble hydrocarbons are present, in which the objective is to predict the evolution of the composition of the multicomponent NAPL pool over time, considering all partitioning that may take place; and (2) the case when natural or synthetic surfactants or hydrophilic organic solvents such as alcohols, ethers, ketones, amines, nitriles are also present, in which the objective is to predict their influence on the resulting chemical equilibria.

The complete expression of chemical partitioning in multicomponent-multiphase systems is achieved by equating the chemical potential, or an auxiliary function, fugacity, for each chemical species between all existing phases (gases, liquids, biotic phases, soil organic matter, matrix solids). A detailed discussion of chemical potential and fugacity is beyond the scope of this report and can be found elsewhere [Mackay, 1979; Mackay and Paterson, 1981; Prausnitz et al., 1986]. Conceptually, it is not the chemical concentrations which are equal between different phases, but the energy states of each species. The energy is measured as fugacity, having the units of pressure. Equilibrium is achieved when all fugacities are identical, that is, when no "hypothetical" pressure gradient exists. Chemical equilibrium expression in a four-phase system consisting of air, water, and soil organic matter and NAPL (Figure 2 1.1), is expressed as:

$$x_{ig} \gamma_{ig} f_{ig} = x_{i\alpha} \gamma_{i\alpha} f_{i\alpha} = x_{i\beta} \gamma_{i\beta} f_{i\beta} = x_{ioc} \gamma_{ioc} f_{ioc} = \dots \quad (13)$$

where the subscripts i, g, α , β and oc denote the chemical species, gas, polar (water), non-polar (NAPL), and organic carbon phases, respectively; x_i and γ_i denote the mole fractions and activity coefficients of species i in the respective phases; and, f_{ix} is the reference fugacity of each phase. The mole fractions indicate actual phase composition. The activity coefficients account for deviations from ideal phase behavior. The reference fugacities which are normally selected at STP conditions (thus making them equal) in environmental applications cancel from the expressions.

The usage of α , and β as the polar (water) and nonpolar (NAPL) phases in equation (13) is deliberate. This usage is taken from the solvophobic theory which recognizes that NAPL-water equilibrium is a subset of the larger, more general class of nonpolar-polar equilibrium interactions which exhibit similar behavior [Sinanoglu and Abdulnur, 1965; Sinanoglu, 1968]. "Nonpolar-polar" equilibrium terminology better accommodates systems in which compounds such as acids, alcohols, caustics, ketones, and amines are the polar solvents instead of water. This terminology also seems better suited for concentrated systems in which the composition and properties of the polar and non-polar phases are significantly changing with time, as would be expected in in-situ acid, caustic, surfactant, and hydrophilic cosolvent soil washing applications. For other less concentrated ground-water systems, it is convenient to refer to the polar phase in terms of the principal solvent, water.

2.4.1 Multicomponent NAPLs

In the discussion of multicomponent NAPLs we assume that the presence of other dissolved chemical species (metals, cosolvents, surfactants) in the system will, in general, not affect partitioning of the individual compounds. This assumption allows the multicomponent NAPL to be treated as an ideal liquid phase. Similarly, the aqueous phase, is also considered as an ideal liquid phase in that all solutes are considered to be infinitely dilute; and therefore, they do not interact. Several of the constants mentioned previously in this chapter including the aqueous solubility ($C_{iw,sol}$), octanol-water partitioning coefficient (K_{ow}), and the sorption coefficient (K_d) are also based on the same assumptions.

Cancelling the reference fugacities in Equation (13) from each liquid phase in the water-NAPL binary liquid system yields the expression:

$$x_{iw} \gamma_{iw} = x_{in} \gamma_{in} \quad (14)$$

or,

$$x_{iw} = \left(\frac{\gamma_{in}}{\gamma_{iw}} \right) x_{in} \quad (15)$$

where the subscripts w and n denote the water and NAPL respectively, and the mole fractions in each phase sum to unity. For fluid phase equilibria of nonelectrolytes, Raoult's Law is used for activity coefficient normalization. This convention states that as $x_{ij} \rightarrow 1$, $\gamma_{ij} \rightarrow 1$ [Prausnitz et al., 1986]. As the multicomponent NAPL is considered as an ideal liquid phase, a further simplification is made that all activity coefficients in the NAPL equal unity ($\gamma_{in} = 1$). In order to obtain the aqueous solubility limit of a hydrocarbon, an excess quantity of single-component NAPL is contacted with water. Under these conditions, the right hand side of equation (14) becomes unity, and upon rearrangement,

$$\gamma_{iw} = 1 / x_{iw,sol} \quad (16)$$

where $x_{iw,sol}$ is the aqueous solubility limit of the hydrocarbon expressed as a mole fraction. The aqueous solubility limits of some of the compounds appear in Table 2.1. The infinite dilution assumption for the aqueous phase is reasonable when $\gamma_{iw} \geq 1000$ [Fu and Luthy, 1986a], and this condition is satisfied in the absence of solubility enhancers. If $\gamma_{iw} \leq 1000$, the mole fraction solubility calculation must account for the appreciable solubility of the compound and that the mole fraction does not approach unity [Fu and Luthy, 1986a]. Substituting $\gamma_{iw} = (1 / x_{iw,sol})$ back into equation (15) provides

$$x_{iw} = (x_{iw,sol.})x_{in} \quad (17)$$

or, in terms of aqueous concentrations (mass hydrocarbon/vol. H₂O),

$$C_{iw} = (C_{iw,sol.})x_{in} \quad (18)$$

Equation (18) states that the aqueous concentration of a hydrocarbon is directly proportional to its mole fraction in the NAPL and its solubility limit. Thus, Equation (18) implies that dissolved concentrations occurring below their respective solubility limits do not preclude the existence of multicomponent NAPL pools [Sitar et al., 1992]. Comparison of equations (15) and (18) reveals that $C_{iw,sol.}$ is none other than the ratio of activity coefficients, or similarly, the partitioning coefficient, between the water and NAPL. The octanol-water partitioning coefficient (K_{ow}) and the soil organic matter sorption (K_d) coefficients can be similarly obtained. These partitioning coefficients can be respectively expressed on a mass basis by equating fugacity between the phases, or:

$$C_{iw} = (C_{iw,sol.})x_{in} = (K_{ow})^{-1}C_{io} = (K_d)^{-1}C_{is} = \dots \quad (19)$$

where C_{io} and C_{is} are the hydrocarbon concentrations in the octanol and solid (i.e., soil organic matter) phases, respectively. Recall that K_d can be expressed as equation (12) [Karickhoff et al., 1979; Karickhoff 1981, 1984]. These three partitioning coefficients can be treated as constants, as long as the solutes in the aqueous phase are infinitely dilute. This may not be the case when surfactants and hydrophilic cosolvents are present in the ground-water environment.

On an equilibrium basis, and considering only one immiscible hydrocarbon, the extent to which the NAPL will be present is limited by the mass of available hydrocarbon [Mackay 1979; Mackay and Paterson, 1981; Mackay and Shiu, 1992]. For example, a NAPL will not form in a well mixed, homogeneous, non-reactive system (i.e., air, water, soil, sediment, etc.) until each preexisting phase is saturated with respect to the given compound. In sub-saturated systems, the hydrocarbon will equilibrate amongst the preexisting phases according to fugacity. Upon saturation, further addition of hydrocarbon results in the formation of a NAPL into which all subsequent hydrocarbon accumulates. Now, if other immiscible hydrocarbons are then added to the system, they will partition among all phases (including the NAPL) according to fugacity. The original hydrocarbon will re-equilibrate among the phases according to changes in its NAPL mole fraction. Hence, if reasonable estimates of porosity, soil organic matter, and water saturation are made, soil concentration data can be used to obtain a first-order estimate of the amount of NAPL (and its composition) in the soil sample [Sitar et al., 1992]. In reality, subsurface systems are heterogeneous, reactive, and mass transfer limited, so even modest addition of a sparingly soluble organic compound may result in NAPL formation.

2.4.2 Surfactants, Cosolvents and Multicomponent NAPLs

The occurrence of hydrocarbons above their solubility limits in ground water has been observed in the presence of surfactants (natural or synthetic) and hydrophilic organic compounds (cosolvents). Surfactants are surface active compounds which accumulate at interphase contacts and increase NAPL solubility primarily by formation of micelles, composite NAPL-surfactant pseudophases consisting of a NAPL interior and surfactant exterior which enable enhanced water solubility of the NAPL [Adamson, 1982; Fountain et al., 1990]. Natural organic matter such as humic and fulvic acids [Chiou et al., 1986, 1987; Abdul et al., 1990a,b] and dissolved organic matter [Kan and Tomson, 1986] may facilitate transport of

hydrocarbons in a micellar and surfactant-like fashion. In contrast, cosolvents do not form micelles per se. Because of their mutual solubility with both water and immiscible hydrocarbons, cosolvents partition into both water and NAPL thereby altering phase properties (i.e., polarity, dielectric constant) such that they become more similar. The net effect is that the electrostatic associations between water and sparingly soluble hydrocarbons are increased, and this is manifested by increased solubility.

In terms of equilibria, surfactants and cosolvents are seen to alter the activity coefficients ratios between phases. Depending on their concentrations, surfactants [Kile and Chiou, 1989; Fountain et al., 1991] and cosolvents [Sørensen and Arlt, 1980; Groves, 1988] have been shown to increase the aqueous solubility of hydrocarbons by several orders of magnitude. Surfactants and cosolvents have been shown to strongly desorb hydrocarbons from soil organic matter and to enhance hydrocarbon partitioning into the aqueous (polar) phase [Fu and Luthy, 1986b; Woodburn et al, 1986; Walters and Guiseppi-Elie, 1988, Zachara et al., 1988; Abdul et al., 1990a,b; Rao et al., 1990]. More specific information on surfactants and cosolvents is presented in Section 4.0.

Whereas the activity coefficients in the NAPL and aqueous phase were formerly treated as constants, the activity coefficients in surfactant and cosolvent systems are seen to vary with chemical species and total system composition. Hence, the limits of the activity coefficient must be determined from partitioning data, phase diagrams, or suitable equilibria models which can account for nonideal behavior.

The solubility enhancement of surfactants is normally measured experimentally and presented in log-linear format. There are currently several approaches to modeling the effects of cosolvents in multiphase multicomponent systems, including: log linear [Fu and Luthy, 1986a,b], excess free energy, molecular surface area (MSA), and group contribution models [Fu and Luthy, 1986a; Prausnitz et al., 1986]. The merits and disadvantages of these approaches are discussed elsewhere [Fu and Luthy, 1986a]. The log linear and excess free energy approaches are extremely accurate, but their infinite dilution activity coefficients must be calculated by group contribution models or equivalent methods when experimental data are lacking. The MSA approach receives limited use because few parameter data are available.

Experimental results are not needed for group contribution models such as NRTL, UNIQUAC and UNIFAC, which can accurately approximate (within a factor of 2) compound solubilities in multicomponent multiphase systems [Prausnitz et al., 1986]. These models employ interaction parameters based on molecular structure and functional groups, and large amounts of data are available on group interaction parameters [Gmehling et al., 1982]. UNIFAC has enjoyed widespread use, but information is not always available for interaction parameters which are specific to certain compounds of environmental concern.

2.5 UNSATURATED AND SATURATED ZONE TRANSPORT MECHANISMS

2.5.1 Unsaturated Zone Transport

Although the emphasis in this report is on the saturated zone, it is necessary to understand transport through the vadose zone because most contaminant releases typically occur at the ground surface or in the vadose zone. The conceptual framework presented here is summarized from several sources [Schwille, 1967, 1981, 1984, 1988; Feenstra and Cherry, 1988, 1990; USEPA, 1992a].

Figure 2.5.1 shows a release of a fixed volume of DNAPL at the ground surface which becomes immobilized in the vadose zone by capillary forces, adsorption, and by forming annular rings and surface films before encountering the saturated zone. The immobilized, or residual, DNAPL is shown by the cross-hatched region. Infiltrating rainwater passing through the residually contaminated soil zone may leach and transport hydrocarbons to the water table [USEPA, 1992a]. Consequently, a dissolved plume is created within the aquifer.

Even if there is no rainwater infiltration through the residually contaminated zone, considerable contamination of the aquifer may still develop [Hinchee and Reisinger, 1987; Schwille, 1988]. Vapor transport of volatile organic compounds, VOCs, acts independently of the leaching mechanism. The stippled areas within the unsaturated and saturated zones in Figure 2.5.1 indicate the regions affected by hydrocarbons emanating from the soil zone contaminated by residual DNAPL.

Denser-than-air vapors emanating from the contaminated soil zone have been observed to migrate downward to spread along the water table [Marrin and Thompson, 1987; Schwille, 1988], and this has been the subject of several recent studies [Hunt et al., 1988a; Falta et al., 1989; Sleep and Sykes, 1989; McClellan and Gillham, 1990; Mendoza and Frind, 1990a,b; Gierke et al., 1990, 1992]. At the water table, vapors equilibrate with the aqueous phase according to Henry's law, and a dissolved plume develops. The lateral spreading and diffusion of vapors at the water table can be significant as vapors may migrate below buildings, parking lots, and other structures [Hinchee and Reisinger, 1987]. Ground-water contamination occurring upgradient of the DNAPL source also has been observed as a result of vapor transport in the vadose zone [Marrin and Thompson, 1987].

2.5.2 Saturated Zone Transport

Figure 2.5.2 shows a conceptual view of a release of a sufficient quantity of DNAPL to overcome the capillary forces and the retention capacities of the vadose zone, capillary fringe and saturated zone. As before, the cross-hatched area in Figure 2.5.2 shows the soil regions which are contaminated by the residual DNAPL. While the vapor transport within the vadose zone is almost identical between Figures 2.5.1 and 2.5.2, the dissolved plume within the saturated zone is noticeably larger because the residual DNAPL and DNAPL pools (layers or lenses) are in direct contact with ground water

Figure 2.5.2 also shows DNAPL pools which can form in the depressions of low permeability strata such as silty or clayey lenses, aquitards, and bedrock. DNAPL pools can form when mobile DNAPL encounters water-wet strata with very small pore throats that result in prohibitively large DNAPL entry pressures. DNAPL accumulation up to saturations of 70-80% of the pore space may occur at the strata interface. Because pooled DNAPL occurs in excess of its residual saturation, it should be considered mobile because it may penetrate into preexisting fissures in the underlying clayey strata [Kueper and McWhorter, 1991]. Preexisting fissures in naturally occurring clays are known to exist at substantial depths below the water table [D'Astous et al., 1989; Sabourin, 1989]. DNAPL pools may also drain through newly created fissures in a clayey strata resulting from clay desiccation, as already mentioned. Upgradient DNAPL migration along horizontal strata is possible also, as shown in Figure 2.5.2. Migration is obviously enhanced when the underlying strata is inclined.

DNAPL will also penetrate into bedrock fractures as shown in Figure 2.5.3, and the resulting downward vertical migration of DNAPL occurring within the fractures may be extensive owing to the low retention capacities of fractured bedrock systems. For example, based on laboratory experiments employing planar fractures with a frequency of 5 fractures/meter and 0.2 mm apertures, Schwille (1988) estimated DNAPL retention capacities on the order of 0.25 l hydrocarbon/m³ for weakly fractured rock systems of moderate hydraulic conductivity. This value is an order of magnitude smaller than that for unsaturated and saturated soils. Hence, once the DNAPL enters a fractured bedrock system, it can contaminate a much larger region, given volumetric considerations.

While the influence of pronounced soil heterogeneities such as clay aquitards and bedrock on DNAPL migration can be dramatic, it is important to note that even subtle hydraulic conductivity changes in clean sands, on the order of a factor of 2, may be sufficient to cause preferential flow of DNAPL [Kueper and Frind, 1991a]. Site heterogeneities on that order is quite common, thus complicating the NAPL flow and often making even the identification of residually contaminated soil zones and DNAPL pools difficult.

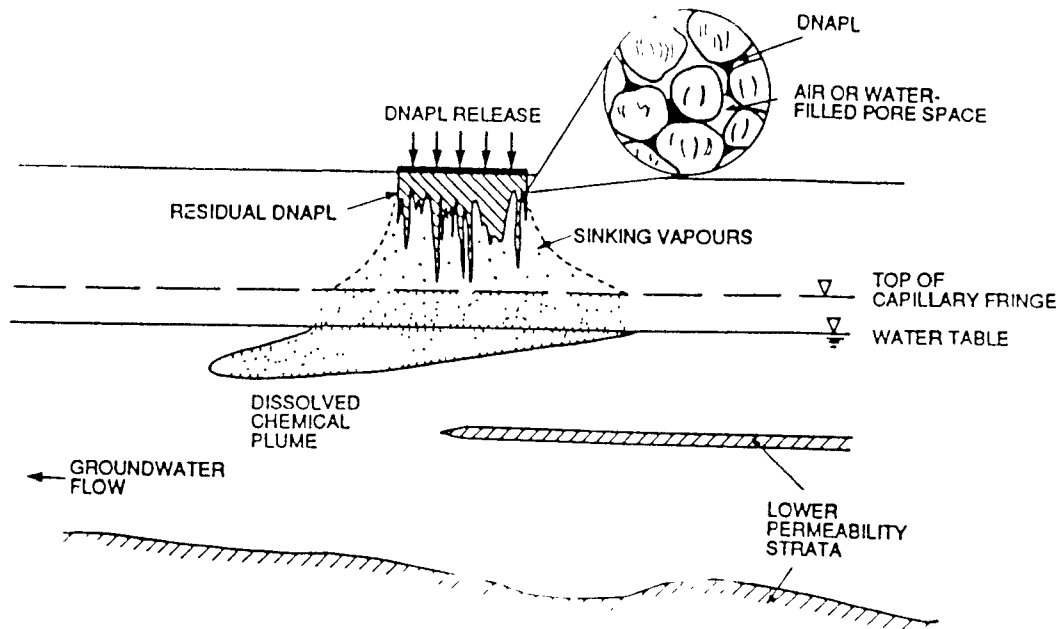


Figure 2.5.1 Schematic of the distribution of subsurface contamination emanating from residual DNAPL source in the vadose zone [Feenstra and Cherry, 1990].

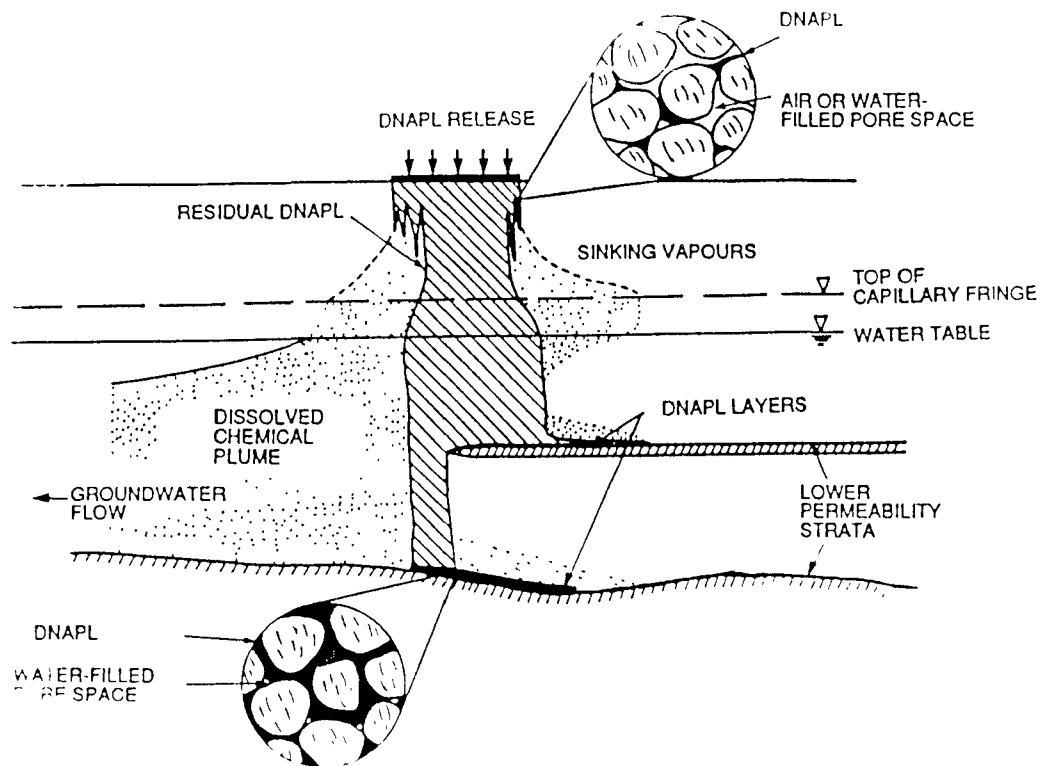


Figure 2.5.2 Schematic of the distribution of subsurface contamination emanating from residual DNAPL sources in the vadose and water saturated zones, and DNAPL pools [Feenstra and Cherry, 1990].

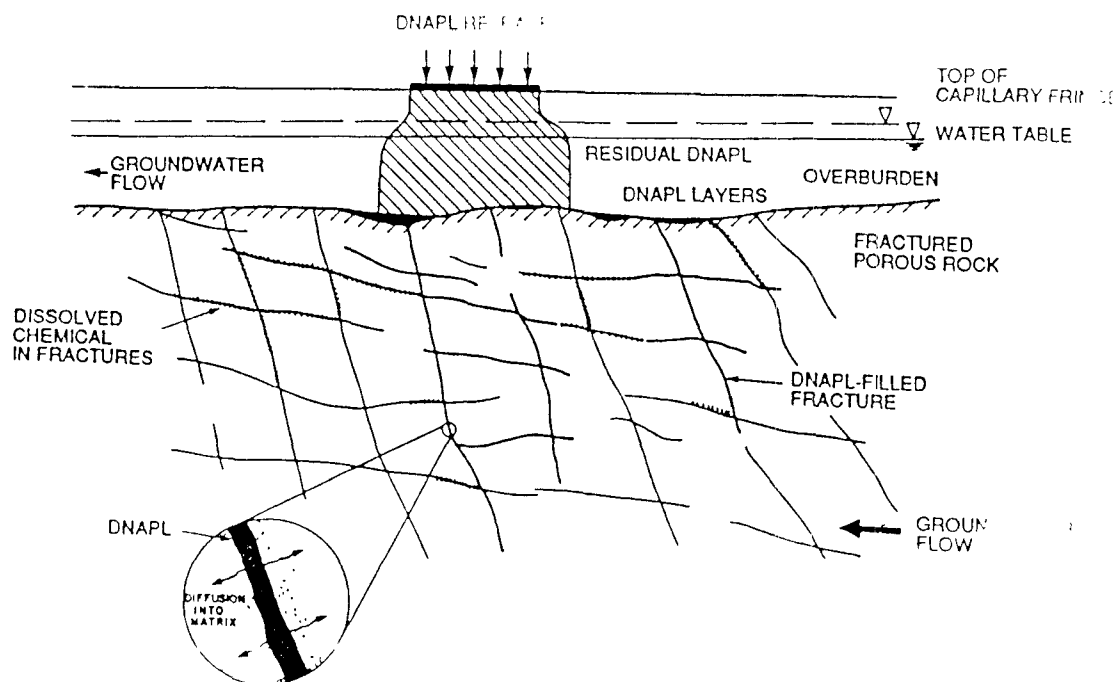


Figure 2.5.3 Schematic of fractured bedrock contamination resulting from mobile and pooled DNAPL [Feenstra and Cherry, 1990].

2.6 ESTIMATION OF THE EXTENT OF SITE CONTAMINATION AND SITE CHARACTERIZATION

Injection, extraction, observation wells and other invasive monitoring, sampling and remedial structures locally disrupt the stratigraphy and therefore introduce bias. Since testing procedures such as well evacuation prior to ground-water sampling perturb resident pore fluids, further bias is introduced. Sampling data themselves can often be misleading relative to the nature and extent of contamination, principally in the delineation of DNAPL in the subsurface. Frequently the importance of multicomponent-multiphase equilibria and interphase transport phenomena has been ignored or underestimated. This section addresses some of these issues and the implicit difficulties regarding data interpretation and estimation of contamination. Since we are ultimately interested in being able to evaluate the effectiveness of the different technologies, these issues must be acknowledged in the technology assessment process.

2.6.1 Ground-water Samples

Ground-water samples are used to delineate the extent of contamination in the saturated zone and to assess the success of remedial applications. Since much emphasis is placed on the "actual" values, it is important to consider the various interpretations that can be made based on the data. For example, both multiphase multicomponent equilibria and mass transfer limitations can have dramatic effects on observed ground-water concentrations. To illustrate this point, the comparison between the partitioning behavior of single- and multicomponent NAPLs is presented. Gasoline (multicomponent LNAPL) and its components are arbitrarily chosen because gasoline spills are reasonably well studied and are helpful in illuminating the limitations of subsurface sampling techniques and data.

Benzene, toluene, ethylbenzene and xylenes (BTEX) are the compounds of primary concern in fresh and weathered gasoline. First, using Equation (18) and assuming that the NAPL is an ideal liquid

phase, the aqueous phase equilibrium concentrations corresponding to a single-component NAPL comprised of either pure benzene, toluene, or xylene, are 1800 mg/l ($C_{bw,sol}$), 540 mg/l ($C_{tw,sol}$), 185mg/l ($C_{xw,sol}$), respectively. Recall that the hydrocarbon mole fraction in a single-component NAPL is unity.

Now, if a bicomponent NAPL consists of a 50/50 mixture of benzene and toluene, the hydrocarbon mole fraction in the NAPL is equal to 0.5. Thus, in comparison to the single-component NAPL, the equilibrium concentration of benzene (C_{bw}) and toluene (C_{tw}) are effectively halved to 900 mg/l and 270 mg/l, respectively. Table 2.4 shows that for a multicomponent NAPL such as gasoline, the typical equilibrium concentrations of benzene, toluene, and xylene amount to an approximate combined total of 47 mg/l. The total dissolved concentration ($C_{gw,sol}$) of all gasoline-derived hydrocarbons is on the order of 100 mg/l. Hence, while BTX compounds are only minor constituents (21%) of gasoline, their combined solubility accounts for almost 50% of the total dissolved hydrocarbons [Sitar et al., 1992]. The significance of the low equilibrium concentrations of the individual components in the presence of a multicomponent NAPL is that they are far below their respective solubility limits, and a convincing argument for the existence of a NAPL cannot be made even though the multiphase equilibria is taken into account. On the other hand, BTEX compounds may be detected in ground water above their solubility limits if gasoline additives such as methanol, ethanol, and methyl tertiary-butyl ether (MTBE) are present [Mihelcic, 1990; Barker et al., 1992; Kan et al., 1992]. Since ground-water data is usually only obtained for regulated compounds unless otherwise specified, it would be easy to overlook the presence of hydrophilic compounds which enhance the solubilities of the regulated compounds.

TABLE 2.4 TYPICAL EQUILIBRIUM CONCENTRATIONS OF PURE AND GASOLINE-DERIVED BTX COMPOUNDS [Sitar et al., 1992]

NAPL	% in Gasoline	Aqueous Solubility (g/m ³)	
		Pure Phase	Gasoline-Derived
Benzene	23	1800	11
Toluene	83	540	24
Xylene	103	185	12

Sub-solubility concentrations can also be caused by other phenomena. Consider the simplified flow geometry depicted in Figure 2.6.1, in which ground water sweeps past a NAPL lens. As shown in Figure 2.6.2a for a single-component NAPL (i.e., TCE), the percent solubility of TCE in the aqueous phase is dependent on such factors as the flow velocity and mixing, as indicated by the value of transverse dispersivity (α). The response of a bi- or multicomponent NAPL lens is more complex [Geller, 1990].

For example, it is possible for the dissolved hydrocarbon concentrations and the mole fractions in the bicomponent NAPL lens to temporally evolve as flowing ground water depletes the more soluble component (benzene) from the NAPL lens more rapidly, as shown in Figure 2.6.3. The preferential removal of soluble components from a NAPL mass via another flowing phase (aqueous or gas) is referred to as selective dissolution or fractionation. As benzene is depleted from the leading edge of the NAPL lens, the toluene mole fraction at the leading edge soon exceeds that of the downstream edge. From the perspective of the aqueous phase, the equilibrium concentration of toluene at the leading edge of the NAPL lens is greater than at the downstream end. Consequently, toluene may dissolve into the aqueous phase at the leading edge only to repartition back into the NAPL lens at the downstream end [Geller, 1990; Adenekan, 1992]. In this way, both temporal and spatial concentration gradients within each liquid phase may develop. In the case of multicomponent NAPLs such as gasoline, this process is very complex.

Other temporal and spatial gradients may develop as a result of the actual flow geometry (see section 2.6.2 for discussion). Because of selective dissolution, the mole fraction ratios at the NAPL lens

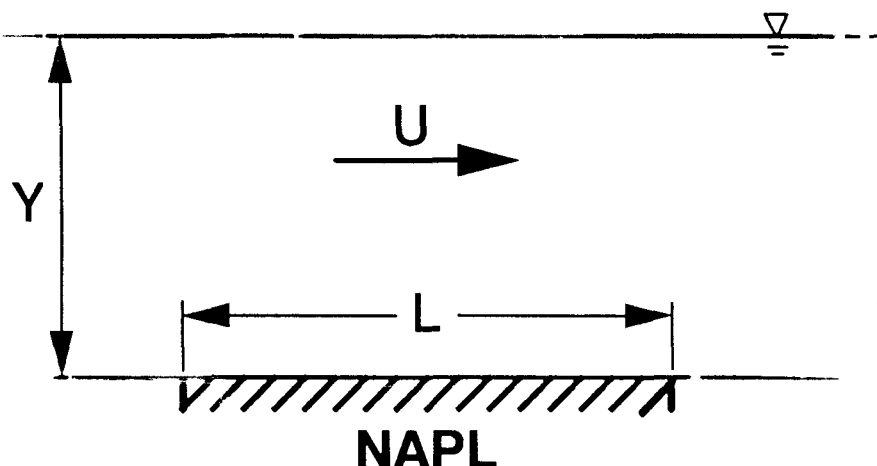


Figure 2.6.1 Schematic of a simplified flow geometry of ground water sweeping past a NAPL lens [Sitar et al., 1992].

interface may be different than in the NAPL interior. Due to mass transfer limitations occurring within the multicomponent NAPL, it therefore takes longer for aqueous concentrations to reach equilibrium with a multi-component NAPL than with a single-component NAPL [Geller, 1990; Adenekan, 1992]. Hence, mass transfer limitations will contribute to aqueous hydrocarbon concentrations appearing below their solubility limits [Hunt et al., 1988b; Miller et al., 1990; Powers et al., 1991; Brusseau, 1992; Sitar et al., 1992]. Sub-solubility limit aqueous NAPL concentrations may result from mixing and dilution within the porous media and at the wellhead [Hunt et al., 1988b; Feenstra and Cherry 1988; Feenstra, 1990; Chiang et al., 1992], and misleading interpretations of ground-water data may result if these factors are not given due consideration.

2.6.2 Soil Gas Samples

Since the gaseous diffusion of volatile compounds is about four orders of magnitude greater than in the liquid phase, soil gas monitoring and vapor extraction are useful in delineating vadose zone contamination, and possible saturated zone contamination. For this reason, soil gas sampling of volatile hydrocarbons has enjoyed widespread use.

Hydrocarbon vapors have been observed in excess of 100 meters from the NAPL source under quiescent conditions [Marrin and Thompson, 1987; Hunt et al., 1988a]. Migration of this magnitude indicates potential success for soil vapor extraction and for the identification of potential volatile DNAPL "hotspots." However, while soil gas measurements can be used to delineate the contaminated region in the unsaturated zone, they yield little information on the actual distribution of DNAPL within the saturated zone [Marrin 1988], as illustrated in Figures 2.5.2 and 2.5.3. Also, nonvolatile hydrocarbons which comprise DNAPLs will not be detected. Soil heterogeneity, density and quantity will limit the DNAPL exposure, access and partitioning to the unsaturated zone. Furthermore, in terms of multiphase equilibria alone, the problems associated with soil gas sampling are essentially identical to those of ground-water sampling [Hunt et al., 1988a; Sitar et al., 1992]. When coupled with mass transfer limitations, interpretation of subsurface sampling data becomes very complex.

For example, as a result of continuous soil gas sampling or extraction, the tailing-off of hydrocarbon concentrations is frequently observed. While this is commonly attributed to successful compound removal from a NAPL lens, numerical simulations have shown that hydrocarbon concentrations in soil gas are a

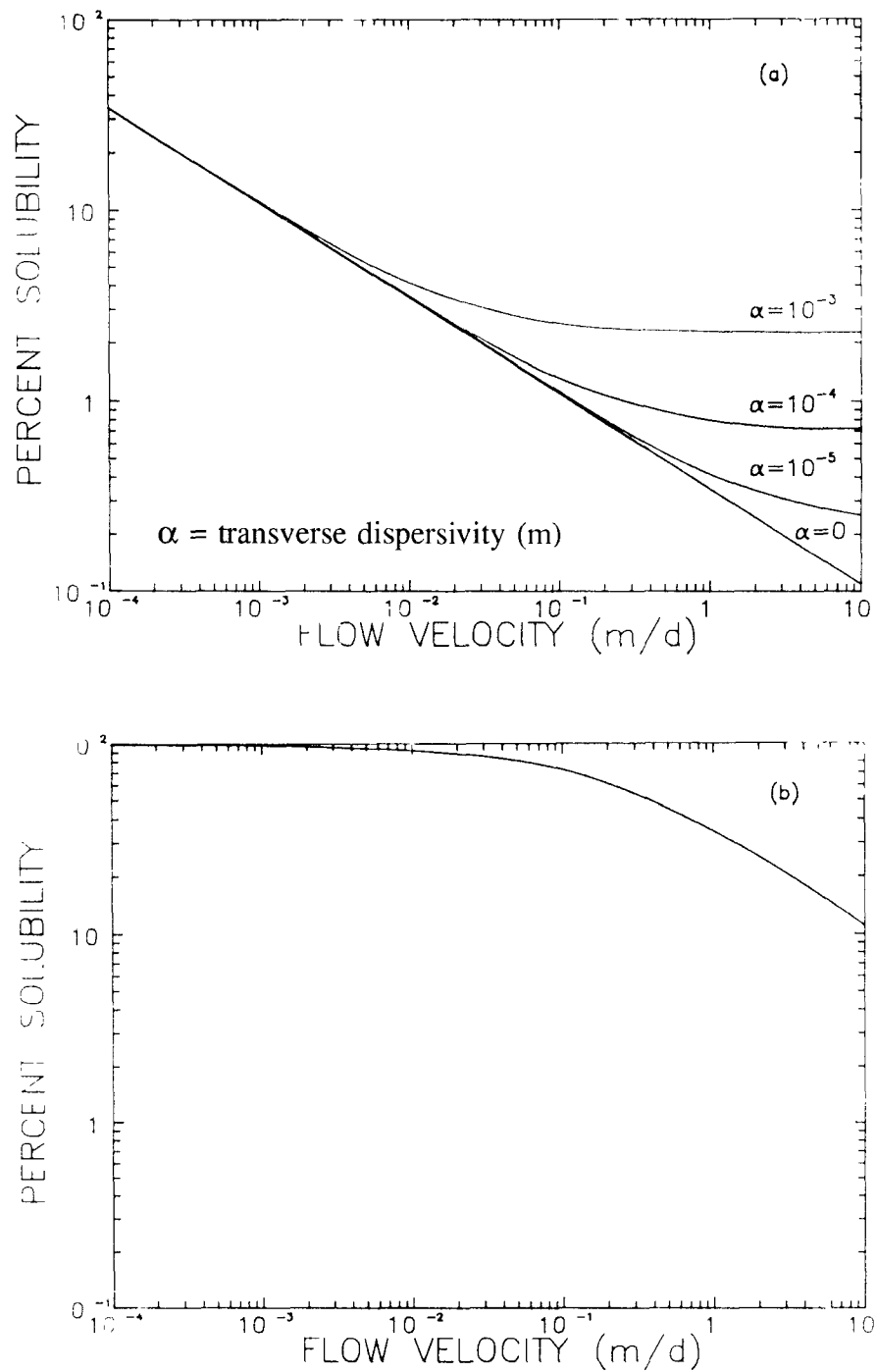


Figure 2.6.2 Computed average TCE concentrations of ground water (a) and soil gas (b) sweeping past a NAPL lens using a simplified geometry (Figure 2.6.1) [Sitar et al., 1992].

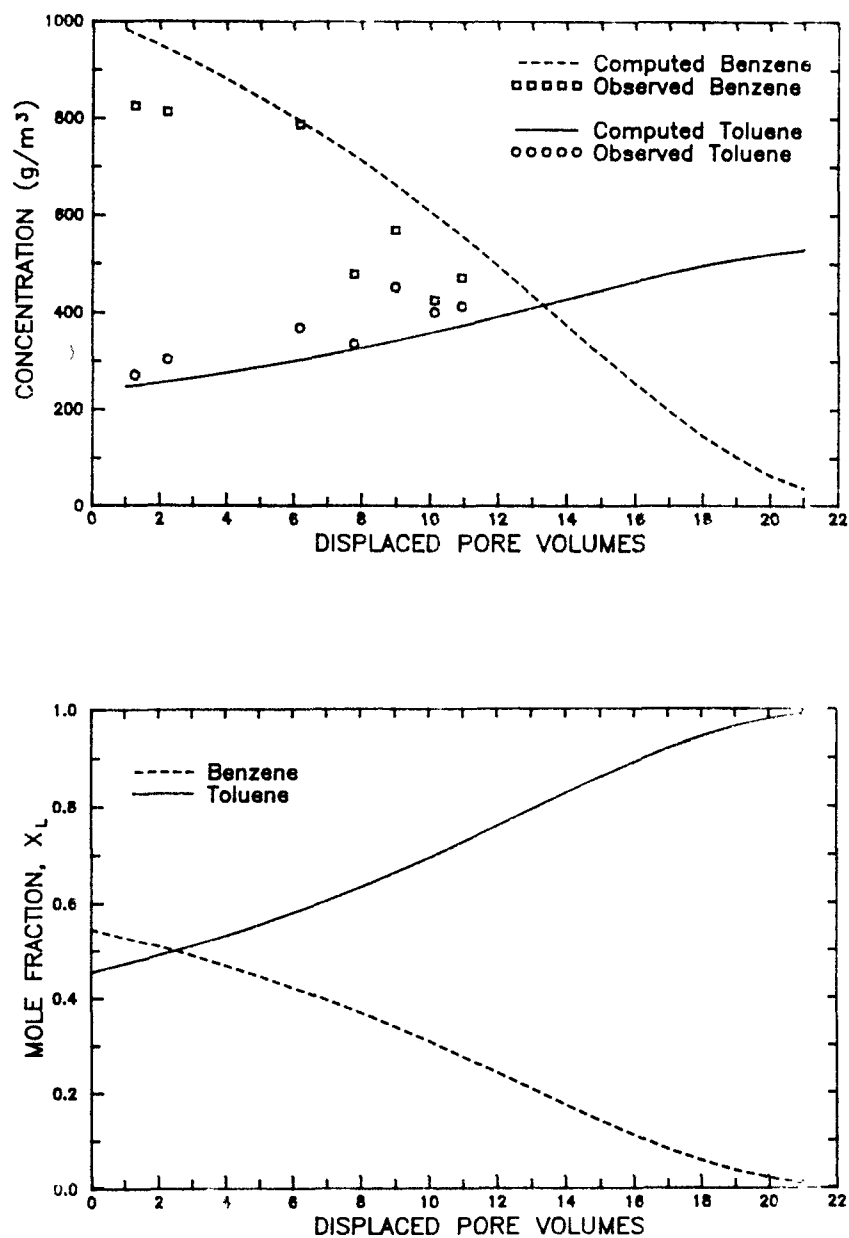


Figure 2.6.3 Predicted and observed evolutions of: (top) aqueous hydrocarbon concentrations in equilibrium with bicomponent NAPL; and (bottom) mole fractions of the bicomponent NAPL [Sitar et al., 1992].

function of the bulk phase sweep velocity [Hunt et al., 1988b; Sitar et al., 1992] and that NAPL removal is limited by gas phase molecular diffusivity. Because liquid phase molecular diffusivities are about four orders of magnitude less than gas phase diffusivities, gas phase removal is more efficient, as suggested by Figure 2.6.2b.

Additionally, the tailing-off of concentrations of volatile compounds is often attributed to the fractionation of the multicomponent NAPL mass, as shown in Figure 2.6.4. The gas phase concentrations imply that the mole fractions of each compound in the NAPL mass are changing with time. Yet, field data obtained by Johnson et al. (1990) reveal that the relative vapor concentrations of BTEX compounds emanating from gasoline (multicomponent LNAPL) in the subsurface remain essentially constant over time, see Figure 2.6.5. In this case, the soil gas concentrations suggest that the mole fractions in the gasoline are constant and that fractionation may not be occurring.

The difference between the observed concentrations shown in Figure 2.6.4 and 2.6.5 can be explained in terms of air flow geometry, i.e., flow-through and/or bypass drying mechanisms. The flow-through drying mechanism is observed to occur when the emplaced NAPL is situated within a homogeneous soil, or within a less permeable soil zone in which the permeability ratio between the adjacent soil layers is less than 10:1 [Ho and Udell, 1992]. Flow-through air flow implies that the air is flowing directly through the DNAPL contaminated soil zone, and compound removal is vapor solubility controlled [Ho and Udell, 1992]. Fractionation of the leading edge (and to a lesser degree the periphery edges) of the NAPL contaminated soil zone occurs as the more volatile components are preferentially vaporized. Depending on the length of the contaminated soil zone in the direction of air flow, the relative soil gas concentrations may not evolve (Figure 2.6.4), but may remain constant for some time (Figure 2.6.5), especially if contamination is extensive. Since DNAPL mass fractionation occurs in the direction of air flow, the effluent soil gas concentrations will sequentially evolve as each component is removed, as shown in Figure 2.6.4.

The bypass drying mechanism is observed to occur when the emplaced NAPL is situated within a less permeable soil zone in which the permeability ratio between the adjacent soil layers is greater than 100:1 [Ho and Udell, 1992]. Bypassing air flow occurs through the more permeable zone, and the removal of the compound is controlled by vapor diffusion within the less permeable soil zone, as shown in Figure 2.6.6. Under these conditions the liquid is stagnant, and although equilibrium is attained at the vapor-liquid interface, fractionation of the DNAPL mass will not be manifested until the mass is nearly diminished or unless liquid-phase mass transfer limitations exist.

Three distinct stages mark the evolution of the soil gas concentrations under bypassing conditions: (1) an early, rapid decrease in the more volatile components arising from fractionation at the DNAPL surface; (2) a period of quasi-steady state compound removal at near constant relative gas concentrations as the DNAPL surface recedes further into the impermeable media; and (3), a long-term gradual decrease in relative gas concentrations as the more volatile species are sequentially removed from the diminishing DNAPL mass. These mechanisms have been observed on the laboratory scale [Ho and Udell, 1992].

Thus, the relative soil gas concentrations emanating from a multicomponent DNAPL mass may be constant under two of the aforementioned conditions: (a) during flow-through vapor flow in an extensive (long) DNAPL mass; and (b) during condition (2) of bypassing air flow. If the flow-through mechanism is operating, the relative soil gas ratios will approximate the relative soil gas solubility limit ratios, whereas the relative soil gas concentrations should be close to the initial compound mass ratios in the DNAPL (from soil samples), if the bypassing mechanism is operating.

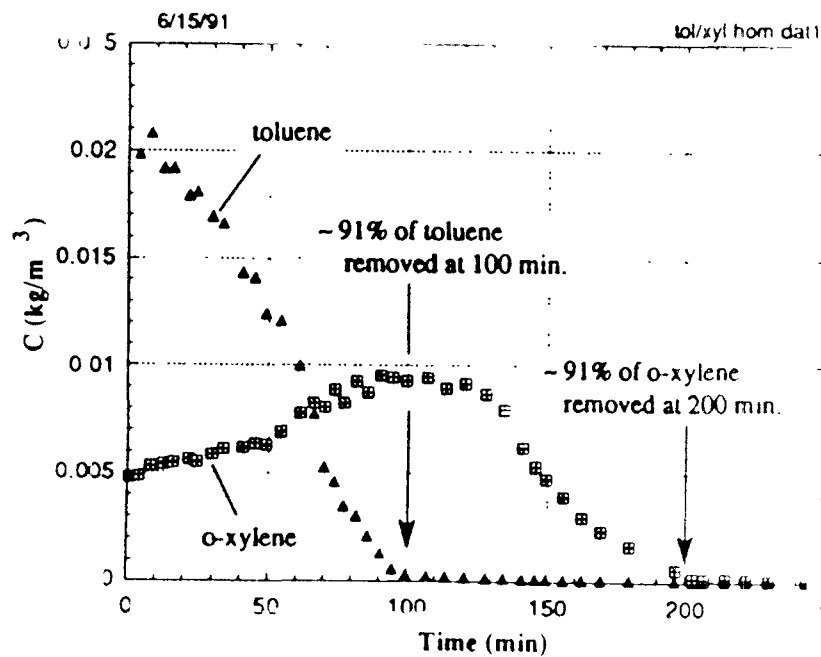


Figure 2.6.4 Evolution of toluene and σ -xylene soil gas concentrations in a homogeneous sand pack [Ho and Udell, 1992].

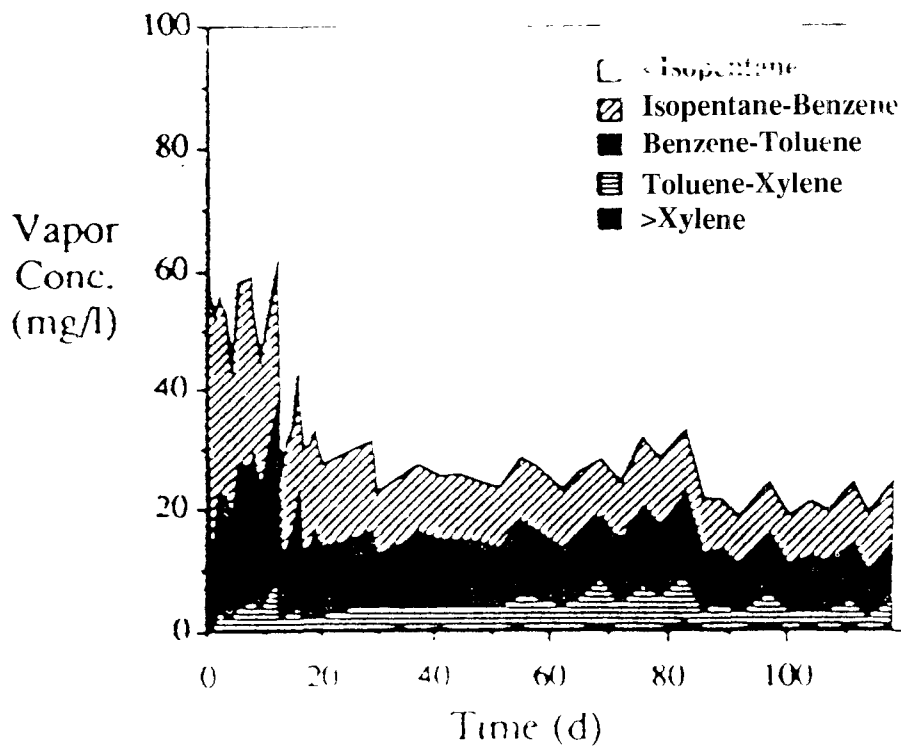


Figure 2.6.5 Soil gas composition as a function of time during soil venting at a gasoline contaminated site [Johnson et al., 1990].

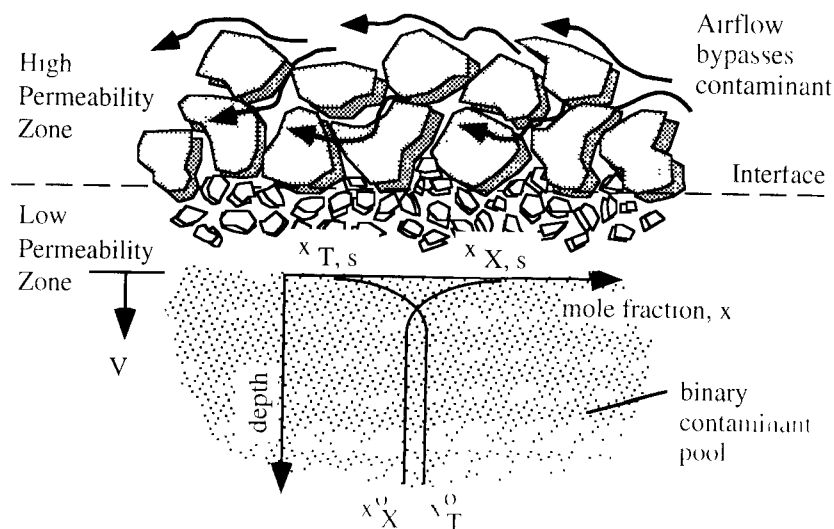


Figure 2.6.6 Bypassing air flow mechanism and its effect on the composition profile of an evaporating bicomponent NAPL pool trapped within low permeability zone [Ho and Udell, 1992].

2.6.3 Well Product Thickness

Evidence of floating LNAPL product in monitoring wells has been used to detect subsurface contamination and to estimate the quantity of recoverable LNAPL [Zilliox and Muntzer, 1975; de Pastrovich et al., 1979; Hall et al., 1984; Abdul et al., 1989; Farr et al., 1990; Kemblowski and Chiang, 1990; Lenhard and Parker, 1990; Mercer and Cohen, 1990]. While these efforts have been made for petroleum spills (LNAPLs), they are of interest to us from the perspective that specific hydrocarbons (see Table 2.1) are often components of multicomponent LNAPLs. Based on the arguments of soil heterogeneity, soil retention capacity and saturation-capillary pressure relationships alone, it should be evident that the absence of floating LNAPL in the monitoring wells does not preclude the existence of NAPLs in the subsurface. While the presence of floating LNAPL in a monitoring well confirms its existence in the subsurface, it indicates little else. For example, LNAPL can become trapped by capillary forces as a result of water table fluctuations. Once immobilized, the LNAPL may no longer be in communication with a pre-existing well, nor will it be easy to locate the trapped LNAPL during subsequent site characterization. Therefore, the use of monitoring wells for detection of NAPLs (consider immobile ganglia) and for NAPL recovery estimations is questionable [Abdul et al., 1989; Lenhard and Parker, 1990].

Similar difficulties are encountered in trying to assess the presence of DNAPL. Most importantly, however, boreholes and completed wells will act as downward conduits for preferential flow, therefore, drilling into suspected DNAPL zones generally is not recommended. In cases when DNAPL is encountered, the height of the DNAPL can be estimated only if the exact bottom of the DNAPL pool is known and if the capillary rise at the DNAPL-water interface is included in the analysis. However, current correlation models do not incorporate the Bond and Capillary number constraints which lead to discontinuous NAPL emplacement under dynamic conditions. Thus, volume estimates of in-situ DNAPL developed using well correlation methods may be highly misleading.

2.6.4 Soil Samples

Because of the complexities introduced by multiphase-multicomponent equilibrium and mass transfer limitations, accurate estimates of the extent of subsurface contamination are difficult to obtain using both ground-water and soil gas samples, as already discussed. The remaining alternative is soil sampling which has the advantage of giving very specific data at discrete locations. However, results of soil sample analyses also require careful interpretation and an understanding of the principles already discussed.

The data of Dresen et al. (1986) illustrate that ground-water and soil samples taken from the same borehole can lead to conflicting conclusions regarding the presence of NAPL [Sitar et al., 1992]. These data are presented in Table 2.5. While the measured ground-water concentration for each BTX compound is well below its individual solubility limit, the concentrations are consistent with saturation concentrations of BTX in contact with separate phase gasoline, as indicated in Section 2.6.1. The reported ground-water concentrations can be used to estimate the amount of adsorbed hydrocarbon in equilibrium with the ground water using Equations (12) and (19), and assuming a conservative value of $f_{oc}=0.01$ and $K_{ow}=135, 490$, and 1300 for benzene, toluene, and xylene, respectively. The computed soil concentrations assuming sorption alone are 22, 76, and 109 mg/kg for benzene, toluene, and xylene, respectively, which are at least an order of magnitude below the measured soil concentrations. Thus, both the ground-water concentration and soil concentration data point to the presence of free product gasoline.

TABLE 2.5 BTX CONCENTRATIONS IN WATER AND SOIL FROM SAME BOREHOLE AT A GASOLINE CONTAMINATED SITE [Dresen et al., 1986]

NAPL	Measured Concentrations	
	in water (g/m ³)	in soil (mg/kg)
Benzene	27	270
Toluene	26	1100
Xylene	14	1100
Total Hydrocarbons	NA	9400

The important point is that once the separate phase is present, its distribution is highly variable, governed by the heterogeneity of the subsurface environment, and the soil concentration data will appear highly variable and inconsistent. Moreover, current soil concentration reporting practices often provide no information on the soil porosity, water content, density or other soil parameters [Sitar et al., 1992]. Hence, volume or mass estimates of each phase (i.e., soil, water, air) are precluded, as are accurate estimates of the hydrocarbon distribution and the volume of NAPL [Mackay, 1979, Mackay and Paterson, 1981; Mackay and Shiu, 1992].

2.7 CHALLENGES FACING IN-SITU TECHNOLOGIES

A variety of the phenomena and technical issues associated with the fate and transport of DNAPLs have been addressed in the previous sections. The migration of DNAPLs was described in terms of their physical and chemical properties and in terms of the porous media characteristics under natural subsurface conditions. In this respect, it is important to distinguish between three major zones of contamination: the source zone, which contains very high concentrations of potentially mobile DNAPL; the residual zone, through which the mobile DNAPL has already traversed, leaving behind considerable contamination; and the dissolved zone (or plume), which emanates from the source and residual zones carrying dissolved hydrocarbons usually at or below their respective solubility limits. In addition, in all zones, hydrocarbons are likely to have partitioned into the solid phase (i.e., organic matter). The major concern with DNAPLs,

in terms of remediation, revolves around the fact that DNAPL sources and residual zones are often quite deep, making access and detection extremely problematic.

Soil heterogeneity is an important factor affecting DNAPL fate and transport. The site stratigraphy affects the distribution of the DNAPL in the subsurface and the contaminant distribution then plays a critical role in the selection of the overall approach for site remediation. Ultimately, the success of any passive or active in-situ technology is largely associated with its susceptibility to soil heterogeneities and its ability to favorably alter the DNAPL properties to facilitate recovery or remediation.

Soil heterogeneity and manipulation of subsurface conditions are not the only challenges facing in-situ DNAPL cleanup technologies. Successful technologies also have to be able to adapt to other site specific conditions such as depth to the water table, depth of the contaminated zone, volume of contaminated soil, site access, and man-made structures and other obstructions.

Finally, current remedial goals often require that a baseline aqueous contaminant concentration (maximum contaminant level, MCL) be attained, or that in excess of 99% of the DNAPL be treated or recovered. This standard by itself poses a significant technical challenge to many technologies even under the most favorable of conditions. Thus, all of these issues and challenges have to be kept in mind when considering the potential viability of the remedial technologies which are discussed in the following sections of this report.

SECTION 3.0

TECHNOLOGY DESCRIPTIONS

3.1 TECHNOLOGY EVALUATION FORMAT

The technology descriptions contain a synthesis of the relevant information about each technology. Focus is placed on attempting to identify in-situ technologies capable of addressing the remediation of DNAPLs situated below the water table; secondary importance is placed on contaminants dissolved in the aqueous phase. Several of the evaluated technologies were not originally developed for remediation of contaminated sites, much less DNAPLs. As a result, some of the technologies have not yet been demonstrated on DNAPLs, and owing to their developmental stage, have not been demonstrated in the field and below the water table. Some in-situ technologies which have potential applicability to remediation of DNAPLs occurring below the water table have been demonstrated in the vadose zone only; but beyond this, the evaluation of technologies used to clean up contamination in the vadose zone has been omitted from this report. Also, several in-situ technologies have been fully demonstrated only in non-environmental applications, and are currently being adapted for environmental applications. In all cases, the applicability to remediation of DNAPLs occurring below the water table is nonetheless considered in order to not rule them out prematurely.

DNAPL treatability data were specifically sought for this report, but were often difficult to obtain for the reasons indicated above. In cases where information on DNAPLs is sparse or not available, performance data relating to treatment/recovery of LNAPLs and metals are provided for illustrative purposes, when applicable. Technologies must therefore be evaluated within the context of the specific application, even though an attempt is made to anticipate the theoretical and practical effectiveness of these technologies to the DNAPL case. With certain technologies such as air sparging or in-situ vitrification, it was very difficult to separate the theoretical background from the field implementation. However, every effort was made to maintain the division.

Effort was made to evaluate the most current information and to select representative applications illustrating the more interesting or impressive capabilities of each technology. However, an exhaustive compilation of relevant case studies (as in the case of slurry wall construction) was beyond the scope of this effort. Thus, the technology descriptions are intended to provide a basic technical assessment of the technology and to identify its problem areas using basic principles.

Technologies are grouped by major process type (i.e., biological, soil washing, thermal) and are arranged alphabetically. An attempt was also made to keep multifaceted technologies separate. For instance, air sparging may enhance in-situ biological degradation of organic compounds. To avoid repetition, this fact is only briefly stated in the air sparging section; and air sparging is reported as an oxygen delivery method in the in-situ aerobic biodegradation section.

The Technology Descriptions, which appear later in this section, are organized into the following subsections:

Theoretical Background--

The theory of each technology is evaluated in terms of the approach, reaction types, dominant phenomena and important considerations or operating parameters. Theory is distinguished from field implementation in order to assess the adequacy of the theory separately from its application in the field. If the theory is poorly understood,

empirical relationships are discussed.

Field Implementation--

A conceptual description or the layout of the technology is presented and evaluated. Details regarding the development, construction, geometry, operating parameters and process rates are provided under this heading, when available.

Level of Demonstration and Performance--

Information on lab-, pilot-, and field-scale performance is provided to demonstrate capabilities of the technology. Information at the most advanced stage of development is presented to the extent possible. Frequency of implementation is stated under this heading and performance assessed versus predictions where possible.

Applicability/Limitations--

Information regarding targeted contaminants, soil matrix limitations, site considerations, health and safety issues, and inefficiencies are addressed under this heading.

Cost and Availability--

The promise and commercial availability of the technology is evaluated. Although necessary technology hardware may be available, the requisite expertise may be lacking. Patent and license information is provided where possible. Total, operating, maintenance, partial, or relative costs are presented where available. Untreated residuals requiring further treatment are usually identified.

References--

The most relevant citations selected and used in each technology description are provided at the end of the report.

Although not formally addressed here, regulatory acceptance and/or approval will be required for most of these technologies and, therefore, plays a major role in the viability of actual technology implementation. Regulatory issues require serious consideration and the involvement of state and federal entities should be sought at the earliest possible date to explore remedial alternatives.

Finally, the significance of site heterogeneity cannot be stressed enough. The effectiveness of all of the reviewed technologies can be affected by the presence of subsurface heterogeneities. However, some technologies are still more susceptible than others; therefore, this issue is an important criterion in determining the potential effectiveness of a given technology.

3.2 BIOLOGICAL PROCESSES

Introduction--

In-situ biodegradation is a process in which aqueous phase organic compounds are completely or partially metabolized by microorganisms situated in the subsurface. Bacteria are largely responsible for the biological transformations which occur in porous media and are generally considered as a stationary phase, either through attachment to solid surfaces or via agglomeration [Criddle et al., 1991]. These organisms convert natural and xenobiotic organic compounds into energy and end products, and utilize a portion of the organic material for cell synthesis [Lee et al., 1988; McCarty, 1988, 1991; Sims et al., 1992]. In this section, some of the general features of biodegradation are presented and the in-situ aerobic and anaerobic biodegradation processes are specifically evaluated in sections 3.2.1 and 3.2.2, respectively.

Metabolic processes of aerobic and anaerobic microbial consortia are distinguished by the nature of carbon substrate utilization, and three metabolic processes are recognized: primary metabolism, secondary metabolism, and cometabolism. The metabolic utilization of a compound depends on such factors as its molecular structure, concentration, environmental conditions, bioavailability of nutrients, presence of competing or inhibitory substrates, the nature of the microbial consortia and the enzymes and cofactors they possess, and toxicity effects.

Primary metabolism of an organic compound occurs when it yields sufficient energy for both cell maintenance and growth, and it is present at concentrations large enough to sustain the microbial population [McCarty, 1988, 1991]. Petroleum hydrocarbons are generally good examples of primary substrates, while compounds such as ammonia can serve as a primary energy source but not a carbon source. Examples of halogenated primary substrates and the conditions under which they are utilized are presented in Table 3.2.1. Many stoichiometric relationships describing the oxidation and reduction of organic compounds by microbes have been enumerated [McCarty, 1975; Criddle et al., 1991]. From the stoichiometric relations, nutrient (electron acceptor, primary substrate, nitrogen, phosphorus, etc.) demands can be estimated and Monod kinetics can be used to relate the growth and decay of the microbial consortia to the degradation reactions [Monod 1942; McCarty, 1971]. Also, provisions can be made to incorporate sorption and biofilm effects [Criddle et al., 1991; Semprini and McCarty, 1992].

Secondary metabolism describes the utilization of trace organic compounds which, by virtue of their low concentrations, cannot sustain microbial growth [McCarty, 1988]. Cometabolism occurs when nonspecific microbial enzymes or cofactors fortuitously biotransform organic compounds that provide insignificant energy and organic carbon for growth [McCarty, 1988]. Cometabolism has been identified as one of the major mechanisms in the transformation of chlorinated hydrocarbons and pesticides [Horvath, 1972].

TABLE 3.2.1 MICROBIAL UTILIZATION OF ORGANIC COMPOUNDS AS A FUNCTION OF BIOLOGICAL PROCESS TYPE AND ENVIRONMENTAL CONDITIONS [McCarty, 1988]

Primary Substrates	Aerobic and Anaerobic	Glucose, acetone, isopropanol, acetate, benzoate, phenol
	Aerobic Primarily	Alkanes, benzene, toluene, xylene, vinyl chloride, 1,2 dichloroethane, chlorobenzene
Co-metabolism (secondary substrates)	Oxidations	Trichlorethylene, dichloroethylene, dichloroethane, vinyl chloride, chloroform
	Reductions	1,1,1-Trichloroethane, trichlorethylene, tetrachloroethylene, dichloroethylene, dichloroethane, carbon tetrachloride, chloroform, DDT, lindane, PCBs

Organic substrates may be oxidized under aerobic conditions and reduced under anaerobic conditions. With increasing degree of halogenation, the carbon atoms within the organic compound become more oxidized, making reductive metabolism more likely than oxidative [Vogel et al., 1987]. Hence, for aliphatic compounds, rates of oxidation generally increase with decreasing degree of halogenation; whereas rates of reduction generally increase with increasing degree of halogenation [Vogel et al., 1987]. The influence of the degree of halogenation on the transformation (reaction) rate is summarized in Figure 3.2.1. Table 3.2.2 presents several compound transformation rates by mixed cultures under a variety of environmental conditions. Carbon dioxide or methane, water and inorganic salts (chlorine, bromine, etc.) are produced by the complete mineralization of halogenated hydrocarbons and other compounds by microbial consortia.

If naturally occurring microorganisms can be identified in the subsurface environment and are capable of degrading the targeted compounds, they are usually enriched or biostimulated with amendments which may include electron donors (primary substrates), electron acceptors (i.e., oxygen, nitrates, etc.), and nutrients such as nitrogen, phosphorus and other trace metals. Many case studies exist where indigenous microorganisms have been successfully biostimulated. Introduction of exogenous cultures into the subsurface is often considered on occasions when indigenous consortia are incapable of degrading the targeted compound, or are non-existent. However, to date, in-situ aerobic biodegradation resulting from introduction of exogenous cultures into the subsurface has not been convincingly demonstrated [Lee et al., 1988; Alvarez-Cohen, 1993a]. Introduction of genetically engineered microorganisms into the subsurface is presently prohibited by law in the U.S. without prior approval [Thomas and Ward, 1989].

Elements common to successful applications of in-situ aerobic biodegradation include: adequate aquifer permeability, usually $K > 10^{-4}$ cm/s [Thomas and Ward, 1989]; prior removal of free product [Thomas and Ward, 1989; Alvarez-Cohen, 1993a]; a suitable microbial population [McCarty 1991; Alvarez-Cohen, 1993a]; sufficient hydrodynamic control for plume containment and delivery of required amendments [Sims

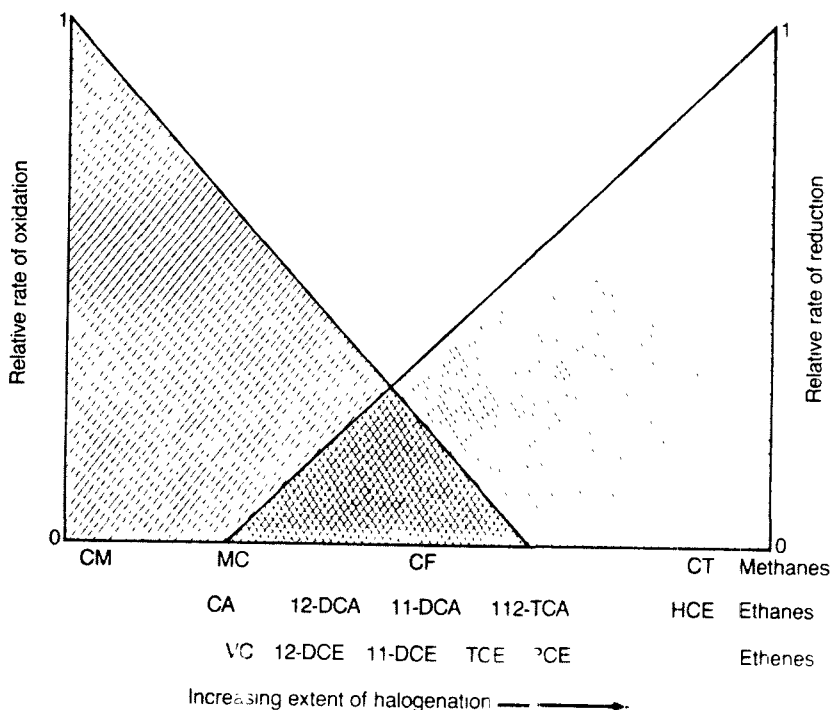


Figure 3.2.1 Relative rates of reduction and oxidation as a function of halogenation [Vogel et al., 1987].

TABLE 3.2.2 COMPARISON OF SUBSTRATE UTILIZATION RATES BY MIXED CULTURES USING DIFFERENT ELECTRON ACCEPTORS [Criddle et al., 1991]

Substrates	k' (L / mg day)			
	Aerobic (O ₂)	Anaerobic ^b		
		Denitrification (NO ₃ ⁻)	Sulfate Reduction (SO ₄ ²⁻)	Methanogenesis (CO ₂)
Primary				
acetate	3.8	1.4	1.0	0.63
Secondary				
chlorobenzene	2.5			
o-dichlorobenzene	10.0			
p-dichlorobenzene	11.0			
1,2,4- trichlorobenzene	5.0			
ethylbenzene	35.0			
styrene	50.0			
naphthalene	40.0			
bromoform		0.23	0.71	2.0
chloroform				0.21
carbon tetrachloride		0.36	0.2	0.63
1,1,1,- trichloroethane		0.002	0.005	0.96
tetrachloroethene				0.094
1,2-dibromomethane		0.0019	0.0076	2.1
dibromochloropropane			0.23	2.4
hexachloroethane		0.056	0.38	0.61

References. ^a Bouwer and McCarty (1985), ^b Bouwer and Wright (1988)

et al., 1992; Alvarez-Cohen, 1993a]; and a complete monitoring system [Sims et al., 1992; Alvarez-Cohen, 1993a]. In common engineering practice, successful in-situ biodegradation is often explained in terms of: changes in dissolved electron acceptor concentrations (oxygen, nitrate, etc.), reduction in dissolved compound concentrations, increased carbon dioxide (or methane) concentrations, increased biomass in-situ, and the ability of indigenous microorganisms to biologically transform the targeted compounds in laboratory microcosms. Evidence of this kind is putative because evaluation of successful in-situ biodegradation is complicated by: uncontrollability of the field sites [Madsen, 1991]; aquifer heterogeneities [Madsen, 1991; McCarty, 1991; Alvarez-Cohen, 1993a]; and, a wide range of competing contaminant fates [Madsen, 1991, Alvarez-Cohen, 1993a]. For example, most abiotic transformations are slow, but are still significant within the time scales commonly associated with groundwater movement [Vogel et al., 1987].

Actual proof and sufficient confirmation of halogenated hydrocarbon destruction by microbial degradation has been provided in only a few studies which rely on several convergent lines of evidence [Madsen 1991; Alvarez-Cohen, 1993a]. Madsen [1991] summarizes sources of evidence which indicate successful in-situ biodegradation: production of specific intermediate metabolic compounds; changes in organic compound, stereoisomer, isotope or electron acceptor/tracer ratios after onset of in-situ biodegradation; amendment utilization and aqueous phase concentration responses coincident with pulsed

injection; and increased presence of microbial predators. Other factors may exist which are compound and site specific.

Because of compound toxicity, in-situ microorganisms cannot degrade the pure phase organic liquids. However, in-situ biological degradation should be considered when these compounds exist in residual or trace amounts in the saturated zone, and for any dissolved plumes emanating from DNAPL source areas. Considerable benefit can be derived from "ground-water polishing" when in-situ biodegradation is used in conjunction with other technologies capable of addressing the removal of the separate phase.

3.2.1 Aerobic Biodegradation

Theoretical Background--

Aerobic biodegradation is a process by which aqueous phase organic compounds are completely or partially metabolized by oxygen utilizing microorganisms. Using oxygen as the terminal electron acceptor, microorganisms convert natural and xenobiotic organic compounds into end products, energy, and utilize a portion of the organic material for cell synthesis [Lee et al., 1988; McCarty, 1988, 1991; Sims et al., 1992]. For low molecular weight chlorinated aliphatics, the metabolic intermediates and end products exuded by aerobes are not usually recalcitrant and/or toxic. However, degradation pathways for more complex aliphatics and aromatics may involve recalcitrant and/or toxic intermediates and end products.

Monooxygenases mediate halogenated hydrocarbon oxidation in three generalized ways in aerobic systems: α -hydroxylation and halosyl oxidation of halide substituted alkanes, which results in the formation of easily biodegradable alcohols and organic acids; and epoxidation of ethene bonds which produces unstable epoxides. Epoxidation is recognized as being the first step in the overall mineralization of several halogenated hydrocarbons in microbial systems [Stirling and Dalton, 1979; Patel et al., 1982; Janssen et al., 1987]. Methanotrophs were among the first bacteria recognized to utilize the epoxidation mechanism during the cometabolism of NAPLs [Leadbetter and Foster, 1959]. The epoxidation mechanism is shown in Figure 3.2.1.1 for the degradation of TCE by methane monooxygenase (MMO) as originally proposed by Hou (1984) and as modified by Henry and Grbić-Galić (1986). Epoxidation is afforded by the unusually broad substrate specificity of MMO [Stirling and Dalton, 1979]. Epoxidation pathways are recognized for several nonspecific oxygenases such as methane, propane, toluene, and ammonia monooxygenases and toluene dioxygenase [McCarty, 1992].

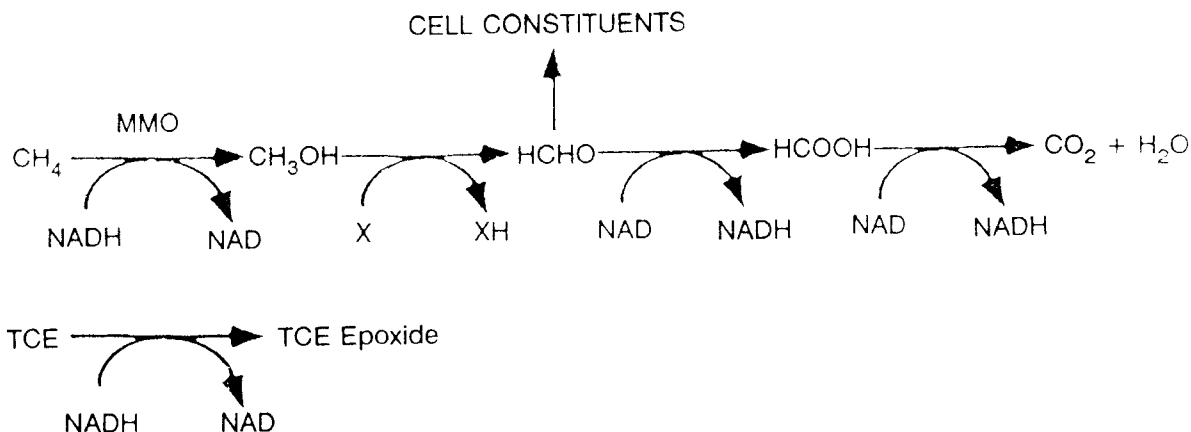


Figure 3.2.1.1 Methanotrophic utilization of methane by Methane Monooxygenase (MMO) and the formation of TCE-epoxide as the initial step of TCE oxidation [Hou, 1984; Henry and Grbić-Galić, 1986].

MMO catalyzes the oxidation of methane (CH_4) to methanol (CH_3OH); and energy is liberated, as indicated in Figure 3.2.1.1. During methane oxidation, energy is expended as TCE is transformed to TCE-epoxide. TCE-epoxide can then undergo hydrolysis (abiotic oxidation) to intermediates which can be easily degraded to carbon dioxide, chloride, and water [Little et al., 1988]. Subsequent oxidation of methanol, formaldehyde (HCHO), and formate (HCOOH) catalyzed by other oxygenases yields additional energy. While the use of methanol, formaldehyde, and formate as alternate substrates appears attractive from the perspective that reduced competition between methane and the targeted compounds for the MMO will result in higher compound removal [Semprini et al., 1991], field [Semprini et al., 1990, 1991] and laboratory [Alvarez-Cohen and McCarty, 1991; Henry and Grbić-Galić, 1991] studies have indicated that MMO enzyme production, and subsequently halogenated hydrocarbon epoxidation, is curtailed when methane is absent. However, MMO can remain active in the cell for extended periods of time.

Finally, some bacteria can oxidize simple chlorinated aliphatics such as vinyl chloride [Hartmans et al., 1985], 1,2 dichloroethane [Stucki et al., 1983], and methylene chloride [LaPat-Polasko et al., 1984] as sole carbon sources for energy. Aromatic degrading bacteria using phenol and toluene as the primary substrates have been shown to degrade di- and tri-halogenated ethenes [Nelson et al., 1987].

Field Implementation--

Most in-situ aerobic biodegradation applications are variations on the approach patented by Raymond (1974). Wellhead injection and infiltration galleries are two common configurations used for in-situ aerobic biodegradation, as shown in Figure 3.2.1.2. In-situ biostimulation is usually achieved using strategies analogous to hydraulic gradient control and pump-and-treat methods except that the injected fluids are amended. Pulsed (cyclic) injection of amendments has been employed to prevent biofouling in the vicinity of the injection well [Semprini et al., 1990]. Conventional injection and extraction well construction equipment can be used. Well placement strategy will depend on the nature and extent of contamination, soil heterogeneities, and anticipated subsurface flow behavior. In-situ biostimulation may initiate changes in fluid flow as a result of: changes in aqueous chemistry, pH, porosity, and fluid viscosity; corrosion of the support media, and surface property alterations [Criddle et al., 1991].

Because the subsurface is usually anaerobic and the oxygen demand for sustained biological degradation can be appreciable, oxygen, the primary electron acceptor, must be supplied to accelerate aerobic processes. Primary substrate, oxygen, and nutrient demands can be ascertained from treatability studies using aseptically obtained aquifer samples. Delivery of primary substrates, nitrogen, and phosphorus amendments is facilitated by aqueous phase injection due to their high water solubilities. However, actual delivery of nutrients to the contaminated soil zone depends on such factors as heterogeneity, hydraulic conductivity, etc.

Oxygen can be supplied in several ways which may require judicious selection given site conditions. The dissolved oxygen (DO) content of injected or recycled water can be increased to saturation (approximately 8 to 12 mg/l) prior to injection [Lee et al., 1988; Semprini et al., 1990; Semprini and McCarty 1992]. Air spargers can locally increase the DO of the saturated zone to approximately 8 to 12 mg/l if air is injected [Lee et al., 1988], or up to 40 mg/l if pure oxygen is used [USEPA, 1988; Thomas and Ward, 1989]. Spargers, as described in Section 3.6.2, may introduce such problems as precipitation of hardness ions and pore clogging under initially reduced subsurface conditions, changes in the local hydraulic gradients due to mounding, and uncontrolled migration of dissolved contaminants and DNAPL away from the treatment zone.

Two patents have been issued on hydrogen peroxide assisted in-situ aerobic biodegradation [Raymond et al., 1986; Lawes and Litchfield, 1988]. Hydrogen peroxide (H_2O_2) solutions can be directly injected into the saturated zone to provide a source of oxygen. H_2O_2 solutions can be stabilized by use of peroxidases, oxidases, or phosphates so that excessive decomposition by iron or soil catalyzed reactions

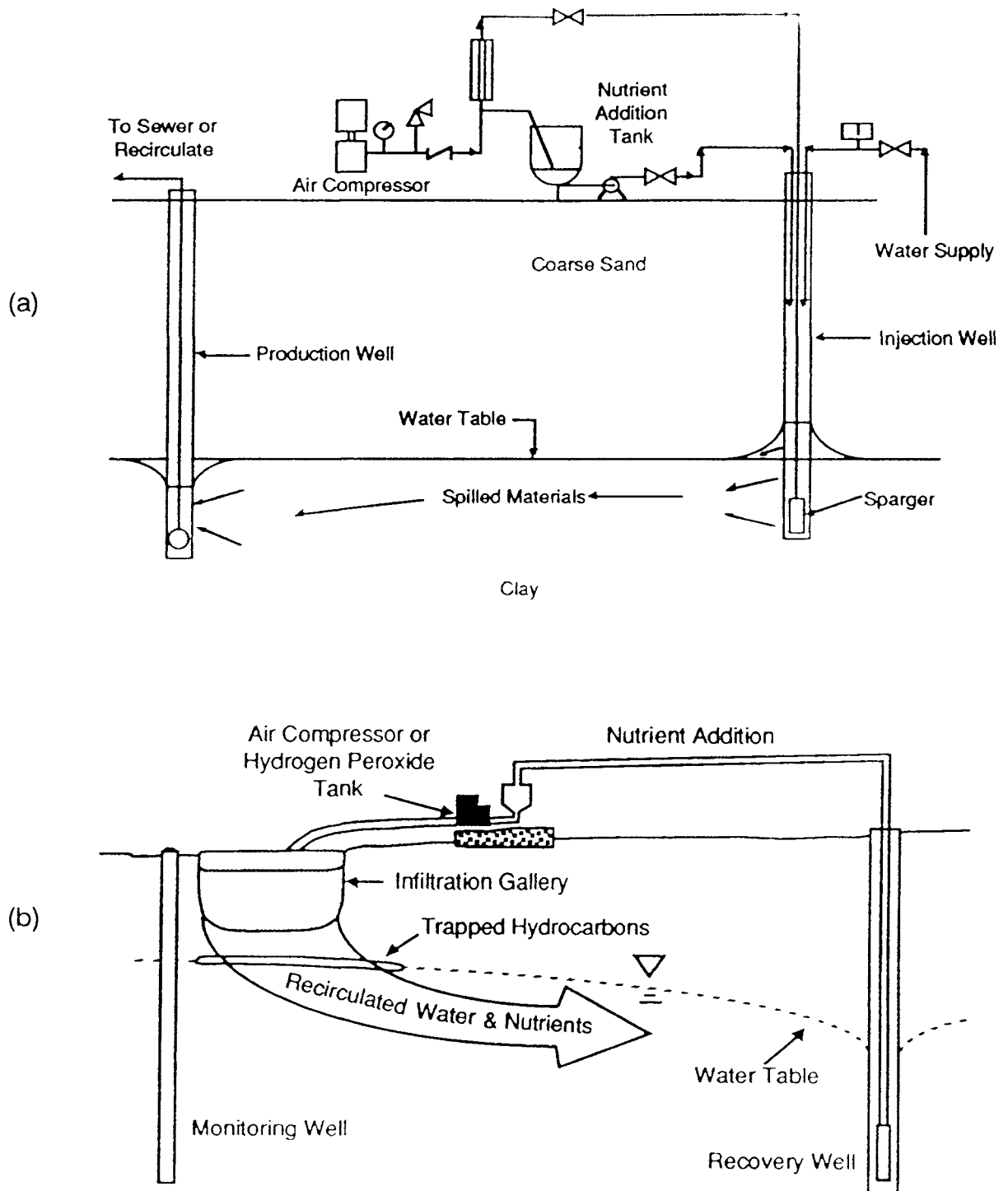


Figure 3.2.1.2 Schematics illustrating oxygen and nutrient delivery using spargers (a) and an infiltration gallery (b) [Thomas and Ward, 1989].

does not occur [Raymond et al., 1986; Lee et al., 1988; USEPA, 1988]. Also, some organic compounds may be oxidized by H_2O_2 and the mobility of inorganic metals such as lead and antimony may be increased via reactions with H_2O_2 [Alvarez-Cohen, 1993a]. Gradually increasing H_2O_2 concentrations from 50 mg/l to as high as 1000 mg/l fosters microbial consortia acclimation to H_2O_2 and mitigates microbial toxicity [Thomas and Ward, 1989]. However, Lee et al. (1988) report that degassing of molecular oxygen may occur at H_2O_2 concentrations > 100 mg/l.

Laboratory studies have indicated that colloidal gas aphrons (CGAs) may be an alternate source of oxygen delivery into the subsurface [Lofti and Michelsen, 1991; Michelsen et al., 1984, 1991]. CGAs, are a colloidal microdispersion of oxygen (65 vol%) in a thin soapy film (surfactant matrix) that have bubble dimensions of 25 to 50 μm in diameter. When injected into the saturated zone, the microbubbles eventually become immobilized and adhere to the solid phase. Oxygen transfer efficiencies of 5.4 to 59% have been achieved in two-dimensional tank studies using sandy soils. However, the viscous fluid (16 cp) may channel when injected or cause ground-water diversion, thus reducing contact efficiency. About 12% of the oxygen transferred is required to biodegrade the surfactant.

Level of Demonstration and Performance--

Numerous sites containing DNAPLs are reported to have been remediated by in-situ aerobic biodegradation, and many are under way [USEPA, 1992b]. An extensive listing of ongoing bioremediation activities is available [USEPA, 1992c]. Approximately 20% of the entries contained within the SITE Demonstration Program Technologies in the USEPA's ATTIC database include bioremediation applications [USEPA, 1992b]. As indicated earlier, actual proof and sufficient confirmation of targeted compound destruction by microbial degradation has only been provided in a few studies [Madsen 1991; Alvarez-Cohen, 1993a].

In 1986-1988, Moffet Field Naval Air Station in Mountain View, California, was the site of several detailed in-situ aerobic biodegradation studies which illustrated the successful biotransformation of chlorinated aliphatics [Roberts et al., 1990; Semprini et al., 1990; 1991; Semprini and McCarty, 1991, 1992]. The studies were conducted in a shallow confined sandy and gravelly aquifer which was not strongly anaerobic. Bromide tracer studies were conducted to define the flow characteristics and capture efficiency, and the sorption and retardation of each compound was evaluated prior to biostimulation. Mass balances performed on trichloroethene (TCE), cis-dichloroethene (cis-DCE), trans-dichloroethene (trans-DCE) and vinyl chloride (VC) revealed that abiotic transformations were negligible. Laboratory [Henry and Grbić-Galić, 1986] and field experiments [Semprini et al., 1990] demonstrated that the indigenous methanotrophic consortia could be biostimulated. Methane and oxygen were pulsed at various intervals, whereas small concentrations of the dissolved hydrocarbons were continuously injected.

In-situ aerobic biodegradation was demonstrated by several corroborating facts. Decreased and increased concentrations of the different compounds were observed to be coincident with the onset and cessation of methane utilization, respectively. The elimination of electron donors/acceptors, and appearance of a specific biotransformation product {trans-dichloroethene oxide (epoxide)} were a further confirmation of actual in-situ biodegradation [Semprini et al., 1990]. More importantly, quantitative knowledge of the contaminant releases and extensive instrumentation and monitoring afforded accurate mass balances that are atypical of most in-situ biodegradation applications.

Madsen et al., (1991) successfully demonstrated in-situ aerobic biodegradation of coal tar constituents (naphthalene and phenanthrene) in a shallow confined aquifer setting. Increased populations of microbes, particularly protozoans (predators), were detected within the plume area. The degradation activities and microbial population comparisons between contaminated and pristine soil samples taken from the site served as indirect and qualitative evidence of in-situ biodegradation.

Applicability/Limitations--

In-situ aerobic biodegradation applies only to the remediation of the aqueous phase. Regions containing the separate phase cannot be treated because the large compound concentrations result in microbial toxicity; therefore, major accumulations of free product must be removed by other means [Thomas and Ward, 1989; Alvarez-Cohen, 1993a]. Many DNAPLs were previously thought to be non-biodegradable, but new laboratory studies continue to demonstrate the biodegradability of DNAPLs. While site data may suggest in-situ biodegradation, it may be difficult to prove because of site conditions and competing mechanisms [Madsen, 1991; Alvarez-Cohen, 1993a].

Site characterization is required and hydraulic gradient control is necessary to effectively deliver nutrients. Hydraulic conductivities should be above 10^{-4} cm/s [Thomas and Ward, 1989]. Soil heterogeneities will greatly affect the ability to implement in-situ biodegradation. At very heterogeneous sites, in-situ biodegradation may be completely ruled out because of the inability to effectively deliver the nutrients to the contaminated areas [Alvarez-Cohen, 1993b].

Treatability studies are required to assess the viability of biostimulation, nutrient demands, ability of culture to degrade DNAPL, and other factors such as pH, redox potential, moisture conditions, DNAPL toxicity, and temperature effects. Microorganisms may convert DNAPLs into more recalcitrant, toxic, or inhibitory intermediate products. In the particular case of petroleum hydrocarbons, in-situ bioremediation can accelerate the time scale of pump-and-treat and natural attenuation of NAPLs from decades and centuries to months and years. However, degradation rates generally decrease as concentrations decrease and total cleanup may not be attainable [Ellison, 1992].

Cost and Availability--

In-situ aerobic biodegradation has been implemented on the full-scale numerous times, but mostly for petroleum hydrocarbons (usually non-halogenated). The technology hardware is generally available for full-scale applications. Although pulsed injection can be accommodated by two wells, more sophisticated (automated) injection systems may require site specific design, fabrication, or assembly. Aerobic biodegradation is a good candidate for dissolved plume management in the saturated zone in granular (aquifer) media. It is not well suited for low permeability and fractured media, or in areas where DNAPL is present.

In-situ aerobic bioremediation often costs less than other remedial technologies [Sims et al., 1992]. The usual cost range is \$15-60/yd³ [Ellison, 1992]. Ex-situ hardware will include such items as nutrient feedstocks, air strippers, and granular activated carbon.

3.2.2 Anaerobic Biodegradation

Theoretical Background--

Anaerobic biodegradation involves complete or partial metabolization of aqueous phase organic compounds by non-oxygen utilizing microorganisms. Using such compounds as nitrates, sulfates, carbon dioxide, or possibly ferric iron and other metal oxides as terminal electron acceptors [Ball et al., 1992], microorganisms convert natural and xenobiotic organic compounds into end products, energy, and utilize a portion of the organic material for cell synthesis [Lee et al., 1988; McCarty, 1988, 1991; Sims et al., 1992]. In certain cases, polyhalogenated aliphatic organic compounds can also serve as electron acceptors [Vogel et al., 1987].

Reduction of halogenated hydrocarbons occurs through two generalized dehalogenation mechanisms under anaerobic conditions: hydrogenolysis and dihalo-elimination. Hydrogenolysis entails the substitution of halogen atoms by hydrogen atoms. Dihalogen-elimination results in the replacement of two adjacent halogen atoms by an ethene bond. Figure 3.2.2.1 illustrates that the hydrogenolysis mechanism

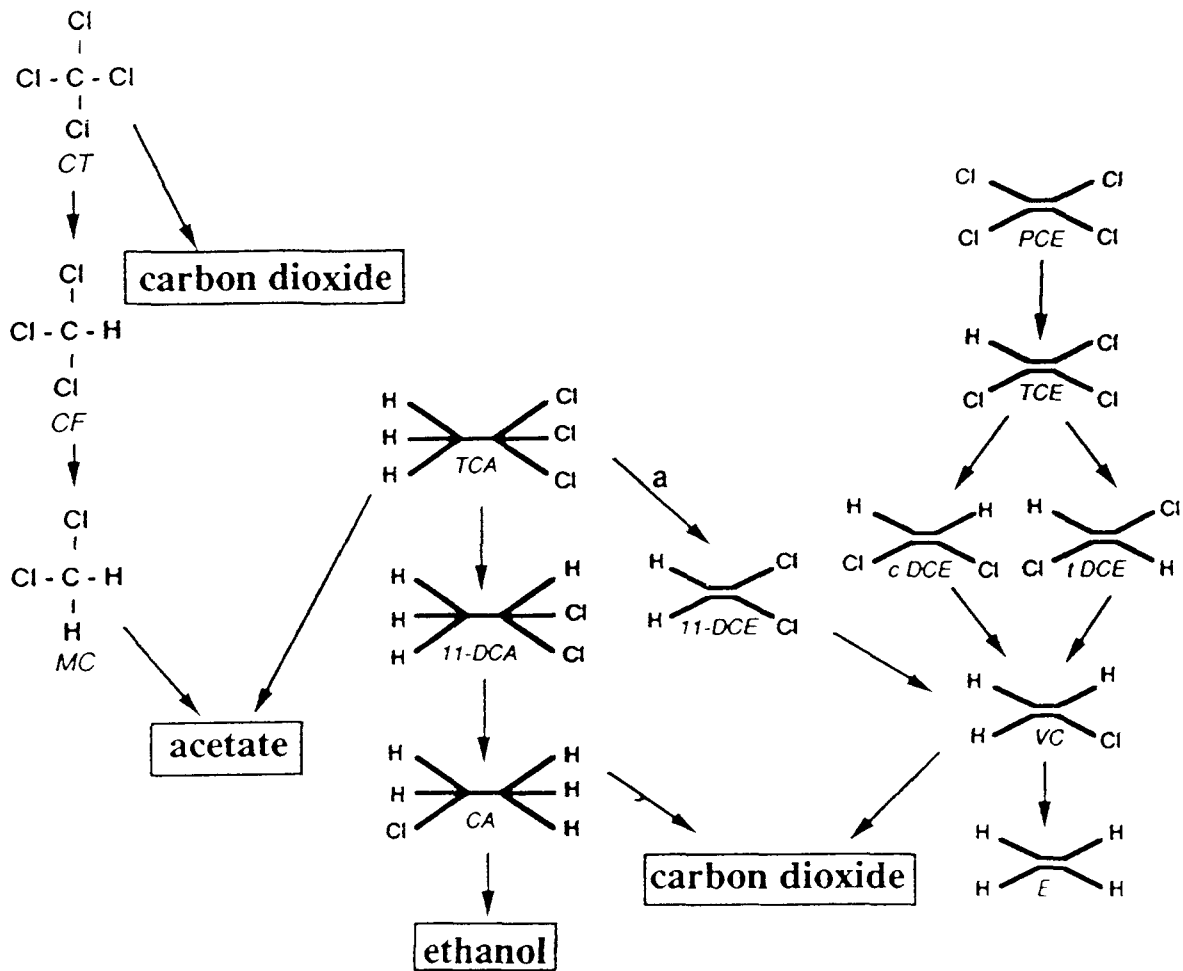


Figure 3.2.2.1 Pathways for anaerobic biotransformation of chlorinated aliphatics including abiotic (a) transformations [Vogel et al., 1987].

is the predominant reductive pathway for aliphatic hydrocarbons. These reductions may be mediated by a variety of enzymes and cofactors. Under severely reducing conditions, such as those typified by methanogenesis, the organic compound can actually serve as the electron acceptor [Alvarez-Cohen, 1993b].

Reductive dehalogenation also occurs in aromatic hydrocarbons. Descriptions of sequential dehalogenation of aromatic compounds and aromatic ring cleavage mechanisms are beyond the scope of this review, but are available [USEPA, 1986a].

Field Implementation--

Most in-situ biodegradation applications are variations on the approach patented by Raymond (1974). In anaerobic systems, wellhead injection is the usual configuration, and the strategy employed is analogous to aerobic processes (section 3.2.1) with the exception of electron acceptor delivery. Unlike oxygen, anaerobic electron acceptors (nitrate, sulfate, etc.) are extremely water soluble. The subsurface is usually anaerobic which makes this process advantageous. Delivery of primary substrates, electron acceptors, nitrogen and phosphorus amendments is easily facilitated by aqueous phase injection owing to

their high water solubilities.

Level of Demonstration and Performance--

Anaerobic processes are naturally occurring and have been observed to occur in-situ. Field studies have been conducted, but no full-scale engineered applications are known to exist. In 1980, St. Louis Park (Minnesota) was the site of a study which evaluated the in-situ anaerobic degradation of creosote constituents [Ehrlich et al., 1982]. The constituents of interest were the phenolics (2-17%). The 20 m thick aquifer consisted of three units: an upper drift of lake deposits and till; a middle drift consisting of glacial sands; and a lower unit consisting of till and deeply weathered bedrock. The presence of methane and methanogenic consortia only within the plume area and their absence elsewhere was evidence of in-situ biodegradation. Disappearance of phenolics relative to other less biodegradable creosote constituents, such as naphthalene, suggested that dilution was not a source of attenuation. Supplemental evidence was provided by laboratory sorption studies using field samples which indicated low phenolic sorption. Methane production in laboratory microcosms, inoculated with indigenous bacteria from the contaminated soil zone, lent further credibility to the qualitative conclusion that phenolics were being biodegraded in-situ under anaerobic conditions.

In 1988-1989, Moffet Field Naval Air Station in Mountain View, California, was the site of a detailed in-situ anaerobic biodegradation study which illustrated the successful biotransformation of chlorinated aliphatics [Semprini et al., 1992]. Experiments were conducted in a shallow confined sandy and gravelly aquifer which was not strongly anaerobic. Bromide tracer studies were conducted to define the flow characteristics and capture efficiency, and the sorption and retardation of each organic compound was evaluated prior to biostimulation. Mass balances performed on carbon tetrachloride (CT) revealed that abiotic transformations were negligible. Two potential electron acceptors were naturally occurring: nitrate (25 mg/l; as nitrate) and sulfate (700 mg/l; as sulfate). Other contaminants present in the groundwater included 50 µg/l trichloroethane (TCA), 6 µg/l Freon-113 and 3 µg/l Freon 11. Field experiments [Semprini et al., 1992] demonstrated that the indigenous consortia could be biostimulated using acetate as a primary substrate without any other amendments. To avoid biofouling near the injector, acetate (320 mg/l) and nitrate (25 mg/l) were pulsed at various intervals, whereas CT (40 µg/l) was continuously injected.

The field response indicated that the main denitrifying population was not responsible for the transformation of CT. While most of the acetate (80-90%) and nitrate were consumed within the first meter of transport, the most rapid rates of CT transformation occurred further downstream. Potential inhibition of CT transformation by high nitrate concentrations may have caused this trend. It was therefore hypothesized that a secondary microbial consortia that utilized the remaining acetate and decay products of the denitrifiers was responsible for the CT transformation [Semprini et al., 1992]. This hypothesis appears to be corroborated by the results of the transient experiments in which no direct evidence was found for the stimulation of sulfate-reducing or methanogenic bacteria when nitrate was completely removed.

In-situ anaerobic biodegradation was demonstrated by several corroborating facts. Decreased organic compound concentrations were observed to be coincident with the onset of acetate utilization, whereas increased organic compound concentrations coincided with the cessation of acetate utilization. Appearance of chloroform (CF), an intermediate biotransformation product which is not produced abiotically, was further confirmation of actual in-situ biodegradation [Semprini et al., 1992]. Transformation of CT was on the order of 70 to 97% within the test zone, and CF accounted for 30 to 40 % of the CT transformed. The other compounds, TCA, Freon 113, and Freon 11 were also transformed, but to a lesser extent. Quantitative knowledge of the compound releases, extensive instrumentation and monitoring afforded accurate mass balances that are atypical of most in-situ biodegradation applications.

Applicability/Limitations--

In-situ anaerobic biodegradation applies only to the remediation organic compounds in the aqueous phase. Via the aqueous phase, sorbed and residual organics can be rapidly biotransformed. The separate phase cannot be directly treated because of compound toxicity, and major accumulations of free product must be removed [Thomas and Ward, 1989; Alvarez-Cohen, 1993a]. Many halogenated organic compounds were previously thought to be non-biodegradable, but new laboratory studies continue to demonstrate the biodegradability of these compounds by mixed or pure cultures and to elucidate the metabolic pathways. While site data may suggest in-situ biodegradation, it may be difficult to prove because of site conditions and competing mechanisms [Madsen, 1991; Alvarez-Cohen, 1993a].

Treatability studies are required to assess the viability of biostimulation, nutrient demands, ability of culture to degrade a targeted compound, and other factors such as pH, redox potential, moisture conditions, compound toxicity, and temperature effects. Site characterization is required and hydraulic gradient control is necessary to effectively deliver nutrients. Hydraulic conductivities should be above 10^{-4} cm/s [Thomas and Ward, 1989]. Soil heterogeneities will greatly affect the ability to implement in-situ biodegradation, and even under the most favorable conditions, total cleanup may not be attainable [Ellison, 1992].

Depending on the environmental conditions and the exact compound and its metabolic pathway, the intermediate or end products exuded by the anaerobic consortia may be recalcitrant, toxic, or undesirable. For example, vinyl chloride is a byproduct which poses a greater human health hazard than the parent compound [Vogel et al., 1987], while formation of chloroform is undesirable from a water quality standpoint [Semprini et al., 1992]. This issue may preclude anaerobic processes from being implemented at certain sites, and it is one of the reasons why much attention has been devoted to aerobic processes. Another aspect to consider is the condition of the aquifer after remediation: it will be anaerobic and possibly very reduced and characterized by relatively high concentrations of Fe, Mn, H_2S , and CH_4 .

Cost and Availability--

In-situ anaerobic biodegradation is naturally occurring. Field studies have been conducted, but no full-scale applications exist. Much remains unknown about the anaerobic mineralization of halogenated hydrocarbons in-situ. At this time, full-scale application of anaerobic biodegradation is generally discouraged because of the formation of potentially toxic end products. However, the hardware is available for full-scale applications.

The cost of anaerobic biodegradation is comparable to that of aerobic processes (\$15-60/yd³ [Ellison, 1992]). Ex-situ hardware may include such items as nutrient feedstocks, air strippers, and granular activated carbon.

3.3 ELECTROLYTIC PROCESSES

Introduction--

In-situ electrolytic processes use applied electric fields to enhance organic contaminant removal. The effectiveness of these processes in soils is controlled by coupled flow phenomena [Mitchell, 1976, 1991; van Olphen, 1977; Mitchell and Yeung, 1990; Yeung 1990]. In most cases, the flow results from the presence of fluid, heat, electrical, and chemical flow potentials; or any of these potentials may be created even though only one driving force is applied [Mitchell, 1991]. These relationships are shown in Table 3.3.1. The electrolytic processes reviewed in this chapter include electro-osmosis (section 3.3.1), and electroacoustic soil decontamination (section 3.3.2) which employs both electrical and acoustical fields to enhance contaminant treatment.

TABLE 3.3.1 DIRECT AND COUPLED FLOW PHENOMENA OCCURRING IN THE SUBSURFACE
[Mitchell, 1991]

Flow J	Gradient X			
	Hydraulic Head	Temperature	Electrical	Chemical
Fluid	Hydraulic conduction: Darcy's law	Thermo-osmosis	Electro-osmosis	Chemical-osmosis
Heat	Isothermal heat transfer	Thermal conduction. Fourier's law	Peltier effect	Dufour effect
Current	Streaming current	Thermo-electricity. Seebeck effect	Electrical conduction. Ohm's law	Diffusion and membrane potentials
Ion	Streaming current	Thermal diffusion of electrolyte Soret effect	Electrophoresis	Diffusion Fick's law

Electro-osmotically and chemico-osmotically driven fluid flows dominate transport in saturated, fine grained soils having hydraulic conductivities less than approximately 10^{-9} m/s [Mitchell, 1991] because the electrical conductivity of a soil is independent of soil particle size and pore size, whereas the hydraulic conductivity is related to particle size [Casagrande, 1952; Mitchell, 1976, 1991; Shapiro and Probstein, 1993]. Also, in clays a portion of the relatively large surplus of cations, which are required to balance the net negative charge of the clay particle surfaces, can be mobilized under applied electrical gradients to produce hydraulic flow that would not otherwise be possible by hydraulic means alone [Mitchell, 1976].

In general, electrolytic methods attempt to mobilize ionic species, namely dissolved heavy metals, radionuclides, and charged organic compounds towards their respective electrodes by applying potential (electrical and acoustical) fields. Recovery of contaminants including neutral compounds transported by advection occurs at the electrodes. Dissolved contaminants are pumped to the surface for above-ground treatment. However, DNAPLs will not be appreciably mobilized by electrolytic methods because of their uncharged, non-polar attributes.

Subsurface structures and objects [Lageman et al., 1989] and electrode corrosion [Segall and Bruell, 1992; Shapiro and Probstein, 1993] are among the factors that will interfere with the electrolytic process. If not properly applied, electrolytic processes may also cause cracking and fabric changes in the porous media [Mitchell, 1991].

3.3.1 Electro-Osmosis (EO)

Theoretical Background--

Electro-osmosis uses current flow and electric potential gradients to enhance organic contaminant removal. The primary mechanisms are: ionic migration of charged species (cations, anions) resulting from the applied electrical potential [Casagrande, 1952]; and advection of neutrally charged species in the direction of the bulk diffusive flow of the major ions, usually cations [Mitchell, 1991]. Other phenomena that may contribute to overall contaminant removal when an electric field is applied to a wet soil mass include: development of osmotic and pH gradients, desiccation of soils due to heat generation at the electrodes, precipitation, electrolysis, hydrolysis, oxidation, reduction, adsorption, and soil fabric changes [Mitchell and Yeung, 1990].

The electrostatic distribution of ions in the vicinity of a negatively charged clay particle surface is schematically shown in Figure 3.3.1.1. When an external electric field is applied, both cations and anions "drag" water with them toward the cathode and anode, respectively. However, the net bulk fluid flow is in the direction of the cathode owing to the abundance of cations, as shown in Figure 3.3.1.2.

Several factors will affect contaminant removal. While the electrical and hydraulic gradients may be held constant during electro-osmosis, chemical gradients evolve from migration of cations and anions [Mitchell and Yeung, 1990]. Chemical gradients acting counter-current to the bulk flow direction will retard contaminant removal. Depending on the applied electrical potential and current flow, joule resistance heating of the porous media may also result [Shapiro and Probstein, 1993; Smith and Hinchee, 1993]. Additionally, hydrolysis of water at the electrodes causes the pH to rise at the cathode and decrease at the anode [Mitchell and Yeung, 1990]. In the initial stages of the process, the pH at the anode and cathode can approach 2 and 12, respectively. This may result in the propagation of an acid front towards the cathode [Shapiro et al. 1989a,b; Hamed et al., 1991; USEPA, 1992d]. The rate of advance of this front will be affected by the buffer capacity of the soil [Acar, 1992] and the pH variations may initiate ionization or valence changes of organic compounds which can affect their removal [Shapiro et al., 1989b]. Alkaline conditions occurring near the cathode can desorb organics, pesticides, and heavy metals from the solid surfaces, thereby enhancing their removal [Segall et al., 1980].

Field Implementation--

A schematic of an in-situ environmental application of electroosmosis is shown in Figure 3.3.1.3. Ions migrate to the respective electrodes in response to the applied electrical field. Recovery of contaminants occurs at the electrodes, and the dissolved contaminants are pumped to the surface for above-ground treatment. Electrode placement strategy depends on the nature and extent of contamination, soil heterogeneities, flow resistance, and response of the electrical potential field to subsurface features. The site must be thoroughly characterized and bench studies are required. The strategy of electroosmosis is in many ways analogous to pump-and-treat, but using current, voltage, and electrical gradients as major design variables.

Electrodes can be placed in conventional injection and extraction wells [Banerjee, 1993]. Electrodes are usually fabricated of a metal such as iron [Mitchell, 1991; Segall and Bruell, 1992; Banerjee, 1993] or graphite [Segall and Bruell, 1992]. Graphite electrodes have non-wetting surfaces which offer greater corrosion resistance, reduce hydrogen gas formation, and can be constructed to facilitate fluid injection, extraction, or recycling [Segall and Bruell, 1992]. To keep the clay saturated in order to mitigate consolidation effects, water or purge solutions containing salts, surfactants, or chelating agents are usually injected at the anode [Acar, 1992].

Dewatering applications can have electrode spacings on the order of 30 ft. In contaminant recovery applications, electrode spacings are usually on the order of 3 to 15 feet depending on the soil type and

applied current. Applied DC potentials on the order of 25-500 volts are typical.

Level of Demonstration and Performance--

Geotechnical applications of electro-osmosis for purposes of clay dewatering and enhancing rates of clay consolidation, and for general site and soil improvement are well known and date back to the 1930's [Casagrande, 1952; Mitchell, 1991; Civil Engineering, 1992]. Environmental applications of electro-osmosis are relatively new and have mostly addressed recovery and treatment of heavy metals and radionuclides [Lageman, 1989]. Muralidhara et al. (1990) provide a brief summary of several electro-osmotic applications. Only laboratory studies have addressed the removal of dissolved organics, including TCE.

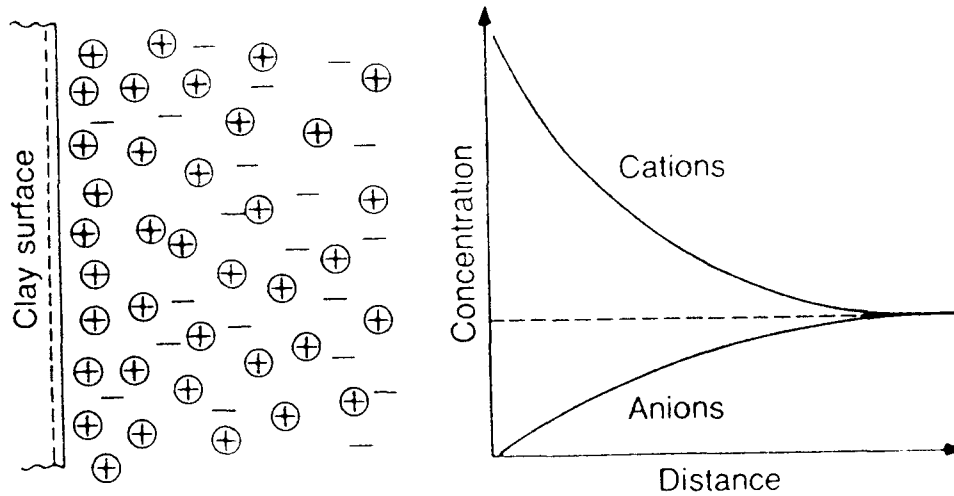


Figure 3.3.1.1 Ion distribution adjacent to clay particle surface [Mitchell, 1991]

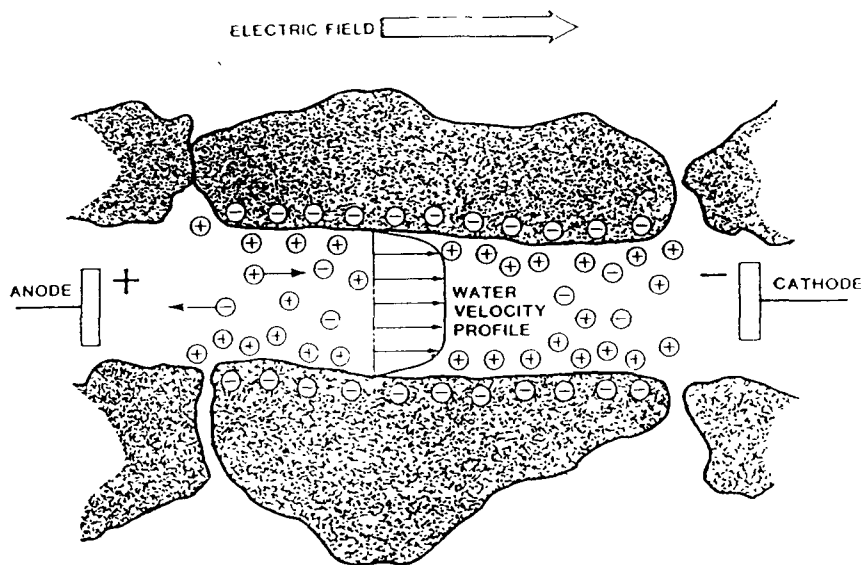


Figure 3.3.1.2 Schematic of electro-osmotic flow resulting from an applied electric field in a charged porous medium [Shapiro et al., 1989b].

In 1986, electro-osmosis was implemented at a former chrome-plating facility in Corvallis, Oregon [Civil Engineering, 1992; Banerjee, 1993]. The subsurface soils consisted mostly of clays and clayey silts, and the water table was located at a depth of 10 ft. Seven electrodes (iron reinforcing bars) were installed in monitoring wells to a depth of 20-22 ft. The seven spot well configuration was used with the anode located in the center of the test cell. The spacing between the central well and perimeter wells was 5 ft. The applied current was on the order of 5-10 amps. Hexavalent chrome and other metals were recovered in the central well. In this test, ground-water concentrations of chrome were reduced from 1,000 mg/l to 35 mg/l [Civil Engineering, 1992].

Most environmental applications of electro-osmosis have been conducted abroad, principally by Geokinetics, Inc., in Europe. Two field tests and one commercial application have been completed [Lageman et al., 1989; Civil Engineering, 1992]. One field experiment [Lageman et al., 1989] was conducted in sandy, clayey soils located near the ground surface (1 m depth) having soil concentrations of zinc of 7,101 ppm (max.) and 2,410 ppm (ave.). After approximately 8 weeks (including some downtime) using an energy supply of approximately 160 kW/ton, the zinc concentrations were reduced to 5,300 ppm (max.) and 1,620 ppm (ave.). Another field experiment was conducted in sediments (peat and fines) located in a drainage ditch which had soil concentrations of copper and lead as high as 5,000 and 10,000 ppm, respectively [Lageman et al., 1989]. In the commercial application, approximately 340 tons of arsenic contaminated clayey soils were treated [Lageman et al., 1989]. Arsenic concentrations were reduced from 110 ppm to 30 ppm in approximately 10 weeks [Lageman et al., 1989; Civil Engineering, 1992].

Electro-osmosis is currently being evaluated as part of the USEPA SITE Program for the removal of tetraethyl lead from clayey soils at a former refinery [Acar, 1992; USEPA, 1992d]. Soil concentrations of lead as high as 100,000 ppm have been measured. For perspective, the drinking water standard is 5 ppm, and the SITE cleanup goal is approximately 500 ppm [Acar, 1992]. The 10 x 25 ft test cell is shown in Figure 3.3.1.4. At this time, soil is being treated to a depth of 3 ft. A central anode array consisting of 7 anodes at 2.5 ft spacings is surrounded by 24 cathodes. Two rows of 11 cathodes are aligned parallel to the anode array. As of fall 1992, initial results indicated that electro-osmosis was unsuccessful and the test program was temporarily suspended [Civil Engineering, 1992]. Enhancement schemes are currently being investigated.

Soluble (and polar) organic compounds such as acetic acid and phenol have been successfully removed from clay soils in laboratory samples [Shapiro et al., 1989b]. More than 94% of dissolved acetic acid (0.5 mole/l) and phenol (450 ppm) were recovered from kaolinitic soils [Shapiro and Probst, 1993]. Ongoing bench studies are examining the viability of electro-osmotically enhanced removal of BTEX, TCE and other non-polar organic compounds [Bruell et al., 1992; Acar, 1992; Marks et al., 1992; Segall and Bruell, 1992]. In one kaolinite soil column study, 25 wt% of TCE (150 ppm) was removed within 5 days [Bruell et al., 1992].

Applicability/Limitations--

Electro-osmosis pertains mostly to the removal of ionic species, namely dissolved heavy metals, radionuclides, and charged (valence bearing) organic compounds whose sign (if any) will depend on the ambient ground-water pH and the compound's pKa. Therefore, it may have applicability to such compounds as pentachlorophenol. The ability of electro-osmosis to recover dissolved organic compounds is dependent on their sorption properties and solubility [Bruell et al., 1992]. It remains to be seen if DNAPLs can be mobilized by electro-osmosis [Mitchell, 1991]. Electro-osmosis is best applied in fine grained soils having active and plastic clays and low void ratios [Mitchell, 1991]. In soils with high concentrations of electrolytes, the soil zeta potential may drop to zero thereby ceasing electro-osmotic flow; or, if the zeta potential is negative, double layer charge reversal may result in electro-osmotic flow to the cathode [Casagrande, 1952]. Subsurface structures like utilities and other objects such as drums and scrap metals will interfere with the electro-osmotic process [Lageman et al., 1989].

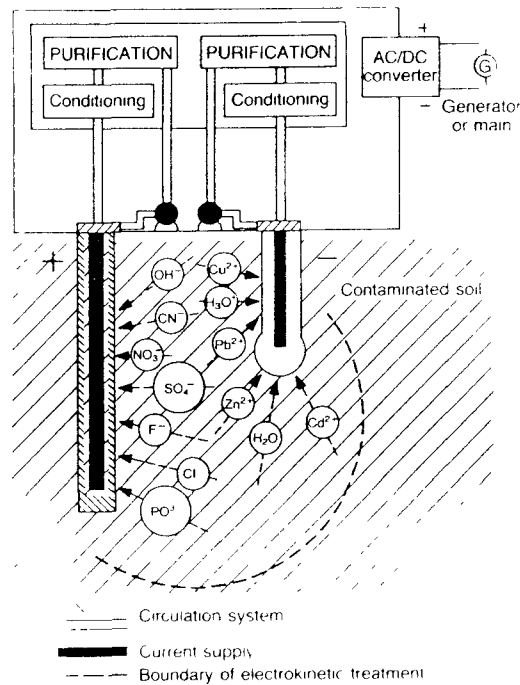


Figure 3.3.1.3 Schematic of an in-situ electro-osmotic extraction system [Lageman, 1989].

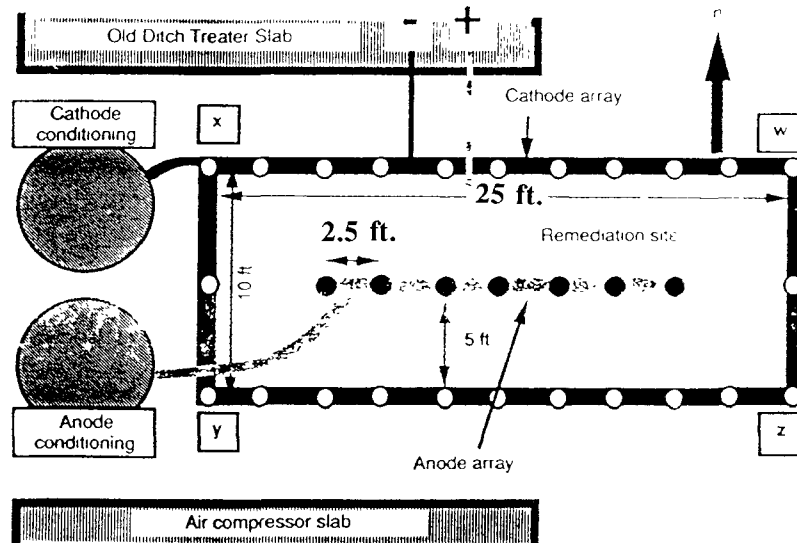


Figure 3.3.1.4 Schematic layout of electrode arrays for the in-situ electrokinetic application at Baton Rouge field test site [Acar, 1992].

Desaturation, thermal drying and pore chemistry changes may result in cracking of the clay soils [Mitchell, 1991]. Corrosion of the electrodes may affect the efficiency of electro-osmosis [Segall and Bruell, 1992; Shapiro and Probst, 1993]. Gases may be evolved at the electrodes depending on electrode composition, power input, and the prevailing electrochemical reactions taking place [Segall and Bruell, 1992]. Electrode corrosion can be mitigated by electrode type and composition (graphite vs. metal), and by cycling or injecting of fluids [Lageman, 1989; Mitchell, 1991; Acar, 1992; Segall and Bruell, 1992].

Cost and Availability--

This technology has been demonstrated on the full-scale in both geotechnical and environmental applications. Electro-osmosis equipment for geotechnical applications is readily available, and the design criteria are well established [Casagrande, 1952]. Geokinetics holds the European patent for in-situ electro-osmosis for electrokinetic remediation. Probst et al. (1991) have been awarded U.S. Patent (5,074,986) for "Electro-osmosis Techniques for Removing Hazardous Materials from Soil." Another U.S. patent (5,137,608) entitled "Electrochemical Decontamination of Soils and Slurries" has been awarded to Louisiana State University [Acar, 1993].

However, no known full-scale applications of electro-osmosis pertaining specifically to DNAPLs in the saturated zone are known to exist. Electro-osmosis is generally not a good candidate for DNAPL cleanup because DNAPLs are generally nonpolar, making them generally unsusceptible to electrical fields. Furthermore, electro-osmosis is best applied in saturated fine (clay) soils where major quantities of DNAPL are usually not found.

Electro-osmosis costs are dependent on initial contaminant concentration, energy supply and time duration. For low energy delivery over long periods (months), the total treatment can be as low as \$50/ton which can increase up to \$400/ton for short (weeks) energy intensive applications [Lageman, 1989]. Of the total cost, the electric power costs are typically in the range of \$2-20/ton of remediated fine grained soils [Marks et al., 1992; Shapiro and Probst, 1993].

3.3.2 Electroacoustic Soil Decontamination (ESD)

Theoretical Background--

Electroacoustic Soil Decontamination (ESD) employs both electrical and acoustical (pressure) gradients to enhance organic contaminant removal. The electrically-induced phenomena and removal mechanisms are identical to electro-osmosis (see section 3.3.1). It may be convenient to think of this technology as a hybrid of electro-osmosis and radio frequency heating (section 3.7.3), except that the lower applied frequencies (usually 100-1000 Hz) do not result in appreciable soil heating; but they do enhance fluid flow through the porous media. The primary removal mechanisms and phenomena derived from acoustical fields which are believed to contribute to overall contaminant removal include: orthokinetic forces, Bernoulli's forces, rectified diffusion, "rectified" Stoke's forces, decreased apparent viscosity and radiation pressure [Muralidhara et al., 1990]. Since the elements of electroosmosis have been discussed previously, attention will be given here to the prevailing acoustical phenomena.

Acoustic fields generate fluctuating (sinusoidal) pressure waves which vary as a function of time and position [Muralidhara et al., 1990]. Buried acoustical sources will produce mainly compression and shear waves and negligible surface waves [Muralidhara et al., 1990]. Wave intensity decreases with the inverse of distance squared, while soil attenuation of waves increases with the square of frequency. Travelling waves impart mechanical energy to particles in the form of velocity. Particle velocities are seen to be a function of applied frequency, and are related to the acoustic pressure through the acoustical impedance of the porous medium [Muralidhara et al., 1990]. Which of the previously mentioned removal mechanisms and phenomena will prevail in-situ is in large part governed by the physical and chemical properties of the porous medium. Since the process is neither fully understood [USEPA, 1992d] nor

accurately predictable (a priori) [Muralidhara et al., 1990], the approach is empirically based.

The following descriptions of the contributing phenomena have been summarized from Hinchee et al. (1989) and Muralidhara et al. (1990). Orthokinetic and Bernoulli's forces refer to the forces that cause small and large particles to agglomerate, respectively. Cavitation of pore fluids and gas bubble generation within soil particle capillaries with the resultant expulsion of trapped pore fluids from minipores and macropores aid in dewatering, this is referred to as rectified diffusion. Decreased apparent viscosities are thought to arise from the high strain rates and localized heating. The nonlinear spatial variation in fluid viscosity, which aids in transport to the source, is referred to as the rectified Stoke's force. Radiation pressure, a static pressure, is a second order effect which adds to the normal pressure differential.

Of the acoustically induced phenomena, particle rearrangement and viscosity reduction are believed to be among the major factors contributing to the contaminant removal. Ex-situ applications of electrical and acoustic fields to dewatering of sludges and soils has indicated that the dewatering effects are synergistic [Hinchee et al., 1989]. It has been postulated [Hinchee et al., 1989; Muralidhara et al., 1990] that the rearrangement of particles creates new flow channels which enhance fluid flow and, therefore, electro-osmosis.

Field Implementation--

A conceptual layout for a vadose zone application of ESD is shown in Figure 3.3.2.1. Since this technology is still under development, details on the construction and configuration of the requisite acoustic sources are not available. However, an acoustical electrode or array is likely to be similar in certain respects to the radio frequency devices (section 3.7.3). The electro-osmotic elements and their implementation have been previously described (section 3.3.1), and the strategy for laying out the electrodes for ESD is essentially analogous to that of electro-osmosis.

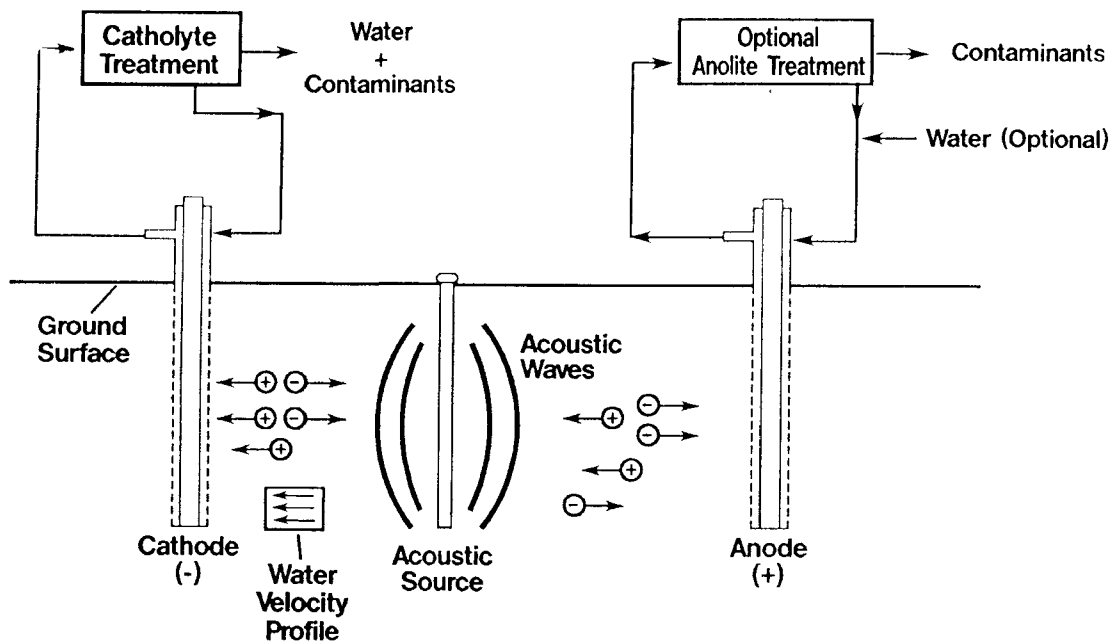


Figure 3.3.2.1 Conceptual layout of the electroacoustical soil decontamination process [USEPA, 1992d].

Level of Demonstration and Performance--

To date, ESD has not been implemented in the field. Bench scale results indicate that metals (zinc, cadmium) were removed more effectively than decane (a non-polar organic compound) [Hinchee et al., 1989; Muralidhara et al., 1990]. The soils tested were classified as clay loam, silty and sandy clays, and clay. The clays were slightly acidic (pH= 5.5) and had organic matter contents of 1.85 wt%. Samples had a diameter of 3.5 in and length dimensions of 2 to 8 in depending on the test. On a dry soil basis, samples were uniformly spiked with either 2,000 ppm zinc, 11,000 ppm zinc, 1,000 ppm cadmium, or 8 wt% decane.

In the zinc removal experiments, the soil moisture contents were on the order of 42 wt%. Constant currents of 50 amps were applied, and the voltage drop across the 4.5 in long samples increased from 0.3 to 20 V/in during the test. Electrical energy consumption was 1.423 watts, and no acoustics were applied. In 100 hours of operation, more than 90 wt% of the zinc was removed from three-quarters of the sample. Precipitation of zinc hydroxide was detected near the cathode. Zinc removal efficiencies were found to increase with longer test durations and elevated power levels. Similar results were obtained for cadmium removal.

The decane spiked soil samples were 2.5 in long and had approximate weight proportions as follows: solids, 52.7%; water, 39.3%; decane, 8%. Four tests were completed with average applied currents of 0.11 amps, with voltage drops ranging from 25 to 45 V/in. Of these four samples, acoustic energy was applied to only one sample at 400 Hz and 0.697 watts. The test duration was 2 hours. Decane removal was estimated to be between 10-25 wt%. However, the positive effect of the acoustical field on decane removal could not be confirmed owing to data discrepancies between the two analytical laboratories [Muralidhara et al., 1990]. Deoiling of petroleum sludges and removal of jet fuel from sandy soils are reported to have been successful with electroacoustics [Hinchee et al., 1989]. However, the exact contribution of acoustics above and beyond that of simple electro-osmosis was not reported.

Applicability/Limitations--

Essentially the same as electro-osmosis.

Cost and Availability--

This technology has been demonstrated on the lab scale only. No field- or full-scale applications of any kind have been attempted. The technology is currently under development by Battelle Memorial Institute as part of the USEPA SITE Emerging Technology Program [USEPA, 1992d]. The process has been patented by Battelle Memorial Institute [USEPA, 1992d].

Electroacoustics does not appear to be a good candidate for DNAPL cleanup because DNAPLs are usually nonpolar making them relatively unsusceptible to electrical fields. Furthermore, electroacoustics is best applied in saturated (fine) soils where major quantities of DNAPL are usually not found.

The cost is similar to electro-osmosis, plus acoustical hardware and incremental energy cost. ESD should be comparable to RF heating coupled with soil venting (i.e., \$40-100/ton) [Muralidhara et al., 1990].

3.4 CONTAINMENT AND GROUND MODIFICATION

Introduction--

Containment systems and ground modification methods are used to contain and immobilize dissolved contaminants and, in certain cases, DNAPLs. Containment systems are usually placed on the periphery of the contaminated area or along specified boundaries so that the encompassed area becomes effectively isolated from its surroundings, thereby preventing further spreading. Impermeable barriers and ground-water injection/extraction systems are examples of containment systems. The ground modification methods are usually confined to DNAPL source areas, and aim to immobilize or neutralize the contaminants. Stabilization/solidification (S/S), vitrification, permeable treatment walls, and variations of these methods are examples of ground modification. Containment and ground modification can be either passive or active, the distinction being made on the required energy expenditure after installation.

Impermeable barriers constructed of soil-bentonite (SB) slurry walls, composite geomembrane-slurry walls, grout curtains, and sealable joint (sheetpile) cut-off walls are the focus of section 3.4.1. The primary issues related to these systems are cost, durability, compatibility, and constructibility [Elsevier Science, 1989; ASCE, 1990; ASTM, 1990a,b]. These are passive systems which rely on low hydraulic conductivity to inhibit contaminant migration [Mitchell and van Court, 1992]. Active ground-water extraction and recharge systems are also briefly evaluated in section 3.4.1.

Stabilization/solidification (S/S) by in-situ soil mixing is addressed in section 3.4.2. Immobilization of contaminants is achieved by neutralization, precipitation, sorption, and physical encapsulation of the contaminants within a solidified soil matrix. In the broadest sense, many treatment technologies can be considered as stabilization technologies [USEPA, 1986b]. In-situ vitrification (ISV) is a good example of a technology which achieves both stabilization and solidification, but has been placed in section 3.7 because solidification and stabilization are attained by heat application. The major issues surrounding in-situ S/S are chemical compatibility, and the durability and leachability of the treated soil mass.

In-situ permeable treatment walls (section 3.4.3) are granular backfill walls which provide treatment of dissolved contaminants but no containment or immobilization. The composition of the porous backfill (additives, surface coatings, etc.,) can promote favorable conditions for in-situ biodegradation, precipitation, and chemical oxidation or reduction. The major issues regarding in-situ permeable treatment walls pertain to changes in ground-water flow direction, clogging, long-term performance, and incomplete treatment of wastes.

Isolation and containment systems and in-situ S/S are commercially available and have been successfully demonstrated on the full scale. In-situ permeable treatment walls are being tested on the pilot scale. All of these technologies except hydraulic controls constitute permanent structures.

3.4.1 Isolation and Containment

Theoretical Background--

Passive systems such as impermeable barriers and active systems such as hydraulic controls are commonly used to attain dissolved plume or contaminant source area isolation and containment. Grout curtains, geomembranes, in-situ soil mixed zones, and clay slurry walls, caps, and liners are impermeable barriers which rely on low hydraulic conductivity to inhibit contaminant migration [Mitchell and van Court, 1992]. Ground-water extraction and recharge via arrays of wells and trenches facilitate hydraulic gradient control, create capture zones, and permit redirection of local ground-water flow [Mercer and Cohen, 1990; Mitchell and van Court, 1992]. The focus here is on slurry walls, grouting, sealable joint cut-off walls, and hydraulic controls. In-situ soil mixing is described in the next section (3.4.2), owing to its similarity to in-situ stabilization/solidification.

Slurry walls can be constructed of clay (usually bentonite), cement, pozzolans (polymers, resins, asphaltic emulsions), and native soils [McFarlane and Holtz, 1992]. The lower cost and hydraulic conductivity, and greater plasticity and chemical resistance of soil-bentonite (SB) slurry walls usually make them preferred over cement-bentonite (CB) walls [D'Appolonia, 1980; Ryan, 1980, 1987]. Plastic concrete and concrete cut-off walls can also be used [Evans et al., 1987; ASTM, 1992]. During the construction of a slurry wall, a filter cake develops on the walls of the trench. The filter cake also serves to reduce the hydraulic conductivity. Experience has shown that the lowest filter cake permeabilities are attained when the slurry mixture contains approximately 5-7 wt% bentonite, producing slurry viscosities greater than 40 sec-Marsh [D'Appolonia, 1980]. The hydraulic conductivity of the SB backfill decreases with increasing fraction of fines appearing in the backfill material and the final percentage of bentonite in the SB wall, as shown in Figure 3.4.1.1. Since the initial composition of the backfill becomes relatively unimportant at bentonite contents greater than 2 wt%, this minimum limit is often recommended or used [D'Appolonia, 1980; Millet et al., 1992; Mitchell and van Court 1992]. In order to decrease the hydraulic conductivity, composite slurry walls have been designed incorporating inclusions such as concrete panels, sheetpiles, and, most recently, geomembranes into the traditional SB cut-off walls [Ryan, 1987; Hayward Baker, 1991; ASTM, 1992]. Design criteria for the use of geosynthetics [Koerner, 1990], and clay cap and liner systems [ASCE, 1990; Goldman et al., 1990] are readily available.

Penetration and jet grouting are the two main grouting techniques for construction of grout curtains [Mitchell, 1981; Ryan, 1987; Mitchell and van Court, 1992]. Penetration (pressure) grouting entails the pressure injection of particulate or fluid slurries to fill interparticle voids and fissures. Jet grouting uses high pressure nozzle injection to destroy the soil fabric thereby mixing the soil and slurry in-situ. Grout design parameters are usually water/solids ratio, viscosity, bleed, and permeability [Weaver et al., 1992]. Penetration grouting hole spacings are usually on the order of 1.3 to 2.5 m. Jet-grouted soil column diameter can be on the order of 0.3 to 1.5 m [Gazaway and Jasperse, 1992; Mitchell and van Court, 1992], and the spacing of the columns is somewhat less to provide for overlap of adjacent soil columns. Overlapping patterns using at least two to three grout injection rows are often used to ensure continuity of the grout barrier as shown in Figure 3.4.1.2 [Gazaway and Jasperse, 1992; Mitchell and van Court, 1992], but in some instances this convention has been waived [Weaver et al., 1992]. Hydraulic conductivities of grouted soil samples can be on the order of 10^{-5} - 10^{-8} cm/s depending on the grouting method and media type [Gazaway and Jasperse, 1992; Weaver et al., 1992].

Sealable joint sheetpile cut-off wall systems have been recently proposed [Starr et al., 1991; Starr and Cherry, 1992]. To reduce leakage through sheetpile joints, the joints are sealed using bentonite slurry or proprietary polymers which lower the overall hydraulic conductivity of the wall. However, because sheetpiles are installed by driving, this technology may cause cracking and damage to aquitards such as stiff clay soils.

Active ground-water controls are often used in conjunction with impermeable barriers to minimize the potential for advective transport of contaminants across the impermeable barrier, as shown in Figure 3.4.1.3. Judicious well pumping may be used to alter the flow direction of plumes. Depending on the quantity of DNAPL and the overall remedial strategy, more aggressive ground-water pumping approaches may be practiced (see section 3.5.4). However, the cost of pumping and water treatment in absence of cut-offs can be very high.

Field Implementation--

The configuration of the containment barrier is dictated by such factors as the overall remediation strategy, cost, site limitations, liability reduction, preservation of uncontaminated or drinking water supplies, and the ability to contain the contaminant by other means. Two approaches are commonly used: (1) the DNAPL source areas and dissolved plumes are completely encompassed with a continuous barrier, or (2) the dissolved plume migration is locally arrested or stalled using discrete barrier sections. Vertical barriers

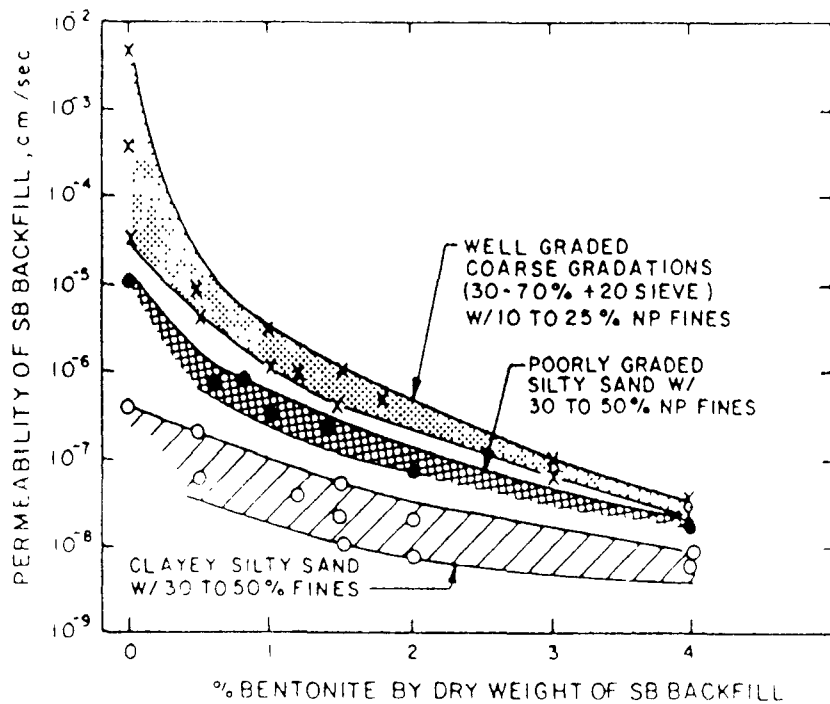


Figure 3.4.1.1 Relationship between the permeability and bentonite content of SB backfill materials [D'Appolonia, 1980].

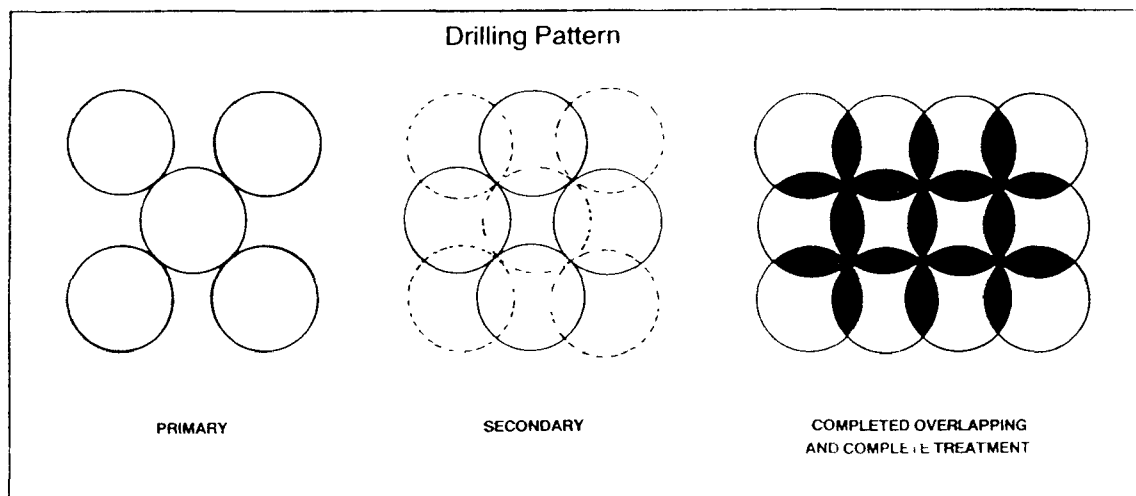


Figure 3.4.1.2 Primary and secondary overlapping patterns for in-situ soil mixing processes [Geo-Con, Inc., 1990].

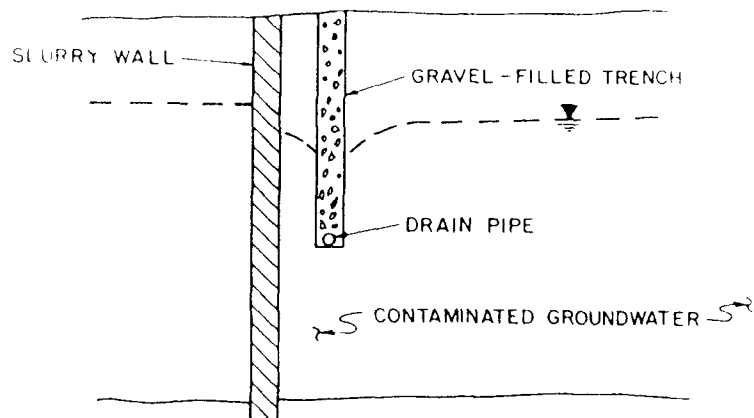


Figure 3.4.1.3 Schematic configuration of a coupled impervious barrier and hydraulic gradient control system. Groundwater flow across barrier is maintained into contaminated groundwater region [Ryan, 1987].

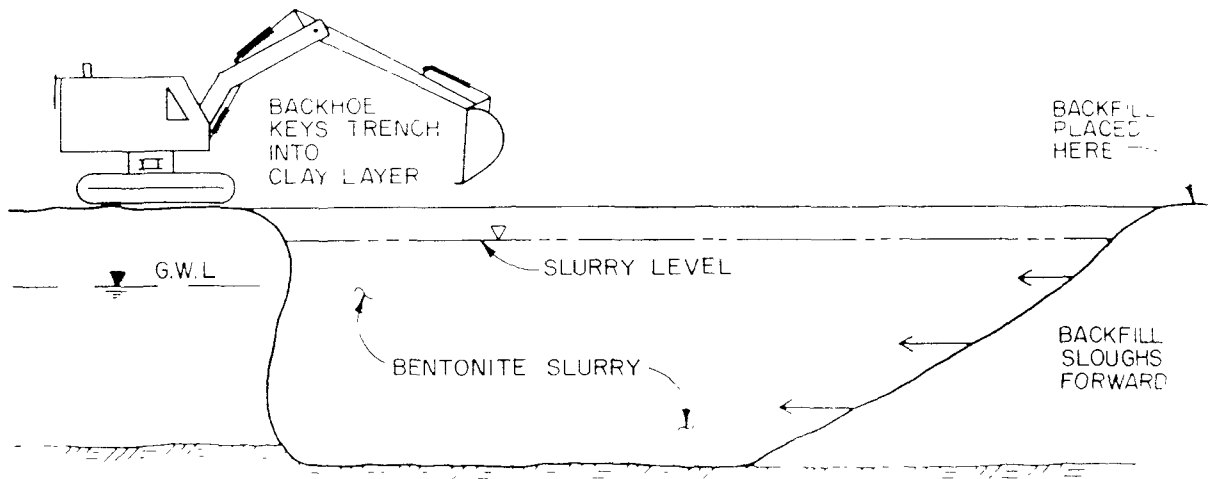


Figure 3.4.1.4 Schematic of SB slurry wall installation process [Ryan, 1980].

are usually grouted into underlying aquitards or bedrock. Detailed descriptions of slurry wall installation and grouting technology are available in a number of publications [D'Appolonia, 1980; Mitchell, 1981; Ryan 1987; ASCE, 1992; ASTM, 1992].

Figure 3.4.1.4 illustrates slurry wall installation using the trench method. Trenches are typically 2-3 ft wide, and trenches more than 100 ft deep and 1,000 ft long have remained stable and open for several weeks between excavation and backfilling [D'Appolonia, 1980]. Construction to depths of 400 ft have been reported [Ressi di Cervia, 1992], and materials such as weathered shales and conglomerates, sands, gravels, clay, and tills have been used successfully as backfill materials in geotechnical practice [D'Appolonia, 1980]. Well mixed SB backfills having a slump of 2-6 in and a minimum viscosity of 40 sec-Marsh are considered as ideal for placement [D'Appolonia, 1980; Ryan, 1987]. To ensure that the SB backfill efficiently displaces the slurry from the trench, its unit weight should be at least 15 lb/ft² greater than that of the slurry [D'Appolonia, 1980; Ryan, 1980, 1987].

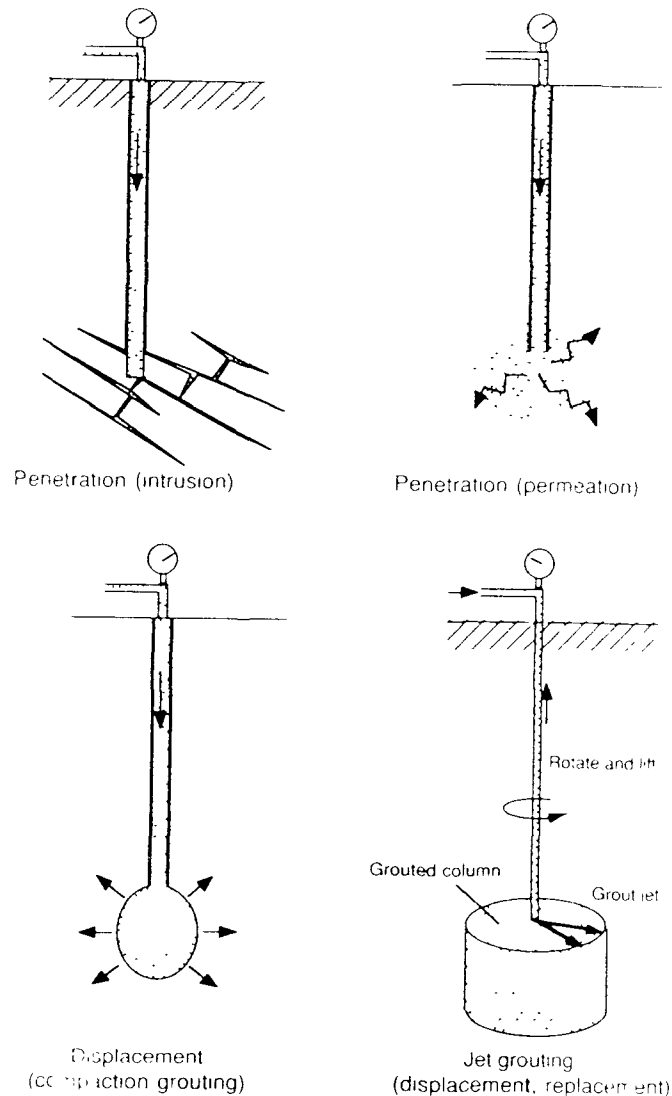


Figure 3.4.1.5 Schematic showing different grouting techniques [Hausmann, 1990].

Figure 3.4.1.5 depicts the penetration and jet grouting installation methods. Penetration grouting can be accomplished within the entire soil horizon by packing off lower sections after grouting. A jet grouted soil column is created as the rotating nozzle injector is removed from the hole. Jet grouting can also be facilitated in panel sections using directional injection [Mitchell and van Court, 1992]. Available grouting materials include particulate grouts (clay, lime, fly ash, microfine cement) and chemical grouts (bitumen, phenolic and acrylic resins, silicates) [Hausmann, 1990; Mitchell and van Court, 1992]. Grout selection is affected by such factors as the hydraulic conductivity of the porous media, cost, permanency, and compatibility [Hausmann, 1990]. Penetration grouting is quite generic and flexible and it can handle a variety of conditions. Typical parameters for jet grouting include: nozzle diameters of 1.8-2.2 mm diameter; injection pressures up to 6,000 psi; and injector rotation rates and lift rates of 1-2 rpm and 1-1.5 ft/min, respectively [Gazaway and Jasperse, 1992].

Level of Demonstration and Performance--

Slurry walls have a long history of use. One recent application features the installation of an approximately 3 km long composite high density polyethylene (HDPE) SB slurry wall at an industrial facility in Liguria, Italy [Manassero and Viola, 1992]. The contaminants were unspecified. The subsurface soils at this site were characterized by 3 to 15 m high permeability sands and gravels underlain by marl. Depth to ground-water at the site was 1 to 8 m. The cross section through the composite wall is shown in Figure 3.4.1.6. The construction sequence entailed the initial installation of a 1.2 m thick provisional slurry wall to bedrock using the clamshell method. After the wall had set, a combination of bedrock drilling and clamshell excavation facilitated removal of the middle 0.5 m of the provisional slurry wall to an approximate depth of 2 m into bedrock. The excavated portions of the wall were kept open using a tremied CB mixture which also served as the final slurry wall. Prior to setting of the cement, 2.5 m wide geomembrane panels having tongue-and-groove connections with hydrolite seals were lowered using guides into the center of the final slurry wall. In-situ tests revealed that the hydraulic conductivities of the keyed areas and composite wall were on the order of 10^{-6} and 10^{-7} cm/s, respectively.

Grouting technology has also been used to handle complex subsurface conditions. Jet grouting was recently implemented at a chemical plant in Michigan with unspecified subsurface contamination [Gazaway and Jasperse, 1992]. The project entailed the construction of a jet-grouted cut-off wall through a utility corridor to join two existing slurry walls as shown in Figure 3.4.1.7. Numerous utilities ranging from diameters of 2 to 48 in appeared within the utility corridor up to depths of 17 ft. The jet-grouted wall with a design permeability of 1×10^{-6} cm/s was installed to a depth of 24 ft and was keyed into both existing slurry walls. Field tests indicated that soil columns with diameters of up to 4-5 ft (1.2-1.5 m) were possible, and a conservative spacing of 2 ft was adopted. Operating parameters included: injection pressures up to 6,000 psi and injector rotation rates and lift rates of 1 rpm and 1.3 ft/min, respectively. The rotation and lift rates were decreased near the larger utilities to ensure good mixing and void filling. In some cases the injection pressures were reduced as well. The 5,700 ft² wall was completed within 3.5 weeks with no detectable damage to the utilities and no stoppage in utility service.

Applicability/Limitations--

Slurry walls [ASTM, 1992] have been installed at sites with difficult and complex conditions [ASCE, 1992; ASTM, 1992; Davidson et al., 1992]. Impermeable barriers are generally used to isolate and contain dissolved phase contaminants. The actual remediation of pure and dissolved phase DNAPL requires other techniques. Hydraulic controls, on the other hand, may be utilized for containment and partial recovery of DNAPL.

The primary issues related to these systems are cost, durability, compatibility, and constructibility [Elsevier Science, 1989; ASCE, 1990; ASTM, 1990a,b]. Chemical compatibility and permanency of slurry walls and grouted barriers are major issues. Clay barriers are susceptible to cracking and leaking when exposed to concentrated solutions of acids, caustics, and non-polar organic compounds [Fernandez and Quigley, 1985; Mitchell and Madsen, 1987; Madsen and Mitchell, 1989; Quigley and Fernandez, 1992]. In general, clay barriers are not affected by dilute organic solutions, and the effects of inorganic solutions are consistent with their effects on clay particle double layers, surface and edge charges, and pH [Madsen and Mitchell, 1989]. While CB walls are more chemically resistant, they are prone to cracking because of their brittle nature. For these reasons, ductile CB walls have received recent attention [Evans et al., 1987; Millet et al., 1992]. Some of the same general trends are observed for grouts, but the actual response is contaminant and grout specific due to the many grout mixes and grout pozzolans available [Spooner et al., 1982, 1984; May et al., 1986; Bodosci et al., 1987]. Sulphate attack is one of the most common problems related to grouts [Jefferis, 1992].

Penetration grouting is best suited for sealing fissures in bedrock [Ryan, 1987]. However, May et al. (1986) indicate that the main disadvantage of penetration grouting is that the grout cannot be controlled

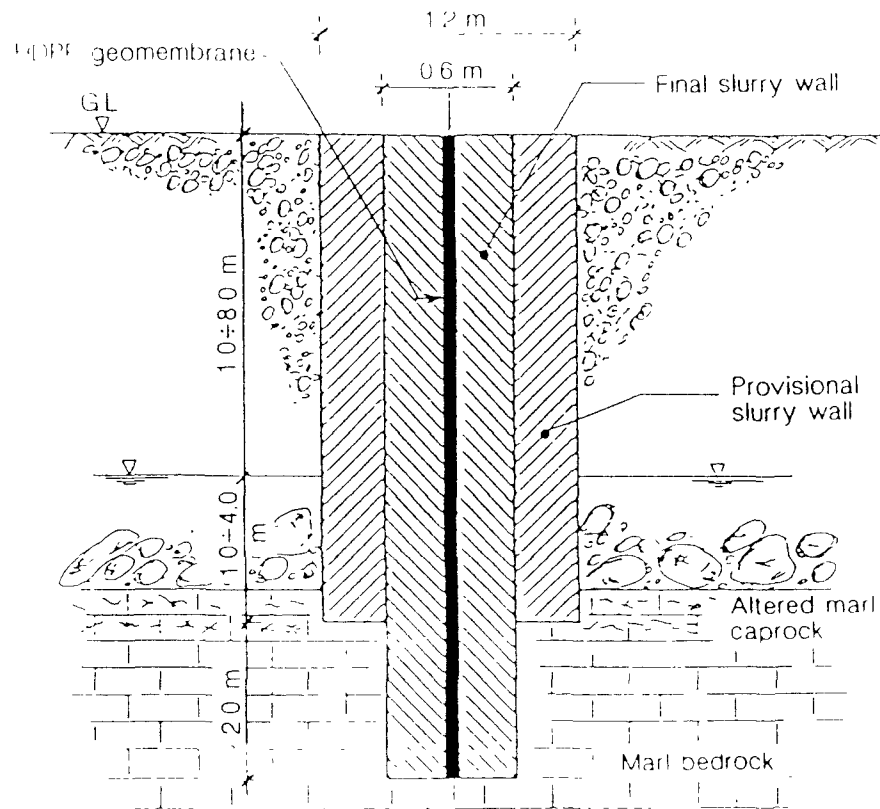


Figure 3.4.1.6 Vertical section taken through a composite geomembrane-SB slurry wall impervious barrier system, Liguria, Italy. [Manassero and Viola, 1992].

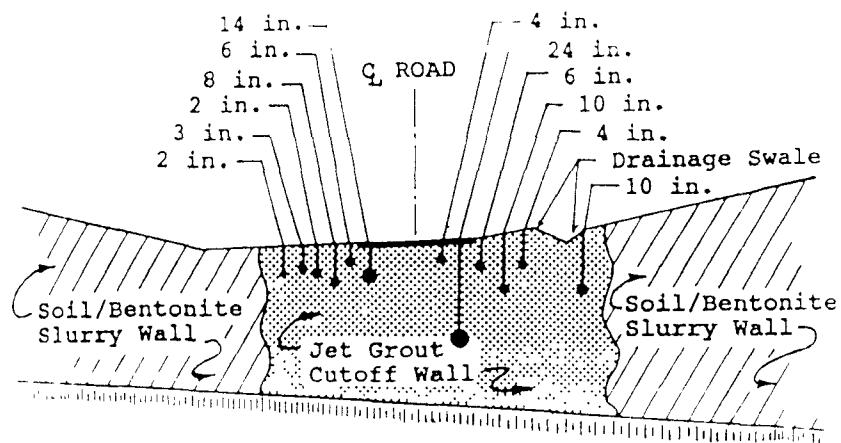


Figure 3.4.1.7 Vertical section taken through utility corridor in which jet grouted impervious barrier was constructed to join SB slurry walls [Gazaway and Jasperse, 1992].

to ensure a complete seal. Grout curtain continuity is difficult to verify, and this is among the reasons why slurry wall installation is favored [Ryan, 1987]. Similarly, poor slurry wall construction will result in the entrapment of pockets of slurry and other wall heterogeneities which may lead to increases in permeability. Composite slurry walls using synthetic panels as inclusions offer challenges regarding wall alignment. Placement of slurry walls is limited to areas without ground structures, buried utilities, other subsurface obstructions, and above bedrock. In such situations, the installation of jet-grouted impermeable barriers in utility corridors has been successful [Gazaway and Jasperse, 1992].

Cost and Availability--

Slurry wall technology has been commercially available for some time, and hundreds of slurry walls have been installed to depths [D'Appolonia, 1980; Ryan, 1987]. Depths of more than 30 m are common. The installation is typically provided by a specialty contractor. While grouting technology dates back centuries [Bowen, 1981] and there are numerous contractors providing this service, the applications in site remediation are relatively new. Slurry walls and grout curtains can be designed by qualified professionals.

If properly installed, impermeable barriers are usually good candidates for isolating the DNAPL source and for preventing the migration of dissolved contaminants. Grout curtains and slurry walls can be used heterogeneous soils; however, their effectiveness in fractured bedrock is limited.

Isolation and containment systems usually cost less than other remedial alternatives [Ryan, 1987; Ellison, 1992]. Backhoe slurry wall construction ranges from \$7-13/ft² and in-situ grouting (using drill rig) ranges from \$60-100/yd³ [Ellison, 1992].

3.4.2 Stabilization and Solidification

Theoretical Background--

Stabilization and solidification (S/S) methods are intended to immobilize dissolved contaminants and, in certain cases, DNAPLs. Stabilization refers to techniques that reduce contaminant hazard potential by converting the contaminants to less soluble, mobile, or toxic forms, which does not necessarily imply a change in physical nature and handling characteristics. Solidification refers to techniques that encapsulate the contaminant in a monolithic solid of high structural integrity [Conner, 1992]. These two ends may be achieved by a variety of means, and often occur simultaneously. S/S has been applied to a wide variety of wastes, including sludges, waste pits, liquids, lagoon sediments, and contaminated soils on an ex-situ and in-situ basis. Good reviews of S/S processes and technology are available [Tittlebaum et al., 1985; Cullinane et al., 1986; Wiles, 1987; USEPA, 1989a,b; Jones, 1990; Conner, 1992]; and, therefore, only a brief overview is given here.

S/S processes are distinguished by reagent type into inorganic and organic processes [Conner, 1992]. Organic systems (urea formaldehyde, polyethylene, bitumen, asphalt emulsions) attain S/S by thermoplastic encapsulation and by polymerization [USEPA, 1989b,c], and these processes pertain mostly to radioactive wastes [USEPA, 1989b; Conner, 1992]. Inorganic systems utilize a combination of cementing agents (cement, lime) and bulking agents to encapsulate and/or mechanically bind the waste material within a solid matrix to restrict contaminant migration [USEPA, 1989b; Conner, 1992]. Bulking agents are admixtures that contribute to the solids content and viscosity of the waste and prevent suspended waste components from settling out before solidification occurs [Conner, 1992]. Bulking agents can be inert or pozzolanic. Pozzolanic S/S admixtures (kiln dust, fly ash, organophilic clays, proprietary admixtures) are aluminosilicate materials that do not possess cementing behavior in themselves, but form cementitious materials when combined with lime, cement and water [USEPA, 1989b; Jones 1990; Conner, 1992]. Data suggest that the use of silicates in conjunction with lime, cement and other setting agents can stabilize a broader range of materials (including oily sludges and soils) than cement based mixtures [USEPA, 1988].

In addition to physical isolation of organics in an impermeable matrix, other chemical fixation mechanisms such as neutralization, precipitation, partitioning and sorption are thought to be active [Martin et al., 1990]. Since cementitious reactions occur at a pH greater than 10, hydrolysis, oxidation, reduction and other compound reactions involving organics may contribute to their immobilization and/or ultimate fate [Conner, 1992].

The exact nature of the reactions occurring in cement-pozzolan-soil-waste systems is not clearly understood [USEPA, 1989b, Jones, 1990, Conner, 1992]. Pozzolan chemistry is not well known, but is thought to be analogous to that of portland cement [Jones, 1990]. Waste components such as polar organics, salts, and certain heavy metals often interfere with cement and pozzolan chemistry and may retard or altogether stop setting and hardening of the paste [Wiles, 1987; Jones, 1990]. Also, admixtures may be used to retard the setting process, but they ultimately produce treated soil of greater integrity and strength [Jones, 1990; Conner, 1992]. Non-polar organic wastes of low volatility should not hinder strength development in cement or pozzolan systems [Jones, 1990]. Because the reaction chemistry and the corresponding immobilization mechanisms are poorly understood, treatability studies are required. The S/S processes are therefore empirical.

The strength and durability of the concrete products are directly related to the number of voids in the final product [Jones, 1990]. The integrity of the monolithic mass is assessed using a number of testing criteria such as [USEPA, 1989b, Jones, 1990]: index property (suspended solids, pumpability); density; permeability; strength; durability (wet/dry and freeze/thaw); and contaminant leaching (EP TOX, TCLP analysis) [USEPA, 1989b].

Field Implementation--

Once the S/S reagent blend is selected, it can be administered in-situ using a variety of conventional construction equipment and techniques [USEPA, 1989b,c]. In order to minimize contaminant volatilization and to ensure more complete mixing [USEPA, 1989c], in-situ soil mixing using rotating auger heads is preferred. For instance, Geo-Con, Inc., has developed shallow (SSM) and deep (DSM) soil mixing technologies which are capable of achieving S/S of subsurface soils to depths of 10 m and 30 m, respectively [Broomhead and Jasperse, 1992]. Furthermore, these processes are generic construction technologies, and any combination of admixtures into the soil for purposes of S/S, soil strength improvement, and reinforced wall and impermeable barrier construction [Jasperse and Ryan, 1992].

The SSM process is depicted in Figure 3.4.2.1. The process uses a crane-mounted multi-blade auger having a diameter of 1 to 3.7 m for mixing of soft soils and sludges. Soil admixtures are fed from the ex-situ mixing plant via hoses and a hollow kelly bar to the SSM auger. The soil admixtures enter the soil via three ports located at the bottom of the mixing auger. Primary and secondary overlapping bore patterns are used for area treatment, as shown in Figure 3.4.1.2.

The DSM process is depicted in Figure 3.4.2.2. This process uses a crane mounted rig consisting of an interlocking series of four 36-in diameter auger flights. Soil admixtures from a mixing plant are introduced into the soil via the hollow auger flights. Overlapping patterns are used to ensure complete mixing and continuity of the treated area, as shown in Figure 3.4.2.1 and Figure 3.4.2.3.

The SSM and DSM processes also incorporate a vacuum hood at the ground surface in order to capture any emissions that may be liberated during in-situ mixing [Jasperse and Ryan, 1992]. A combination of horizontal and vertical leads, and template and guide systems are employed to ensure proper alignment of soil mixed zones [Geo-Con Inc., 1989, 1990].

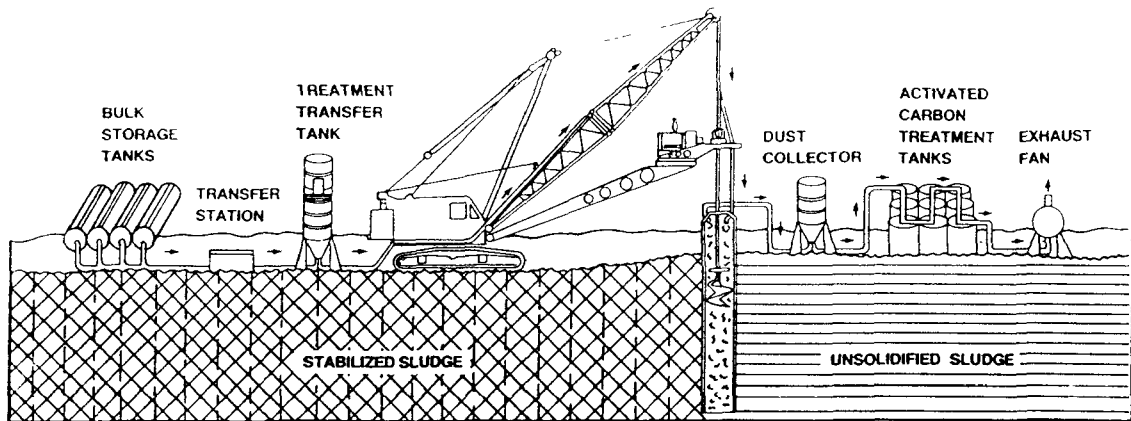


Figure 3.4.2.1 Schematic of crane mounted shallow soil mixing (SSM) process [Geo-Con, Inc., 1990].

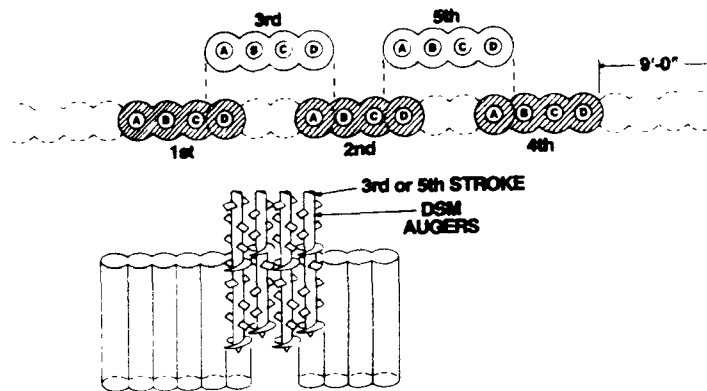


Figure 3.4.2.2 Schematic of drilling pattern for deep soil mixing (DSM) process [Geo-Con, Inc., 1989].

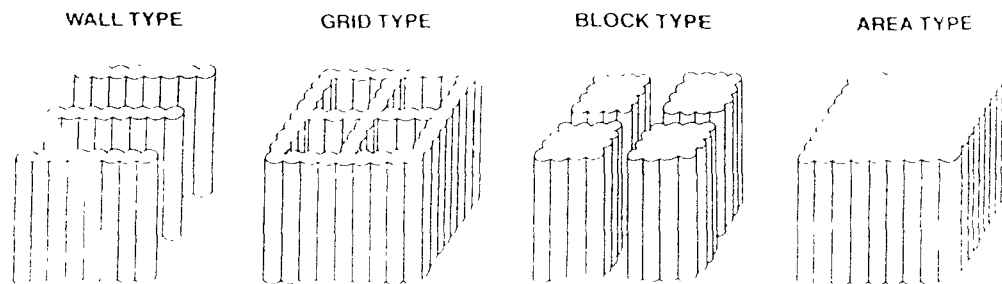


Figure 3.4.2.3 Schematics of various final soil treatment patterns of SSM and DSM in-situ stabilization/solidification processes [Geo-Con, Inc., 1989].

Level of Demonstration and Performance--

Soil mixing technology was developed in the US in the 1950s, but to date it has been used mostly in Japan for a variety of construction related purposes [Ryan, 1987; Broomhead and Jasperse, 1992]. The SSM and DSM soil mixing technologies have been used more than a dozen times for stabilization/solidification purposes [Jasperse and Ryan, 1992]. Environmental applications include waste lagoons, sludges, pits and subsurface soils [Jasperse and Ryan, 1992]. In at least one case, DSM has been applied to soils contaminated with DNAPLs (PCBs).

In 1988, DSM utilizing S/S admixtures supplied by International Waste Technologies was demonstrated as part of the USEPA SITE Program at a site in Hialeah, Florida [USEPA, 1990a]. The soil profile at the site consisted of sands, silty sands and karstic lime rock. The water table was situated at a depth of 2 m. The average hydraulic conductivity of the soils was approximately 1.8×10^{-2} cm/s. Initial PCB concentrations varied between non-detectable to approximately 1,000 ppm. Soil was contaminated to a depth of 15 m, and in the affected areas PCB concentrations ranged from 200-600 ppm.

Bench scale studies indicated that a proprietary pozzolanic additive containing a treated clay adsorbent was effective in chemically binding the PCBs and other organics [Jasperse and Ryan, 1992]. Two 10x20 ft test cells were treated to depths of 14 and 18 ft using a 3-ft diameter SSM auger. The auger was rotated at 15 rpm, and the reagent addition rate was 0.18 lb reagent/ 20lb of dry soil. Thirty-six soil columns were used in an overlapping pattern to completely treat each test cell. The average properties of the treated soil included: hydraulic conductivity 4×10^{-7} cm/s; unconfined compressive strength of 410 psi; and a volume increase of 8.5%. The treated soil performed satisfactorily on the wet/dry test but not in the freeze/thaw test.

TCLP analyses were performed on both untreated and treated soil samples. Untreated soil samples containing PCBs below 60 ppm had no PCBs detected in the leachate by the TCLP, whereas untreated soil samples having above 300 ppm PCBs had PCBs detected in their leachates. Between these limits, the TCLP results were varied. The maximum PCB concentration in the treated soil samples was 170 ppm, with most being below 100 ppm [Jasperse and Ryan, 1992]. Blending of high- and low-contaminated soils by the SSM auger is likely to have contributed to lower contaminant levels in the treated soil [USEPA, 1989a]. Since no PCBs were detected in the leachate, it appeared that they were effectively immobilized according to TCLP analyses [USEPA, 1989a]. However, because of detection limit problems (as indicated above), effective treatment could not be absolutely confirmed [USEPA, 1989a; Jasperse and Ryan, 1992]. Subsequent to the test, complete treatment of the site began in late 1990 and was completed in 1991 [Jasperse and Ryan, 1992].

Applicability/Limitations--

"S/S is one of the most important Best Demonstrated Available Technologies (BDATs) for both 'listed' and 'characteristic' wastes and will continue to be in the future" [Conner, 1992]. Effective treatment of non-polar organic compounds (which include DNAPLs) has been demonstrated under certain conditions [USEPA, 1989b]. However, many organics have been claimed to be effectively treated by S/S processes, but little data is available for confirmation [Conner, 1992]. Treatability studies are required to assess contaminant effects on the physical properties of the treated soil mass.

S/S is a good candidate for sites extensively contaminated with DNAPLs since the DNAPL will become mixed throughout the treated soil column. However, to date, DSM has not been specifically used for DNAPLs and it is not clear whether DNAPL migration from the treatment zone can be prevented. Metals and organics can be treated simultaneously. Dissolved phase plumes and DNAPL in fractured rock are better addressed by other techniques.

Although PCBs constituted only ~1 wt% of the soil to be treated in the USEPA SITE demonstration, the IWT/Geo-Con system is thought to be capable of treating wastes containing up to 25 wt% organics [USEPA, 1990a,b]. The in-situ mixing process is intrusive, and surface and subsurface obstructions such as boulders and concrete blocks must be removed. Drums, trash, and other refuse may be penetrated and incorporated into the treated soil mass [USEPA, 1988]. Although S/S is a BDAT, durability, leachability and longevity are matters which still require attention on a site specific basis.

Cost and Availability--

Cements, pozzolans and other S/S admixtures are commercially available, as are in-situ mixing technologies such as the Detoxifier [USEPA, 1988] and SSM and DSM technologies [Jasperse and Ryan, 1992]. In-situ soil mixing technologies can also be used to deliver steam to the subsurface to drive off volatiles during S/S [USEPA, 1988]. Typical costs for the SSM and DSM technologies are \$20-50/m³ and \$100-200/m³, respectively, excluding reagent cost [Jasperse and Ryan, 1992].

3.4.3 Permeable Treatment Walls

Theoretical Background--

In-situ treatment walls are permeable and reactive structures installed using conventional slurry wall construction technology. The walls are constructed of granular materials to permit ground-water flow through the structure under ambient ground-water gradients. Treatment is achieved by using a combination of reactive granular backfill and a variety of additives or surface coatings such as [Gillham and Burris, 1992]: *nutrients and bacteria for in-situ biodegradation; redox controls and/or metal catalysts to aid in metals precipitation and chemical dehalogenation* [Blowes and Ptacek, 1992; Xu and Schwartz, 1992; O'Hannesin and Gillham, 1993]; *organic carbon for enhanced denitrification; and selective sorbents to increase the retardation capacity of the in-situ wall* [Burris and Antworth, 1992; Chapman, 1992]. The dissolved phase contaminants are exposed to the reactive amendments and/or microbial consortia in the permeable treatment wall. Factors such as rates of reaction and the maintenance of favorable conditions will affect the wall thickness and its longevity.

The remedial strategy requires that the treatment wall either span the entire width of the contaminant plume or the plume be directed through the treatment wall. Figure 3.4.3.1 schematically illustrates two possible wall configurations; an independently acting wall system (Fig. 3.4.3.1a), and a system employing impermeable wing walls which aid in the channeling of contaminated ground water to the reactive sections (Fig. 3.4.3.1b).

Field Implementation--

Installation of in-situ treatment walls will depend on the desired wall configuration and its composition. For example, continuous treatment wall sections such as that shown in Figure 3.4.3.1a, can be constructed in a manner analogous to slurry cut-off walls using biodegradable polymer slurries rather than bentonite [Gillham and Burris, 1992]. For the geometry shown in Figure 3.4.3.1b, large diameter borings filled with soil amendments are used in conjunction with cut-off walls. Using conventional construction technology, installation depths greater than 100 ft are possible [O'Hannesin and Gillham, 1992]. In addition, in-situ treatment walls with hydraulic feed controls can be installed to deliver gaseous or liquid phase amendments [Gillham and Burris, 1992].

Level of Demonstration and Performance--

In most cases, current development of in-situ treatment walls is at the conceptual and laboratory scales [Blowes and Ptacek, 1992; Burris and Antworth, 1992; Xu and Schwartz, 1992]. At the laboratory scale, many chlorinated aliphatics have been transformed under abiotic (iron reducing) conditions and appear to be first order in nature [Gillham et al., 1993]. Zinc and iron appear to transform halogenated aliphatics faster than other metals, and transformation rates were pH dependent [Gillham et al., 1993].

Gillham and O'Hannesin, 1993].

No full-scale applications are known to exist [Gillham and Burris, 1992]. However, in 1991, one pilot test was completed at the Canadian Forces Base (CFB) Borden in which dissolved TCE and PCE were treated [Gillham and O'Hannesin, 1992; Gillham et al., 1993]. At the site, the depth to ground water was approximately 1 m and the ground-water velocity was approximately 9 cm/d. The centroid of the dissolved plume was 3 m below the water table and had a thickness and width of 1 m and 2 m, respectively. The maximum dissolved concentrations of PCE and TCE were 43 and 250 ppm, respectively.

A sheetpile system permitted local dewatering and excavation of aquifer soils and their replacement by amended soils. The in-situ treatment wall consisting of a mixture of iron grindings (22 wt%) and sand (78 wt%) was constructed 5 m downgradient from the DNAPL source. The wall was constructed in the depth interval of 3.8-6.0 m, and was 1.6 m thick and 5.5 m long. Rows of multilevel sampling wells were placed in the aquifer approximately 0.5 m from the upgradient and downgradient faces of the wall, and within the wall at distances of 0.5 and 1.0 m from the upgradient face. The 348 sampling points were monitored for 500 days. Most transformation occurred in the first half of the wall. The results indicated that the plume did not bypass the wall; and reductions of 91% and 95% in PCE and TCE concentration, respectively, were achieved. Mass balances confirmed that chlorine concentrations appearing downgradient of the wall were consistent with degradation of the two compounds. Trace amounts of dichloroethene were detected which may have potentially resulted from abiotic or biotic transformations.

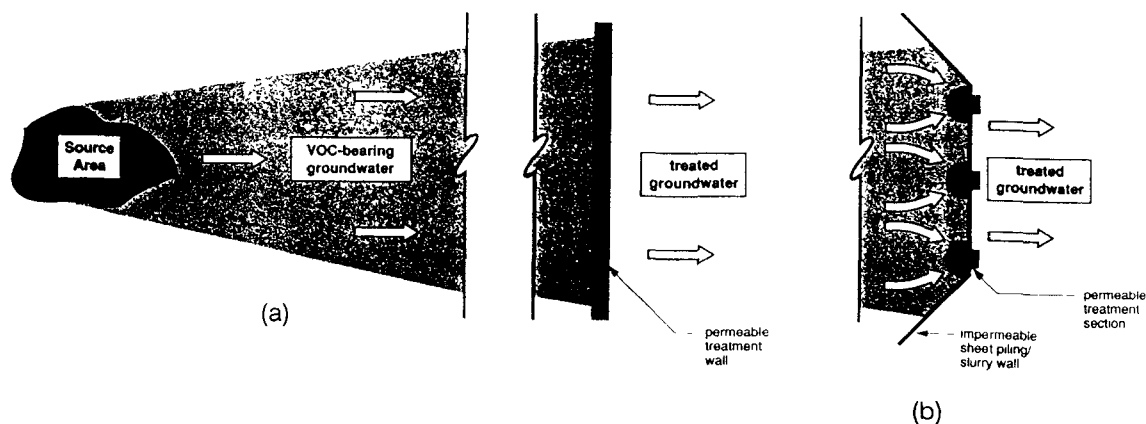


Figure 3.4.3.1 Conceptual plan views for possible configurations of in-situ permeable treatment walls [Envirometal Technologies, Inc., 1992]

Applicability/Limitations--

Laboratory column studies have shown that in-situ soil amendments (treatment zones) can effectively treat both inorganic and organic dissolved phase compounds [Blowes and Ptacek, 1992; Burris and Antworth, 1992; Xu and Schwartz, 1992; Gillham et al., 1993]. Since most DNAPL is immobile, once emplaced, the intended use of this technology is the management and treatment of the dissolved phase

in aquifers; extension to fractured media is unlikely.

The active amendments must be reactive, non-toxic, and must be both soluble enough to supply ample reagent mass for reactions and stationary enough to persist for long periods of time. Excessive biological growth and precipitation may compromise the long-term performance of the permeable wall. Use of inorganic catalysts that promote organic compound reduction may also foster anaerobic biodegradation which may potentially occur within the wall or downgradient. If the treated compounds are not completely dehalogenated, formation of toxic products such as vinyl chloride is conceivable. Since abiotic reactions are aspecific, formation of toxic intermediate degradation products is also conceivable.

The placement of permeable treatment walls and impermeable wing walls is limited to areas without ground structures, buried utilities, and other subsurface obstructions and heterogeneities. By design, in-situ permeable treatment walls are intended to be passive; and no ex-situ treatment is needed. Thus, the treatment costs associated with pump-and-treat can be eliminated. Because the system is passive, site heterogeneity greatly affects site selection to ensure the plume flows through the wall. Seasonal effects may cause the plume migration direction to change, making additional hydraulic controls necessary; i.e., hydraulic gradient controls such as slurry and sheetpile cut-off walls, and/or judicious well pumping.

Cost and Availability--

Degradation of dissolved contaminants has been shown on the pilot scale only. The technology and elements required to construct and implement permeable treatment walls are readily available. The Waterloo Centre for Groundwater Research (Canada) has patents pending on in-situ treatment wall technology [O'Hannesin and Gillham, 1993].

Permeable treatment walls have potential promise for dissolved plume treatment in aquifers providing the plume continues to flow through the wall. Since DNAPLs are generally immobile under ambient groundwater conditions, it is expected that they will remain unaffected. In-situ permeable treatment walls are thought to be less expensive than pump-and-treat [O'Hannesin and Gillham, 1993].

3.5 SOIL WASHING PROCESSES

Introduction--

In-situ soil washing (or fluid flushing/flooding) relies on fluid-fluid displacement processes to enhance contaminant removal. Fluids (alkalis, cosolvents, surfactants, water, etc.) can be injected into the porous media in order to mobilize the resident pore fluids, water and DNAPL, by a combination of physical forces which can be aided by favorably altering chemical partitioning so that bulk fluid properties change, i.e., solubility enhancement and interfacial tension reduction. The exact nature of the displacement and the prevailing physical and chemical behavior occurring in these systems depends on the liquid properties and environmental conditions. In-situ soil washing using alkalis, cosolvents, surfactants, and water are evaluated in sections 3.5.1 through 3.5.4, respectively.

The effectiveness of the displacement process is controlled by phase equilibria and the hydrodynamics of frontal propagation in porous media. The mechanics of miscible and immiscible fluid front propagation in homogeneous, isotropic porous media are well established [Buckley and Leverett, 1942; Miller, 1975; McWhorter and Sunada, 1990]. Factors affecting the orientation and shape of the advancing saturation front include: matrix heterogeneities, fluid properties, geometry of the aquifer and injection strategy, initial moisture and boundary conditions, and injection rates.

As a liquid progresses through the porous media, two types of fluid displacement may occur. Miscible displacement characterizes the removal of resident pore fluids by a mutually soluble displacing liquid (i.e., cosolvent) in which the displacing-resident fluid interfacial region is a continuous liquid phase that is free of interfacial tension. Immiscible displacement occurs when the two fluids are mutually insoluble and capillary forces arising from interfacial tension exist between the two fluids. Both displacement processes consist of two recovery phases: primary and secondary. In a successful primary recovery phase, a very large and concentrated "bank" of resident pore fluid is removed just prior to breakthrough of the injected liquid. Secondary recovery occurs as a result of increased hydrocarbon solubilization or leaching after the breakthrough of the injected liquid.

In saturated homogeneous isotropic porous media, the stability of the propagating front is related to M and N_G (mobility ratio and gravity number, see section 2.1) These ratios have been shown to be very important in terms of viscous fingering, gravity override and effective sweep-out [Saffman and Taylor, 1958; Basel and Udell, 1989]. If viscous forces dominate in saturated porous media, a propagating front is stable with respect to gravity, and propagation can be reasonably predicted and controlled [Buckley and Leverett, 1942; Morrow et al., 1985; Udell and Stewart, 1989].

The mobility ratio, which neglects gravity and interfacial forces (Buckley-Leverett assumption), is often used to evaluate the potential success of a proposed displacement. A value of $M \leq 1$ usually indicates a favorable displacement [Buckley and Leverett, 1942; Muskat, 1982]. System miscibility may not seriously affect primary recovery if M is low enough. For example, Everett et al. (1950) found that for very low mobility ratios, miscible and immiscible displacement of oil from unconsolidated clean sands using water at flow velocities on the order of 20 m/d could lead to primary recoveries as high as 100% and 91%, respectively. Since ground-water flow velocities of 20 m/d are unrealistic, alternative methods have been sought to favorably affect recovery at ambient ground-water velocities (1-5 m/d).

Alkalis enhance the removal of NAPL, heavy oils, creosotes, etc., that contain organic acids such as carboxylic acids, phenolics, and asphaltenes by saponifying the organic acids from the NAPL which results in natural surfactant production and, thus, interfacial tension reduction. Alkalis also disrupt adsorption, precipitation and ion exchange processes between the pore fluids and the porous media which reduces surfactant losses.

Cosolvents rely on viscosity and density differences between the injected and resident fluids and on solubility enhancement to overcome the capillary forces and to mobilize the DNAPL. For enhanced primary recovery, a concentrated cosolvent slug is injected to locally create a displacing front that is essentially one fluid phase composed of water-cosolvent-DNAPL which is free of surface tension effects.

Surfactants rely on interfacial tension reduction and enhanced hydrocarbon solubilization to improve DNAPL recovery. The surfactant can be injected as a concentrated slug followed by a polymer for mobility control to maximize primary recovery. If this is undesirable, a secondary recovery approach emphasizing continuous injection of surfactants at low concentrations can result in significant compound recovery.

Waterflooding and ground-water extraction usually do not lead to appreciable recovery of DNAPL and are therefore primarily used for containment purposes. However, at extensively contaminated sites, certain pumping strategies can enhance DNAPL mobilization.

All of these processes have been utilized separately and in combination for enhanced oil recovery in the petroleum industry with varied success. The technologies are available, but are highly compound- and site-specific. If administered properly, they can lead to significant DNAPL recovery. At this time, environmental applications are being explored.

3.5.1 Alkali Soil Washing

Theoretical Background--

In-situ alkali soil washing involves the injection of alkaline agents such as sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), and sodium orthosilicate (Na_4SiO_4) to enhance contaminant removal. Alkalis enhance NAPL recovery by a number of mechanisms: formation of natural surfactants via NAPL-alkali reactions; the porewater salinity is altered to enhance surfactant formation; precipitation of calcium and magnesium hardness which enhances interfacial activity; reduction of surfactant adsorption to aquifer solids; NAPL wettability changes; emulsification and coacervation of NAPL into a middle-phase emulsion; enhanced NAPL ganglia mobilization as a result of interfacial tension reduction; coalescence of individual NAPL ganglia into a NAPL bank; and displacement of the NAPL bank to a recovery well by viscous forces. Alkalis have been frequently used in enhanced oil recovery methods either alone [Breit et al., 1981; Janssen-van Rosmalen and Hesselink, 1981; de Zabala et al., 1982; Mayer et al., 1983], or in conjunction with cosolvents and surfactants (see sections 3.5.2, 3.5.3) [Reed and Healy, 1977; Krumrine et al., 1982a,b; Clark et al., 1988; Manji and Stasiuk, 1988; Peru and Lorenz, 1990; Surkalo, 1990].

The effect of alkalis on the subsurface transport of petroleum NAPLs is complex. Johnson [1976] and de Zabala et al. [1982] have enumerated the sometimes contradictory mechanisms taking place during alkaline flooding of petroleum reservoirs: emulsification and entrapment; emulsification and entrainment; emulsification with coalescence; wettability reversal (NAPL-wet to water-wet, or water-wet to NAPL-wet); wettability gradients; oil-phase swelling; disruption of rigid films; and low interfacial tensions. The presence of acidic components in petroleum NAPLs appears to be one unifying factor which is common to the observed phenomena [de Zabala et al., 1982]. However, no correlation between the acid number of the NAPL (oil) and its recovery has been established [Ehrlich and Wygal, 1977; Janssen-van Rosmalen and Hesselink, 1981; Mayer et al., 1983]. The acidic components such as carboxylic acids, carboxyphenols, phenolics, porphyrins, and asphaltene fractions of multicomponent petroleum NAPLs can form hydrolyzed surfactant products when saponified in-situ by alkalis [de Zabala et al., 1982; Mayer et al., 1983]; and the hydrolyzed surfactants, which are negatively charged, are presumed to be responsible for enhanced NAPL recovery, not the alkalis themselves [de Zabala et al., 1982].

Alkali and surfactant soil washing differ in the nature of the passage of the surfactant through the system. In surfactant flooding, the surfactant can either be continuously supplied or pulsed. In alkali soil

washing, in-situ surfactant production is coincident with the hydroxide (OH^-) front created by the concentrated alkali; and it continues until the surfactant precursors are completely depleted from the NAPL mass [de Zabala et al., 1982]. Since the amount of surfactant precursors is finite, the surfactant effluent history resulting from this in-situ process is analogous to a single pulsed injection of surfactant. Hence, if the NAPL has not been mobilized by the time its acidic components have been saponified and the alkali front has passed it by, the NAPL will probably remain emplaced, since no other surfactant will be supplied to reduce its interfacial tension.

As the alkaline front propagates through porous media, the aqueous phase pH is elevated and diffusion of acidic NAPL components into the aqueous phase is initiated. The frontal advance of alkali is retarded by saponification of acidic NAPL components at the NAPL-water interface and, more importantly, by reversible and irreversible reactions involving dissolved cations and the porous media [Ehrlich and Wygal, 1977; de Zabala et al., 1982; Jensen and Radke, 1988]. Interactions with the porous media include bulk mineral dissolution and reversible sodium-hydrogen ion exchange at mineral surfaces [Jensen and Radke, 1988]. The saponification and reversible ion exchange reaction equilibria are depicted in Figure 3.5.1.1. The frontal propagation is chromatographic, and its rate of advance has been shown to be dominated by reversible ion exchange reactions [de Zabala et al., 1982; de Zabala et al., 1986; Jensen et al., 1986; Jensen and Radke, 1988]. While there is a tendency to use optimal pH-interfacial tension relationships as the sole basis of design, the beneficial use of alkalis at the optimal pH may be annulled because ion exchange interactions will involve alkali and thus alter pH [de Zabala et al., 1982].

High pH alkalis such as NaOH are obviously desirable because: the reversible ion exchange reactions are overpowered allowing the OH^- front to propagate faster; the surfactant precursor solubilities concomitantly increase with increasing pH; and surfactant adsorption is mitigated by anion exclusion at high pHs [de Zabala et al., 1982]. The pH behavior of several alkalis is shown in Figure 3.5.1.2. At high pHs, solubilization of carbonaceous materials up to 0.5 wt% has been observed after alkali breakthrough [de Zabala et al., 1982]. However, considerable alkali consumption and accelerated rock dissolution make NaOH undesirable [Burk, 1987; Jensen and Radke, 1988; Peru and Lorenz, 1990]. Therefore, alkali buffers such as Na_2CO_3 and Na_4SiO_4 are desirable because they effectively solubilize surfactant precursors and achieve NAPL mobilization at lower pHs, can be used at lower concentrations, and buffer against the reversible sodium-hydrogen ion exchange reactions which consume OH^- and cause its frontal attenuation [Jensen and Radke, 1988]. Buffered systems are usually characterized by an intermediate pH region which occurs from ion exchange and alkaline buffer respeciation [Jensen and Radke, 1988]. The disparity of breakthrough times for alkaline buffers vs. a non-buffered alkali (NaOH) is shown in Figure 3.5.1.3.

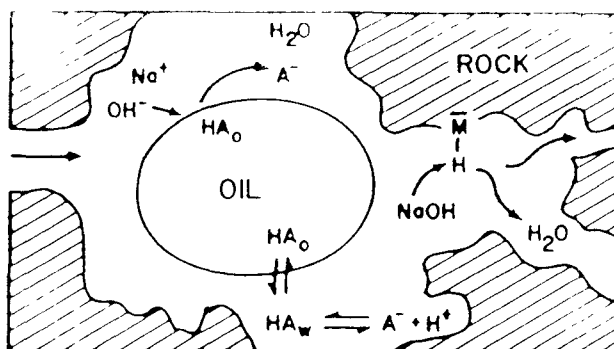


Figure 3.5.1.1 Schematic of alkali recovery process [de Zabala et al., 1982].

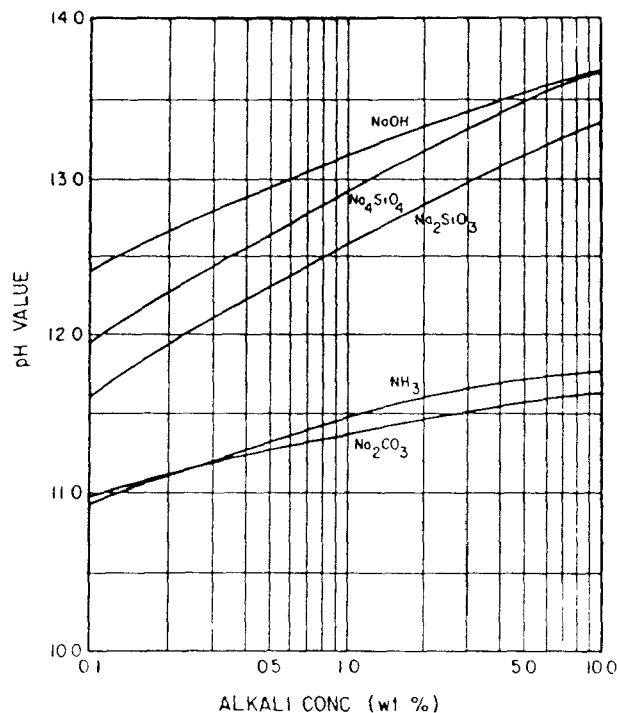


Figure 3.5.1.2 pH comparison of commonly available alkali chemicals [Mayer et al., 1983].

Alkalis can significantly reduce interfacial tension, producing values on the order of 0.01 mN/m, as shown in Figure 3.5.1.4. Figure 3.5.1.5 illustrates that interfacial tension reduction can be synergistic in alkali-surfactant floods [Campbell, 1981; Manji and Stasiuk, 1988]. Co-injection of surfactants may also circumvent NAPL recovery limitations imposed by the finite amount of in-situ saponification that can be realized. Mobility control agents can be used with alkalis to improve sweep efficiency of alkaline flooding [Burk, 1987]. Sodium chloride (NaCl) is often pre-injected or co-injected with alkalis to achieve the optimal salinity for interfacial activity [de Zabala et al., 1982; Mayer et al., 1983].

Field Implementation--

The petroleum engineering literature is replete with field applications of alkaline flooding. Mayer et al. [1983] provides a good summary of alkaline flooding projects. Details on the necessary equipment are also available [Clark et al., 1988; Manji and Stasiuk, 1988; Sale et al., 1989].

Maximum NAPL recovery occurs when a concentrated and viscous middle-phase microemulsion and NAPL bank are created near the advancing front of the alkali. This can be accomplished using a concentrated alkali slug, usually followed by a mobility control agent [Mayer et al., 1983; Burk, 1987], or via continuous injection [Mayer et al., 1983; de Zabala et al., 1982]. Alkaline injection can be continuous for several pore volumes until breakthrough of the alkali and OH⁻ front and/or the saponification capacity of the residual NAPL is exhausted (i.e., in-situ surfactant production ceases). Tertiary injection of mobility control agents may then commence if they were not co-injected with the alkaline agent.

Conventional injection and extraction well construction equipment can be used for in-situ alkaline soil washing [Sale et al., 1989]. For extremely corrosive injectates, stainless steel well construction may be required. Both horizontal and vertical well configurations have been successfully used (see below). Well placement strategy depends on the nature and extent of contamination, soil heterogeneities, and anticipated subsurface flow behavior once washing commences.

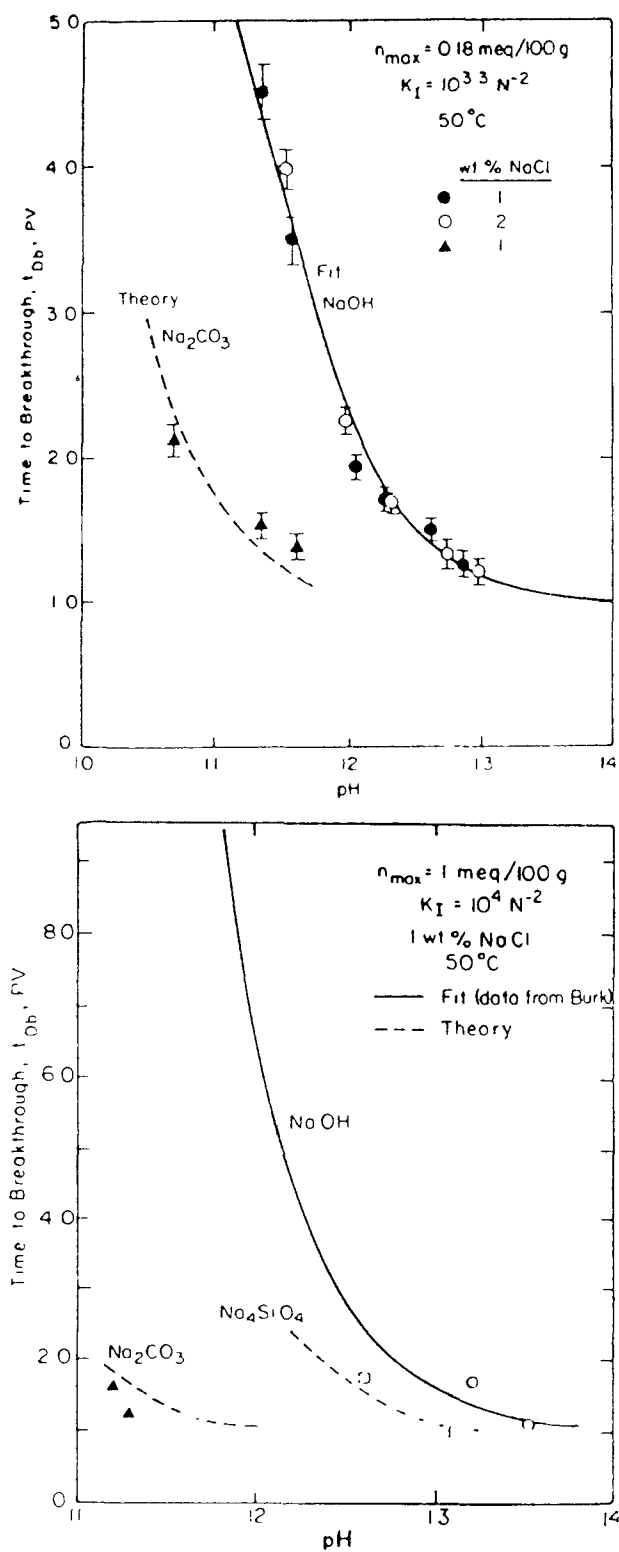


Figure 3.5.1.3 Comparison of experimental and theoretical alkali breakthrough times for NaOH, Na₄SiO₄, and Na₂CO₃ as a function of pH [Burk, 1987; Jensen and Radke, 1988].

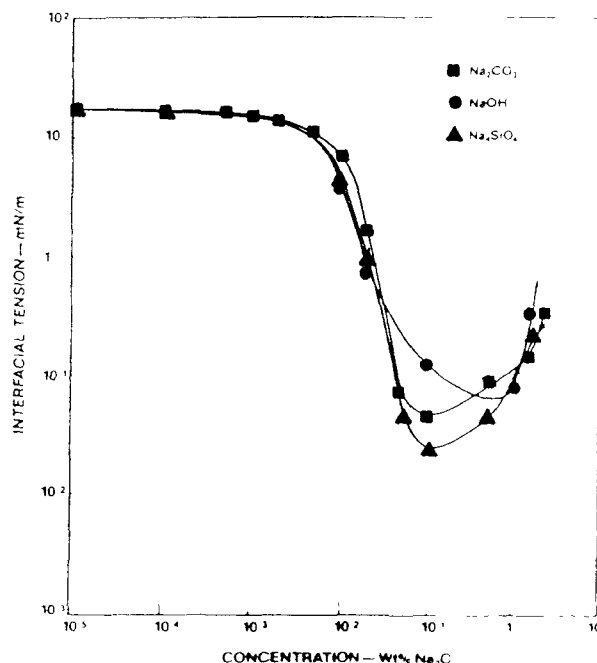


Figure 3.5.1.4 IFT values of Wilmington Ranger zone crudes with alkalis at 52°C [Burk, 1987].

Level of Demonstration and Performance--

Enhanced recovery of petroleum hydrocarbons from oil reservoirs using alkalis either alone or in combination with surfactants, cosolvents, and mobility control polymers has been found to significantly more effective than conventional water-flooding [Mayer et al., 1983; Manji and Stasiuk, 1988; Clark et al., 1988]. Alkaline agents were employed with surfactants to enhance recovery of dense oils ($SG=1.04$, $\mu=54$ cp) from a shallow alluvial aquifer at a former wood-treating site [Sale et al., 1989]. The description of the field test is provided in section 3.5.3.

Applicability/Limitations--

Alkalis can be incorporated into almost any soil washing treatment of DNAPLs, providing a compound can be selected such that the phase behavior and the resultant changes in bulk liquid properties are favorable. Since most multicomponent DNAPLs are not likely to contain acidic components, in-situ saponification is precluded, and surfactant must be supplied in these instances. The favorable influence of alkalis will still be realized with respect to such factors as optimal salinity, hardness precipitation, surfactant adsorption mitigation, and interfacial tension reduction. However, water-DNAPL interfacial tension reductions below 5 dynes/cm have resulted in rapid downward vertical migration of DNAPLs in laboratory studies [Fountain et al., 1991].

Engineered alkaline flooding in petroleum reservoirs has an entirely different focus than that of environmental applications. In petroleum engineering, the scale of application, profit motive, and reservoir conditions such as high NAPL viscosity and saturations, salinity, and geologic confinement favor approaches geared toward high primary recovery; that is, the creation of concentrated and viscous middle-phase microemulsions and banks having low interfacial tensions which promote good sweep efficiency. In general, this approach is not well suited for environmental applications because of the relatively small scale of contamination, environmental sensitivity, and liability. However, high primary recovery applications can be considered as appropriate at sites having large scale contamination, as was the case at the former wood treating facility in Laramie, Wyoming [Sale et al., 1989].

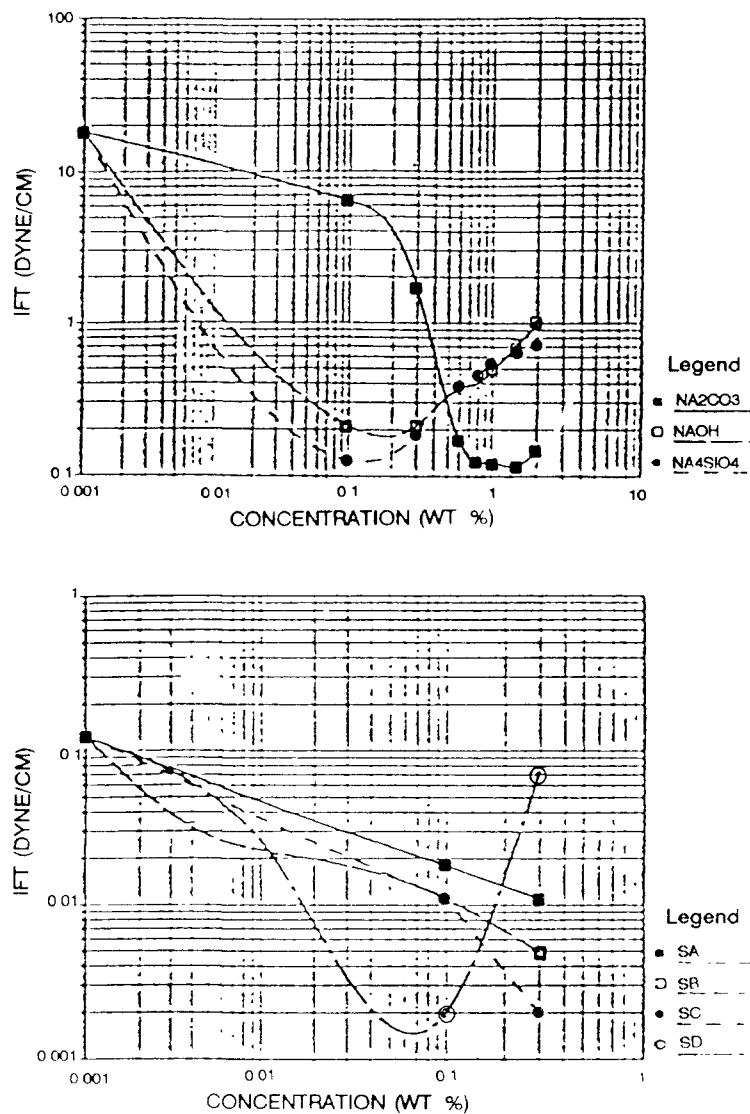


Figure 3.5.1.5 IFT values of Dome Lloydminster "A" pool crude as a function of alkali and surfactant addition [Manji and Stasiuk, 1988].

Alkalis themselves often reduce the viscosity of water, which often promotes unfavorable mobility ratios. If a more displacement-like operation is preferred over solubilization, any combination of compounds such as polymers (density enhancement) and viscosifiers may be added to the alkaline agents to ensure more favorable mobility ratios [Burk, 1987].

Compatibility issues also arise and a careful study of the interactions of the alkali (including co-injected surfactants, cosolvents and brine) with the field soils and pore fluids is essential or pore clogging, excessive alkali consumption, or insufficient pHs may lead to poor NAPL recovery. Alkali consumption and rock dissolution may be excessive for long applications [Breit et al., 1981]. Clayey soils may cause dispersion of the alkali and OH⁻ fronts which will delay and affect NAPL recovery, as well a potentially increasing alkali consumption and surfactant adsorption [Jensen et al., 1986].

The condition of the aquifer upon completion of alkali soils washing is likely to be reduced with a relatively high pH. Therefore, it may be desirable to oxygenate or neutralize the groundwater.

With the exception of borings, in-situ alkali soil washing is not likely to be intrusive; therefore, few limitations exist with respect to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The above ground hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

Cost and Availability--

The hardware required for in-situ alkali soil washing is readily available, but there are few experts on this technology within the environmental community. Many full-scale applications have been completed in the petroleum industry. A field scale application using compatible surfactants and alkalis has been successfully completed.

Alkalis appear to be good candidates for aquifer remediation of DNAPLs, probably serving best as complements to surfactants because most DNAPLs lack acidic components required for saponification (natural surfactant production). Alkalis will have their biggest impact on DNAPL source areas.

Cost information from petroleum applications is not directly applicable. No information is available at this time for environmental applications. Major issues requiring consideration are surfactant costs, surfactant recycling, tankage requirements, and effect of field-scale soil heterogeneity on displacement efficiency. Since the emulsions created can be very stable and the quantity of extracted fluids can be large, management of produced fluids must be carefully considered.

3.5.2 Cosolvent Soil Washing

Theoretical Background--

In-situ cosolvent soil washing uses hydrophilic organic compounds (i.e., alcohols, ethers, ketones) to enhance contaminant removal. The primary mechanisms are: displacement of the contactable NAPL by a propagating cosolvent front; and solubility enhancement and interfacial tension reduction of NAPLs which assists in their recovery. Although the exact displacement application differs, this process is in many ways identical to enhanced oil recovery methods utilizing steam, surfactants, hot-water, or caustic floods [Shah, 1981; Janssen-van Rosmalen and Hesselink, 1981].

Figure 3.5.2.1 shows the relationships between the resident fluid, r , and the displacing fluid, d , in a column of porous media inclined at an angle θ from the horizontal. The interfacial region possesses a mixing length ϵ , and is inclined at an angle α to the direction of flow. The importance of the mobility ratio, M , on advancing cosolvent front stability is clearly shown in Figure 3.5.2.2 as pure isopropanol (IPA) miscibly displaces naphtha ($M=0.271$) [Gatlin, 1959]. Conversely, the effluent history for an unstable miscible displacement of IPA by naphtha ($M=3.69$) suggests that viscous fingering of naphtha into IPA precludes effective sweep-out of IPA.

While miscible displacement is preferred so that interfacial forces are eliminated, pore level mixing within interfacial regions will almost certainly lead to emulsification. This generally does not inhibit removal because cosolvents may introduce a high degree of non-linearity in fluid phase properties such as viscosity, density, and interfacial tension [Gatlin, 1959]. The degree of non-linearity is ternary specific. For example, Figure 3.5.2.3 shows the viscosities of equilibrated liquid pairs for the water-IPA-naphtha ternary as a function of IPA content in each phase. Gatlin (1959) found that while the miscible displacement of naphtha by pure IPA yielded $M=0.271$, a water-IPA slug can be chosen with $M=0.147$ to induce a potentially equivalent immiscible displacement.

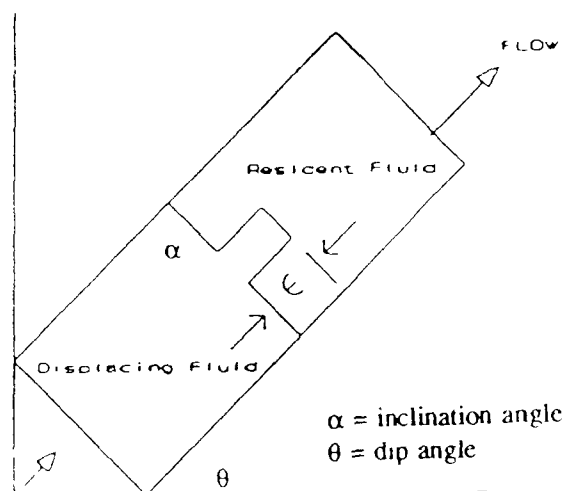


Figure 3.5.2.1 Schematic of the fluid-fluid displacement process [adapted from Boyd and Farley, 1992].

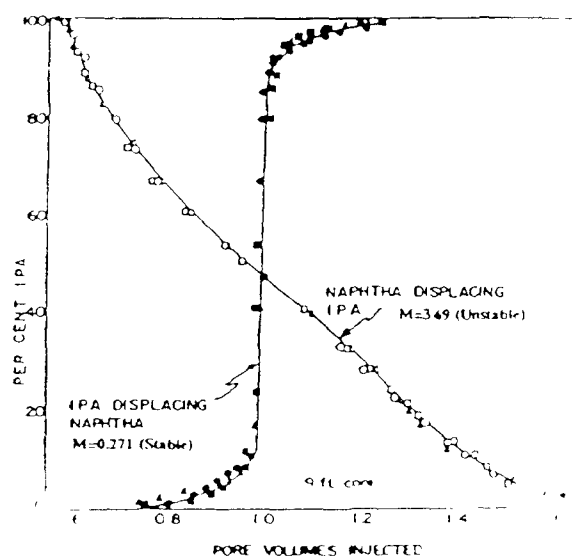


Figure 3.5.2.2 Column effluent histories of miscible displacements [adapted from Gatlin, 1959].

To estimate or optimize M for displacement, the selection of an appropriate cosolvent requires specific knowledge of the phase behavior of water-cosolvent-NAPL ternary systems. The differences in phase behavior can be pronounced for small differences in cosolvent structure. Figure 3.5.2.4, for example shows the ternary phase diagrams for the IPA-water-Soltrol and tert-butyl alcohol (TBA)-water-Soltrol ternary phase diagrams [Taber et al., 1960]. The miscible (single) liquid phase and binary (immiscible) liquid phase regions are situated above and below the binodal curve, respectively. The small area under the binodal curve indicates good cosolvent solvation ability. The end of the tie lines on the binodal curve show the compositions of equilibrated liquid pairs. The location of the plait point and the tie lines illustrates that for the entire range of possible compositions, IPA remains hydrophilic, while TBA becomes more hydrophobic with increasing TBA content. Given the commensurate changes in bulk liquid properties that result from partitioning, accumulation of TBA ($\mu=2.9\text{cp}$) in the Soltrol ($\mu=1.5\text{cp}$) phase may produce less favorable mobility ratios than would be possible with IPA ($\mu=1.9\text{cp}$). Among the other factors that must be considered when selecting a cosolvent include: low human health hazard; biodegradation potential;

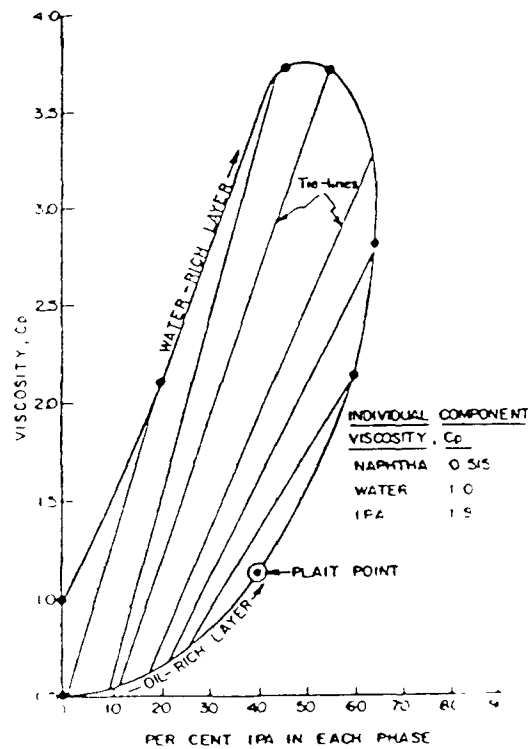


Figure 3.5.2.3 Viscosity enhancement of water and NAPL by isopropanol (IPA) in the H₂O-IPA-Naphtha ternary liquid system at 20°C [Gatlin, 1959].

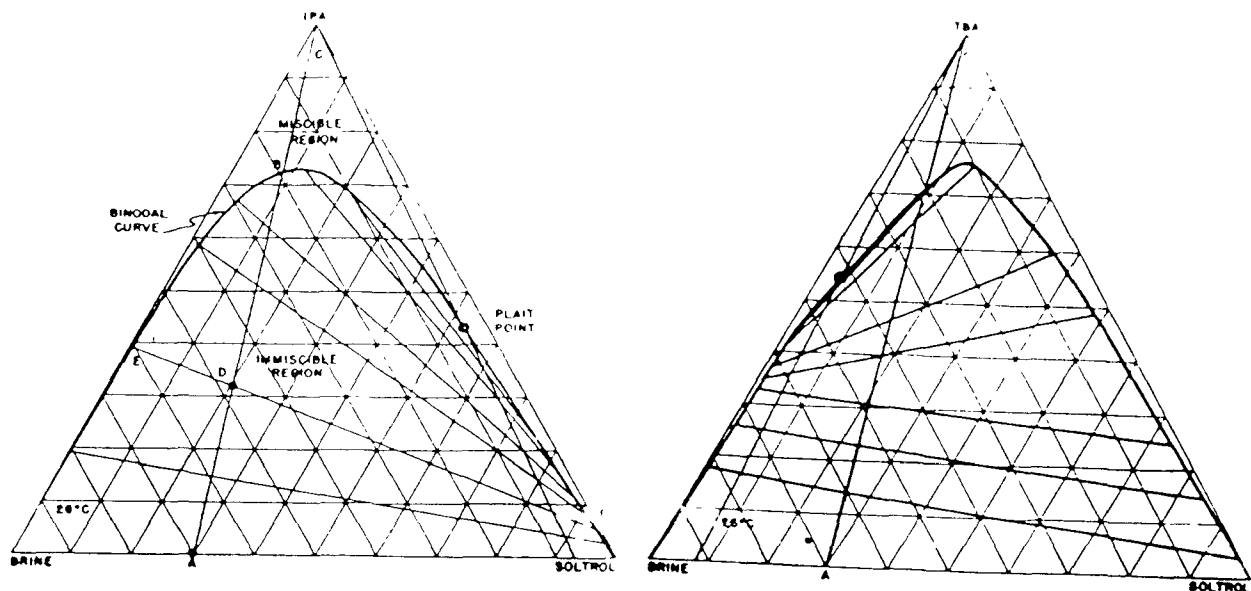


Figure 3.5.2.4 Equilibrium phase diagrams for the IPA-Soltrol-Brine (2% CaCl₂) and TBA(tert-butyl alcohol)-Soltrol-Brine (2% CaCl₂) systems showing binodal curves and inclination of tie lines [Taber et al., 1960].

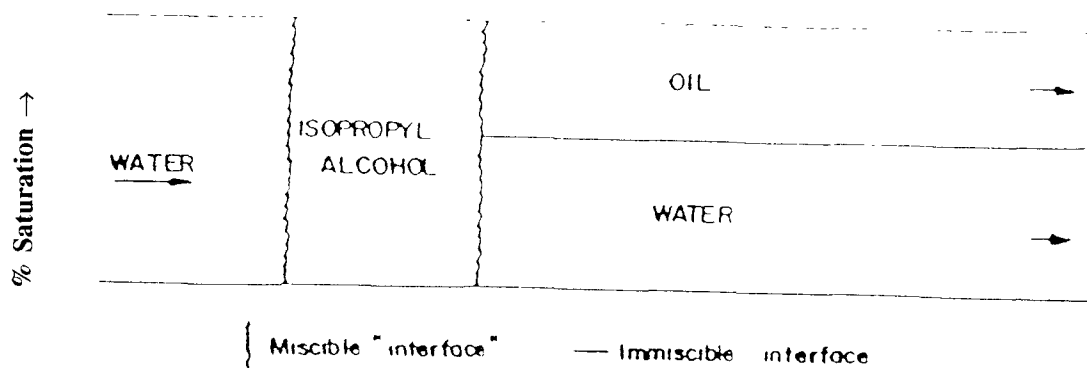


Figure 3.5.2.5 Idealized fluid-fluid displacement using a cosolvent (IPA) slug [adapted from Gatlin, 1959].

cosolvent losses to the DNAPL phase (excessive partitioning into DNAPL phase), strong ability to desorb DNAPLs from soil organic matter; and low sorption to solids.

Field Implementation--

The displacement process entails the injection of the cosolvent as a finite, concentrated "slug" into the porous medium which is then followed by a driving fluid. Injection of a dilute cosolvent may result in solubility enhancement of the hydrocarbons, but not physical displacement of the NAPL. A slug is preferred over continuous cosolvent injection for economic reasons. The driving fluid, water, pushes the cosolvent slug through the porous medium and the cosolvent, in turn, miscibly or immiscibly displaces the resident DNAPL and water in a plug flow manner. This process is schematically shown in Figure 3.5.2.5 for the water-IPA-naphtha system.

The cosolvent slug is bounded by the water/cosolvent interface on the upgradient side and by the cosolvent/resident fluid interface on the downgradient side. Stability at both interfaces must be considered to avoid excessive viscous fingering and/or gravity override/underdrive which deteriorate slug integrity. The size of the slug is then related to interfacial mixing at its upgradient and downgradient boundaries [Sievert et al., 1958; Blackwell et al., 1959; Habermann, 1960]. If the resident fluids are locally contacted by essentially pure cosolvent, a local condition may be created which plots very close to or within the miscible phase region of the ternary phase diagram. Under these conditions capillary forces arising from interfacial tension can be mitigated or altogether eliminated.

While the effects of cosolvents on dissolved plume behavior have been studied [Barker et al., 1992], no known field applications of in-situ cosolvent soil washing have been reported in the environmental literature. Site selection is currently under way for a pilot study of in-situ cosolvent soil washing of trichloroethylene (TCE) using ethanol which will be conducted in conjunction with the Robert S. Kerr Environmental Research Laboratory (RSKERL) in Ada, Oklahoma [Wood, 1992].

In 1959, it was reported that 39 miscible displacement projects (some of which included cosolvents) were being performed in the US for enhanced oil recovery from deep reservoirs [Habermann, 1960]. Displacements performed under these conditions are not directly transferable to the environmental industry owing to differences in hydrogeologic context and purpose. Although the field implementation cannot be adequately evaluated, certain aspects of its implementation are analogous to in-situ alkali and surfactant soil washing (sections 3.5.1 and 3.5.3) and the CROW® process (section 3.7.1).

Level of Demonstration and Performance--

Previous work in the area of chemical displacements, floods, and soil washing was principally

conducted using one-dimensional cores and LNAPLs, in which the LNAPL was displaced using a stable flood configuration with respect to either density or viscosity, or both [Everett et al., 1950; Offerlinga and van der Poel, 1954; Sievert et al., 1958; Gatlin, 1959; Gatlin and Slobod, 1960; Morrow et al., 1985]. Gatlin (1959) performed numerous alcohol floods of LNAPLs using methanol, IPA and tert-butyl alcohol (TBA) in various combinations. Floods were conducted in 1.059-inch ID, 100 ft long, galvanized steel pipes packed with Ottawa sand to porosities on the order of 35% and permeabilities of about 4 darcys. Cores were oriented vertically, and frontal advances were on the order of 6 ft/hr. Figure 3.5.2.2 shows the removal of naphtha by IPA for a stable slug size of 13.5 % pore volume. Gatlin (1959) examined the LNAPL removal for a variety of slug sizes and injection strategies and found that comparable LNAPL removal and smaller IPA requirements were possible when methanol was injected prior to the IPA slug, because methanol preferentially displaced the residual water.

Horizontally oriented, two-dimensional, miscible displacement experiments have been conducted by Habermann (1960). Radial displacement experiments using sands having permeabilities between 4.5 and 20 darcys were conducted for a variety of mobility ratios. The effect of adverse mobility ratios on displacement efficiency is illustrated in Figure 3.5.2.6. For $M \leq 1$, uniform propagation of the slug front occurs until the influence of the extraction point on the flow field causes rapid breakthrough of the slug.

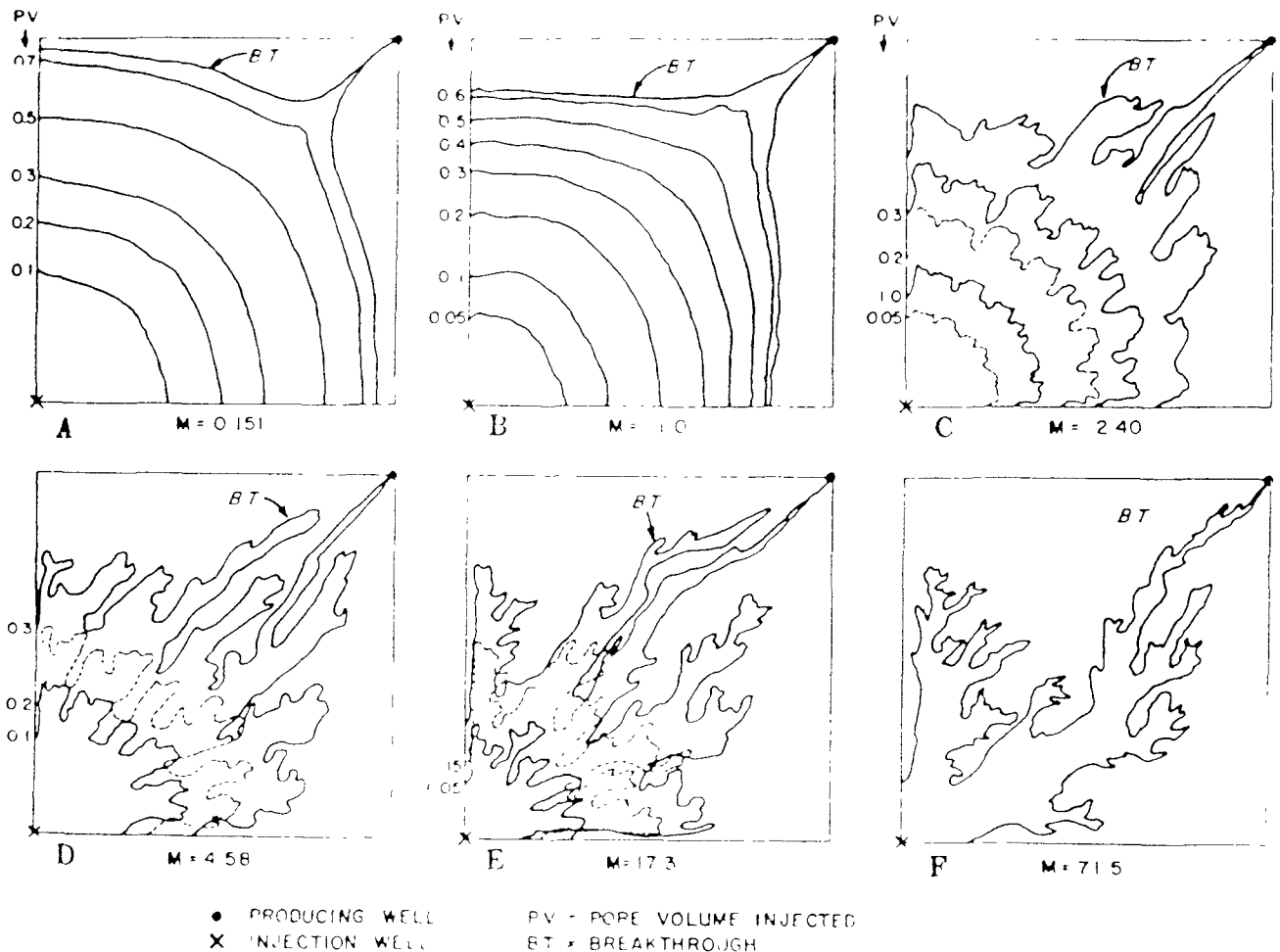


Figure 3.5.2.6 Effect of mobility ratio on displacement fronts and injected pore volumes until breakthrough using quarter of five-spot method [Habermann, 1960].

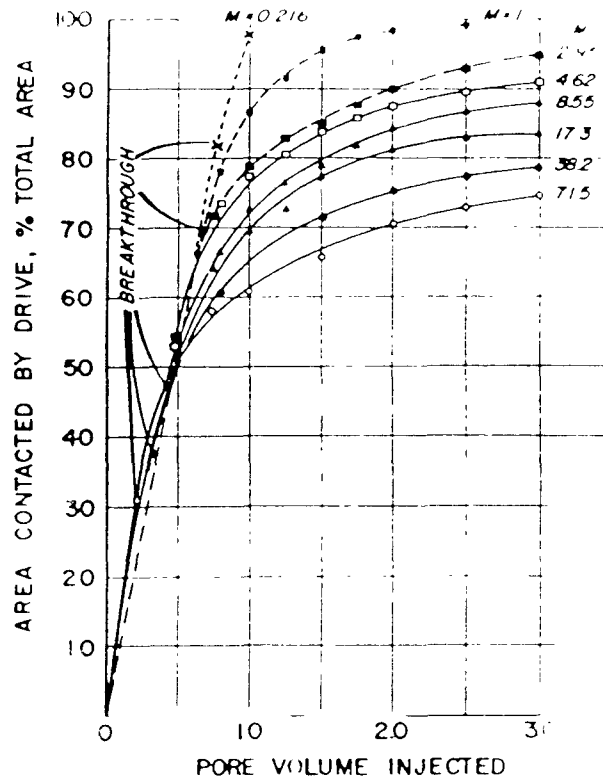
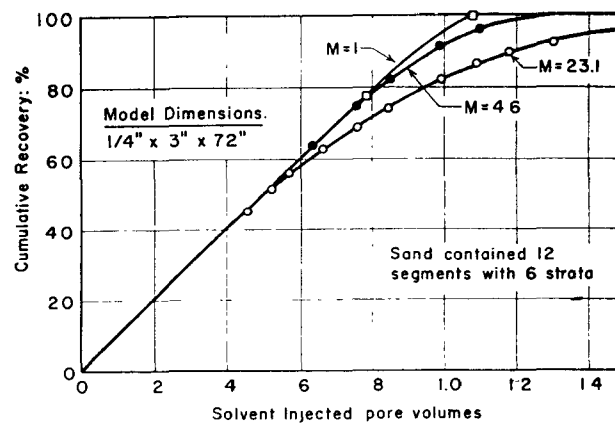


Figure 3.5.2.7 Area contacted by fluid drive after breakthrough, quarter of five spot method [Habermann, 1960].



PERMEABILITY PATTERN FOR SEGMENTED-STRATIFIED MODEL												
Layer	Segment											
	A	B	C	D	E	F	G	H	I	J	K	L
1	9.5	33.0	16.2	9.5	41.5	56.0	16.2	41.5	33.0	9.5	33.0	41.5
2	56.0	16.2	41.5	56.0	16.2	33.0	6.5	16.2	9.5	56.0	6.5	16.2
3	6.5	41.5	33.0	6.5	33.0	41.5	9.5	6.5	56.0	33.0	41.5	9.5
4	41.5	6.5	56.0	33.0	6.5	9.5	41.5	56.0	6.5	16.2	56.0	33.0
5	16.2	56.0	9.5	16.2	56.0	6.5	33.0	9.5	16.2	41.5	9.5	6.5
6	33.0	9.5	6.5	41.5	9.5	16.2	56.0	33.0	41.5	6.5	16.2	56.0

Figure 3.5.2.8 Effect of mobility ratio on fluid recovery from segmented-stratified porous media model [Blackwell et al., 1959]

At breakthrough, primary recovery accounts for a sweep efficiency of approximately 70% on an area basis, and appreciable secondary recovery can lead to total recoveries in excess of 90%, as shown in Figure 3.5.2.7.

Blackwell et al. (1959) investigated miscible displacement in lucite models containing heterogeneously packed sands. In one series of two-stratum experiments, a 3/8x6x72 in Lucite model was packed with two 3-in wide sand strata having permeabilities of 190 and 43 darcys, respectively. For an $M=1$, 4.6 and 75, oil recovery from the model after 2.5 pore volumes of cosolvent injection amounted to 88, 72, and 60%, respectively. Cross flow of cosolvent into the more permeable stratum and bypassing of the oil in the tight sand were observed. A second series of experiments was conducted in a 1/4x3x72 in Lucite model in which the sand was packed in a segmented-stratified configuration. Flow velocities of 41 to 72 ft/day were used. Sand "segments" (1/2 in wide and 6 in long) having permeabilities ranging from 6.5 to 56 darcys were arranged such that adjacent sand segment permeabilities were different, as shown in Figure 3.5.2.8. Oil recovery is also shown for three mobility ratios, illustrating that oil recovery can be appreciable in heterogeneous soils under controlled hydraulic conditions.

Boyd and Farley (1992) studied the 1-D displacement of TCE by IPA and examined flow stabilities and TCE recovery in upflow, downflow and horizontal configurations using flow rates of 18 ft/day. Displacement ($H_2O \rightarrow IPA \rightarrow TCE$) was conducted in 2.5 cm diameter, 80 cm long, glass chromatography columns packed with glass beads. As shown by the effluent concentrations presented in Figure 3.5.2.9a, TCE recovery in the downflow displacement occurred within two pore volumes, since viscous and gravity forces at the IPA/TCE interface complemented one another. However, IPA recovery was much slower since both M and buoyancy forces at the water/IPA interface were unfavorable in the direction of flow. The effluent history for the horizontal displacement shown in Figure 3.5.2.9b, illustrates that displacement efficiency is strongly influenced by the orientation of viscous and density forces.

Results of analogous experiments employing soils with a clay content of 16 wt% and using flow rates of 9.5 ft/day were consistent with the glass bead experiments except at small slug sizes. Poorer TCE removal at small slug sizes was attributed to possible TCE adsorption on clay surfaces [Boyd and Farley, 1992]. Considering that hydrophobic organic compound sorption to clay surfaces is low [Karickhoff, 1981], a more likely explanation is that pore clogging caused by migration of fines led to TCE entrapment. Sequential permeation of hydrocarbon contaminated water-wet clays by ethanol and water (in that order) resulted in the successful leaching of benzene by ethanol, and subsequently a two order of magnitude reduction in hydraulic conductivity after benzene removal [Fernandez and Quigley, 1985]. Similar results were obtained for other cosolvent-hydrocarbon pairs

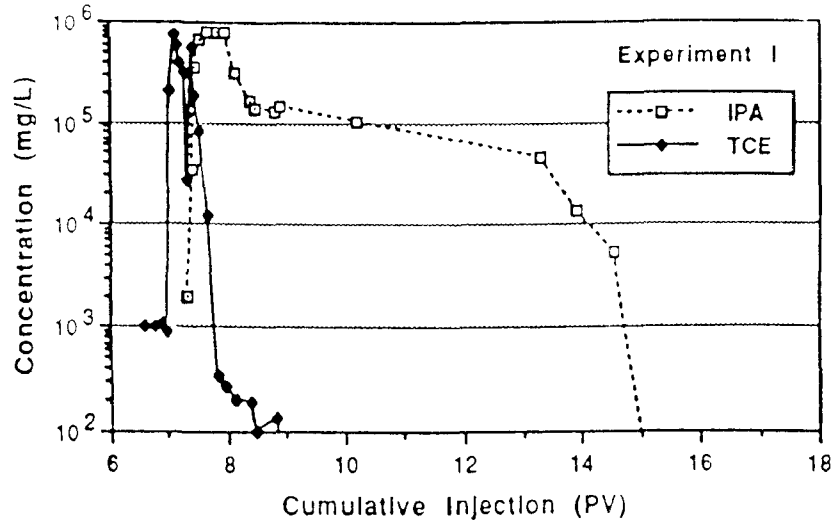
Wood et al. (1992) conducted elution experiments of 2.3 ± 0.3 ppm poly chlorinated biphenyl (PCB) contaminated soils using ethanol-water solutions in 2.54 cm diameter columns of 5 cm length. The soils possessed 2 g/kg organic matter content. PCB displacement efficiencies of 85.1, 96.1, and 98.3% were achieved for binary ethanol-water mixtures containing 47.5, 57, and 76% ethanol, respectively.

Applicability/Limitations--

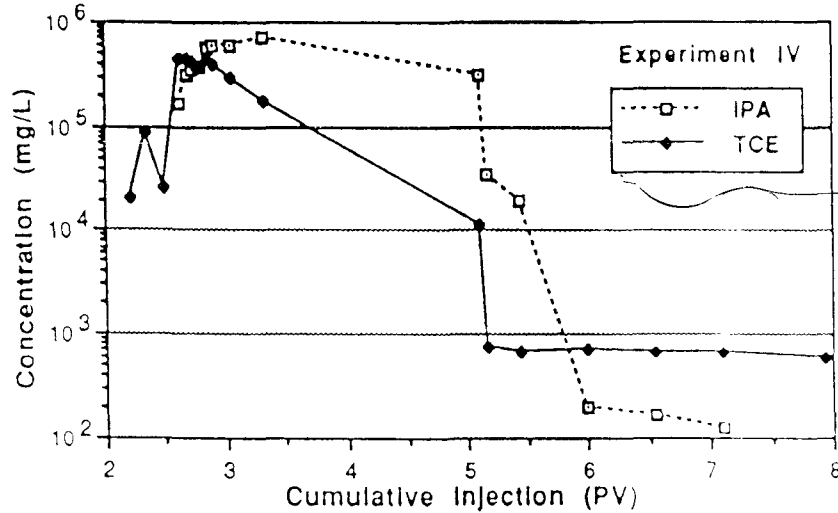
Theoretically, this technology can be applied to almost any DNAPL providing a cosolvent can be selected such that the phase behavior and the resultant changes in bulk liquid properties are favorable. Solubility enhancement and desorption of hydrophobic hydrocarbons from soils by cosolvents are widely acknowledged [Sørensen and Arlt, 1980; Fu and Luthy, 1986a,b; Prausnitz et al., 1986; Woodburn et al., 1986; Groves, 1988; Zachara et al., 1988; Rao et al., 1990; Broholm et al., 1992; Kan et al., 1992; Wood et al., 1992].

Interfacial instability ($M \geq 1$) caused by large viscosity differences (5-200 cp) of reservoir oils was among the primary reasons for deterioration of miscible slugs observed in petroleum recovery. Any

combination of compounds such as alkaline agents, surfactants, polymers (density enhancement) and viscosifiers may be added to the injectates to ensure a more favorable mobility ratio between the cosolvent and the DNAPL or to enhance the solubility of DNAPL components. Finally, displacement efficiency will be greatly affected by soil heterogeneities and cosolvent buoyancy.



(a) Experiment I. 100% IPA Injection. Free product recovery, IPA flood, and follow-up waterflood were conducted in the downflow direction



(b) Experiment IV. 100% IPA Injection. Free product recovery, IPA flood, follow-up waterflood were conducted in the horizontal direction

Figure 3.5.2.9 Comparison of effluent histories for (a) vertical and (b) horizontal $H_2O \rightarrow IPA \rightarrow TCE$ miscible displacements in soil cores. IPA \rightarrow TCE mobility ratios stable for both displacements whereas $H_2O \rightarrow IPA$ are not. The IPA \rightarrow TCE interface in (b) is unstable due to gravity effect, while the $H_2O \rightarrow IPA$ interfaces in both (a) and (b) are unstable [Boyd and Farley, 1992].

With the exception of borings, in-situ cosolvent soil washing is not likely to be intrusive; therefore, there are few limitations due to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The above ground hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

To prevent chemical interactions between well construction materials and pore fluids, stainless steel well construction may be required. Chemical interactions occurring between concentrated organic pore fluids and clayey soils may result in clay desiccation and cracking [Fernandez and Quigley, 1985; Mitchell and Madsen, 1987]. Co-metabolic assimilation of the remaining contamination by indigenous microorganisms may potentially occur after the main DNAPL displacement.

Cost and Availability--

Cosolvents have been employed on the full-scale in petroleum engineering applications. At present there is limited experience with this technology within the environmental community. Environmental applications are on the lab scale at this time, and a pilot study has been proposed.

Cosolvents appear to hold promise for cleanup of NAPL source areas, but many issues are unresolved at this time. However, because of density considerations, it is likely that cosolvents will probably be more effective for LNAPL cleanup rather than DNAPLs.

No cost information is available at this time. Major issues requiring consideration are cosolvent costs, cosolvent recycle, and effect of field scale soil heterogeneity on displacement efficiency.

3.5.3 Surfactant Soil Washing

Theoretical Background--

In-situ surfactant soil washing employs cationic, anionic or non-ionic surface active compounds to enhance contaminant removal. The primary mechanisms are: micellar solubilization of sparingly soluble hydrocarbons into the aqueous phase; coacervation of NAPL into a middle-phase emulsion; enhanced NAPL ganglia mobilization as a result of interfacial tension reduction; coalescence of individual NAPL ganglia into a NAPL bank; and the displacement of the NAPL bank to a recovery well by viscous forces. Although the exact displacement application differs, this process is in many ways identical to enhanced oil recovery methods utilizing steam, cosolvents, hot-water, or caustic floods [Shah, 1981; Janssen-van Rosmalen and Hesselink, 1981]. In fact, cosolvent and alkalis have often been used to complement surfactants [Reed and Healy, 1977; Shah, 1981; Clark et al., 1988; Manji and Stasiuk, 1988].

Two regions of low interfacial tensions may occur in surfactant systems: at low surfactant concentrations (0.1-0.2 wt% and often less) which corresponds to a two-phase system [Rosen, 1978; Shah, 1981; Vignon and Rubin, 1989]; and at high surfactant concentrations (2-10 wt% and often up to 30-40 wt%), which corresponds to a three-phase system containing a middle-phase microemulsion that is in equilibrium with the two bulk phases [Reed and Healy, 1977; Shah, 1981; Chan and Shah, 1981; Radke, 1993].

Micellization describes the process in which surfactant monomers form spheroid or lamellar structures possessing organic pseudophase interiors. At low surfactant concentrations, low interfacial tensions and pronounced solubility enhancement normally coincide with the onset of micellization in the aqueous phase, as shown in Figure 3.5.3.1 [Rosen, 1978; Shah, 1981; Chan and Shah, 1981]; under these conditions, the surfactant is described as being at its "apparent" critical micelle concentration. This will differ from the critical micelle concentration measured in pure water. Factors such as the aqueous phase salinity, hydrocarbon chain length (degree of hydrophobicity), and surfactant type (hydrophile-lipophile balance, HLB) and concentration affect the exact value of the apparent critical micelle concentration and

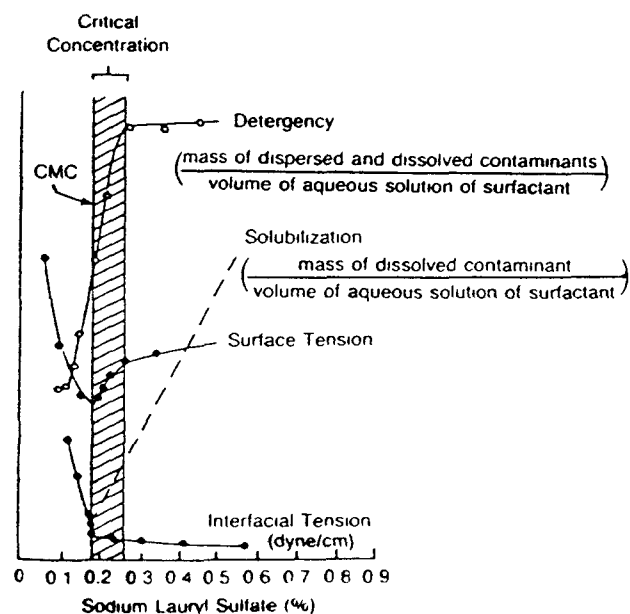


Figure 3.5.3.1 Physical property changes of aqueous solutions of sodium lauryl sulfate in vicinity of critical micelle concentration [Rosen, 1978]

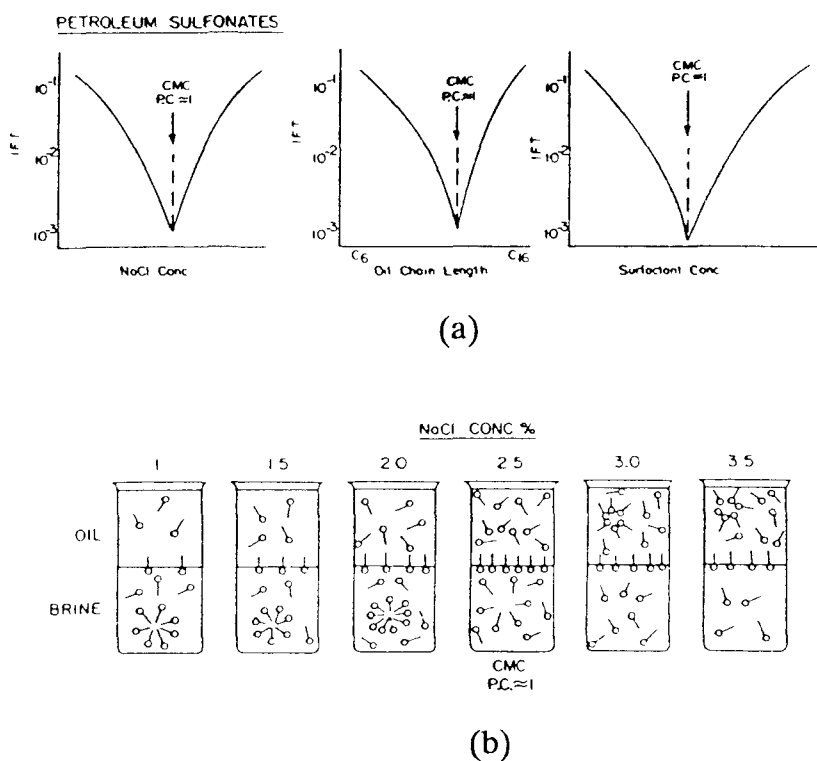
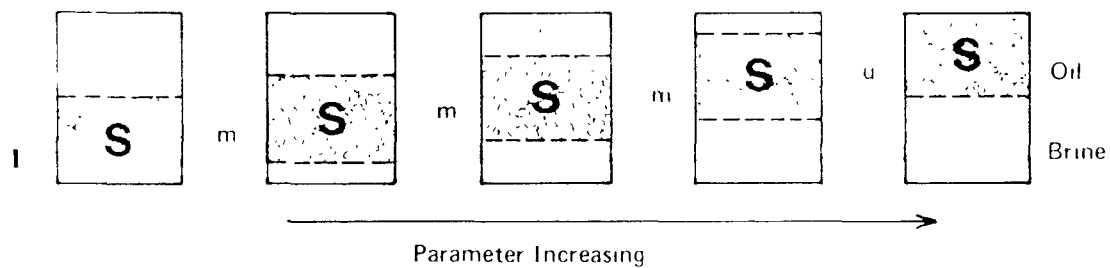


Figure 3.5.3.2 Relationships between salt concentration, oil chain length, surfactant concentration on (a) interfacial tension, and (b) surfactant partitioning and micelle formation in petroleum sulfonate systems [Chan and Shah, 1981].



The transition $I \rightarrow m \rightarrow u$ occurs by:

- 1 Increasing Salinity
- 2 Decreasing oil chain length
- 3 Increasing alcohol concentration (C_4, C_5, C_6)
- 4 Decreasing temperature
- 5 Increasing total surfactant concentration
- 6 Increasing brine/oil ratio
- 7 Increasing surfactant solution/oil ratio
- 8 **Increasing molecular weight of surfactant**

Figure 3.5.3.3 Schematic illustrating the $I \rightarrow m \rightarrow u$ transition and the factors influencing its determination in surfactant/oil/brine/alcohol systems [Shah, 1981].

extent of surfactant partitioning [Chan and Shah, 1981]. For example, Figure 3.5.3.2 illustrates the generalized effect of salinity on surfactant partitioning and phase behavior. At low salinity, the surfactant and micelles prevail in the aqueous phase, but as the salinity increases, "salting out" of the surfactant results in its partitioning into the NAPL.

Concentrated (>10 wt%) surfactant systems are characterized by complex phase behavior and middle-phase microemulsions whose formation is precluded at lower surfactant concentrations simply from mass considerations. Since water is more dense than oil, an emulsion resulting from surfactant accumulation in the denser aqueous phase is referred to as a lower (I) phase emulsion, using the petroleum engineering convention [Reed and Healy, 1977]. To avoid confusion arising from density considerations, it can also be referred to as Winsor type I emulsion [Winsor, 1954]. A middle (m) phase or Winsor type III microemulsion forms when the surfactant is concentrated at the water-NAPL interfacial region. Surfactant accumulation in the NAPL phase is referred to as an upper (u) phase or Winsor type II emulsion. These relationships are shown in Figure 3.5.3.3.

Much like Figure 3.5.3.2, Figure 3.5.3.3 shows that a continuum of phase behavior, and I-m-u transitions can be achieved by changing any of the following variables: aqueous salinity, surfactant concentration, hydrocarbon chain length, molecular weight of surfactant, cosolvent structure and chain length, surfactant/oil ratios, and surfactant/brine ratios [Reed and Healy, 1977; Salager et al., 1979; Shah, 1981; Graciaa et al., 1982]. Middle-phase or Winsor type III microemulsions are the most favorable emulsions for the displacement process because this emulsion: has ultra-low interfacial tensions (~ 0.01 - 0.001 dyne/cm) making displacement at realistic hydraulic gradients possible; contains large quantities of NAPL which enhances primary recovery; and is viscous, thus promoting residual NAPL mobilization and formation of a NAPL bank ahead of the microemulsion which enhances primary recovery.

Field Implementation--

Two strategies are considered, depending on the surfactant concentration used and whether simple

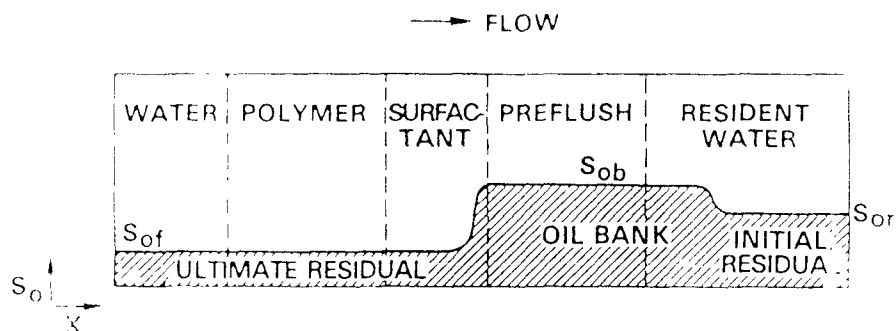


Figure 3.5.3.4 Schematic illustrating fluid bank formation as a function of saturation and distance in a surfactant/polymer flood [Reed and Healy, 1977].

solubility enhancement or a more displacement-like process is desired. Solubility enhancement entails continuous surfactant injection for a specified number of pore volumes in order to leach hydrocarbons out of the porous media. Low surfactant concentrations (<1 wt%) are usually employed for this purpose.

The displacement process is analogous to the cosolvent slug displacement process (section 3.5.1). Liquid-liquid displacement requires the injection of highly concentrated surfactant (10-40 wt%) as a finite slug. At the down-gradient interface of the slug, a concentrated and viscous middle-phase microemulsion and a NAPL bank are created. Successful mobility control of the middle-phase microemulsion and NAPL bank requires that the surfactant slug be driven by a polymer slug(s) of greater viscosity [Reed and Healy, 1977; Shah, 1981; Manji and Stasiuk, 1988]. This process is depicted in Figure 3.5.3.4.

Conventional injection and extraction well construction can be used for in-situ surfactant soil washing. Horizontal and vertical wells have been used (see below), and well placement strategy depends on the nature and extent of contamination, soil heterogeneities, and anticipated flow behavior once washing commences.

Level of Demonstration and Performance--

Solubility enhancement and desorption of hydrophobic hydrocarbons from soils by surfactants are widely acknowledged and documented [Winsor, 1954; Saito and Shinoda, 1967; Reed and Healy, 1977; Akstinat, 1981; Shah, 1981; Ellis et al., 1985; Kile and Chiou, 1989; Edwards et al., 1990; Aronstein et al., 1991; Rixey et al., 1991; Kan et al., 1992]. Numerous laboratory batch and column studies have demonstrated that NAPL recovery from porous media is greatly enhanced by surfactants [Thornton, 1980; Hesselink and Faber, 1981; Ellis et al., 1985; Vignon and Rubin, 1989; Abdul et al., 1990a,b; Abdul and Gibson, 1991; Kan et al., 1992; Soerens et al., 1992].

Several field applications of in-situ soil surfactant washing of DNAPLs have been conducted. An in-situ surfactant soil washing pilot study was conducted in a fire training pit at the Volk National Guard Base (WI). Subsurface soils had been contaminated with chlorinated organics (including DCM, chloroform, TCA, TCE) up to 3.5 ppm, and ground water contained total organics in excess of 300 ppm [Nash, 1988]. The sandy soils had a cation exchange capacity of 0.5 meq/kg, and organic matter content ranged from 0.037 to 1.5 wt% [Nash, 1988]. Chawla et al. (1989) cite data from two reports indicating that the soil had 5 to 15 wt% fines, hydraulic conductivities of 5.2×10^{-4} to 1.7×10^{-2} cm/s, and a depth to water table of 12 ft. Pits with dimensions of 1x1x1 or 2x2x1 ft were dug around each borehole (10 total) to aid in surfactant delivery. Laboratory testing indicated that a 1.5 wt% blend (50/50) of Adsee 799 (Witco) and Hyonic NP-90 (Diamond Shamrock) was capable of 74 to 94% NAPL recoveries within 12 pore volumes [USEPA, 1991c].

Based on these results, the aforementioned blend and six other synthetic and natural surfactant blends (3 each) were administered into the pits four times a day at an equivalent rate of 1.9 gal/ft² per day for a period of 4 to 6 days [Chawla et al., 1989; USEPA, 1991c]. This application rate corresponded to approximately 14 pore volumes of fluid. Three test holes clogged by the third day. Chemical analysis of soil samples taken from 2 to 4 and 12 to 14 inches below the bottom of the test holes revealed that no statistically significant contaminant removal had occurred [USEPA, 1991c]. Several mechanisms have been proposed: high contaminant sorption to soil organic matter [Chawla et al., 1989]; surfactant bypassed contaminated zone [Nash, 1986]; migration of fines caused pore clogging [USEPA, 1991c]; formation of micelles caused pore clogging [USEPA, 1991c]; and biological activity caused pore clogging [Vignon and Rubin, 1989].

In 1988, a field study of in-situ surfactant soil was conducted at a former wood treating facility in Laramie, Wyoming [Sale et al., 1989]. Sheetpiling was used to create a 27x27 ft test cell in alluvial soils to a depth of 12 ft where bedrock (shale) was encountered. The cell had an estimated pore volume (PV) of 5,000 to 5,500 gallons. Wood treating waste contaminated soils (SG=1.04, μ =54 cp) saturated the lower 3 ft of the alluvium. Soil contamination within the test cell was estimated to be approximately 93,000 ppm. A 4-inch surfactant delivery injection line and a vertically nested dual drain line were placed in parallel, and spaced 15 ft apart. The dual drain line had a 3 ft vertical spacing and was designed to simultaneously extract water and denser oils at different flow rates from the upper and lower drains, respectively [Sale and Pointek, 1988; Sale et al., 1988, 1989]. The test cell is schematically depicted in Figure 3.5.3.5.

Two surfactant/alkali/polymer blends were selected. Alkalis and polymers were selected because of wetting, surfactant sorption, pore clogging and mobility considerations. Blend 1 (10,000 gal) was used as a prewash to increase the amount of reusable oil and Blend 2 (20,000 gal) to attain lower cleanup levels. The blend compositions were: (Blend 1) 1.0 wt% sodium dodecyl benzene sulfonate (Polystep A-7®), 0.72 wt% NaHCO₃, 0.1 wt% Na₂CO₃, and 1,050 mg/l Xanthum Gum Biopolymer; and (Blend 2) 1.4 wt% ethoxylated nonphenol (Makon-10®, Stepan Chem. Co.), 0.65 wt% NaHCO₃, 0.825 wt% Na₂CO₃, and 1,050 mg/l Xanthum Gum Biopolymer. The primary waterflood (140,000 gal) and surfactant flood (30,000 gal) recovered 1,600 and 260 gal of oil, respectively. Residual oil concentrations of 15,500 and 5,100 ppm (soil) were estimated from an analysis of soil cores taken after water flooding and surfactant flooding, respectively. This constitutes an overall reduction of approximately 95% by weight. Water quality data indicated that approximately 99 wt% of the surfactants were recovered.

In 1990-91, a surfactant soil washing pilot study was conducted at the Canadian Forces Base Borden in Ontario, Canada [Fountain et al., 1990, 1991; Wunderlich et al., 1992; Fountain, 1992b, in press]. The Borden sands have a hydraulic conductivity in the order of 1×10^{-4} m/s. The organic carbon content and cation exchange capacity of these soils are very low. The Borden sands are extensively described elsewhere [Sudicky et al., 1983; Sudicky, 1986]. A sheetpile test cell having the dimensions of 3x3 m was socketed into the underlying clay aquitard located at a depth of 4 meters. A secondary sheet pile isolation system was also installed. Five surfactant and five injection wells were installed at opposite sides of the cell, as shown in Figure 3.5.3 6. Multilevel monitoring wells each with six sampling points were placed 0.3 m from each injection and extraction well [Fountain et al., 1990]. A total of 231 liters of PCE were released via a pipe into the center of the test cell, and undisturbed migration of PCE was permitted for two months. Pumping of pure PCE product which accumulated in the wells during this period recovered 48 liters of PCE. As part of the study, PCE infiltration was studied. Excavation of near surface soils to a depth of 1 m recovered 52 liters of PCE. The cell was subsequently backfilled with bentonite [Fountain, in press]. A water flood was then initiated which recovered an additional 12 liters of PCE.

After extensive surfactant testing [Fountain, et al., 1991], a 2 wt% solution of a 50/50 blend of nonylphenol ethoxylate (Alkasurf NP-10, Alkaryl Co.) and a phosphate ester of a alkylphenol ethoxylate (Rexophos 25/97, Hart Chem.) were finally selected for the pilot test. This blend lowered the water-PCE

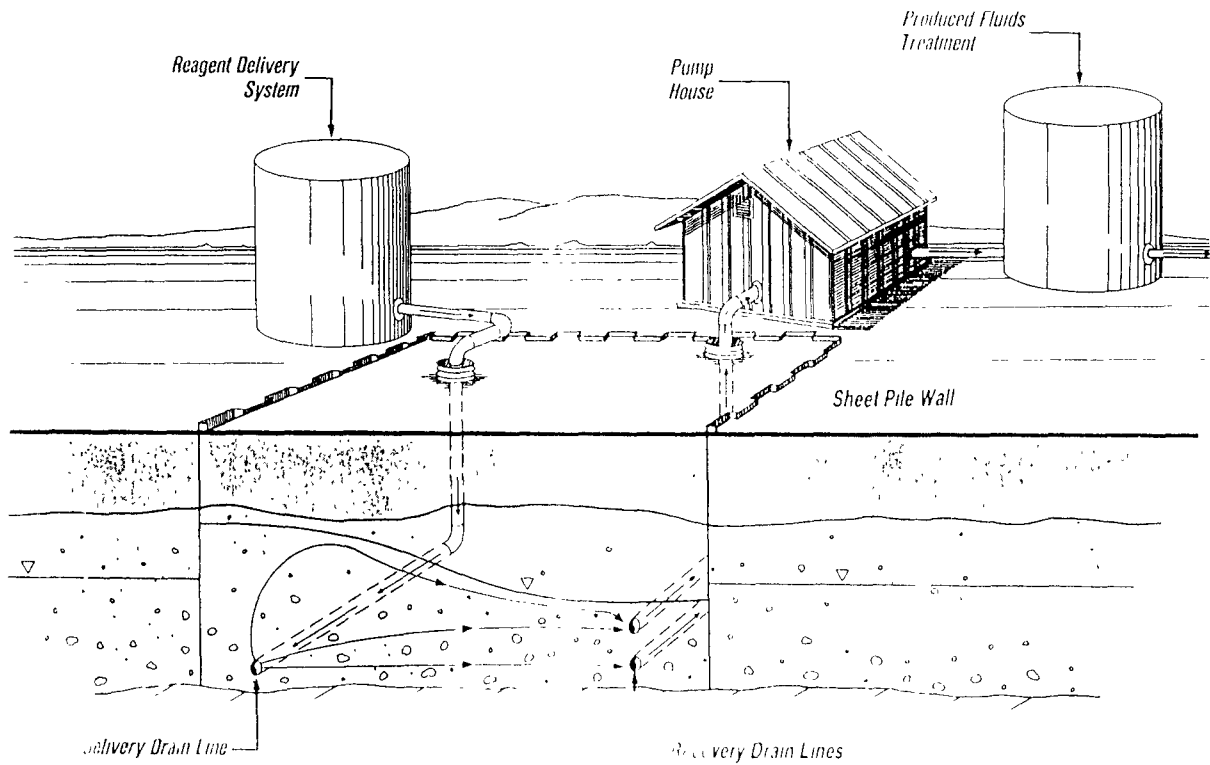


Figure 3.5.3.5 Schematic of dual drain line system for the 1988 field test using water and combined alkali/surfactant flooding of heavy oils [Sale et al., 1989].

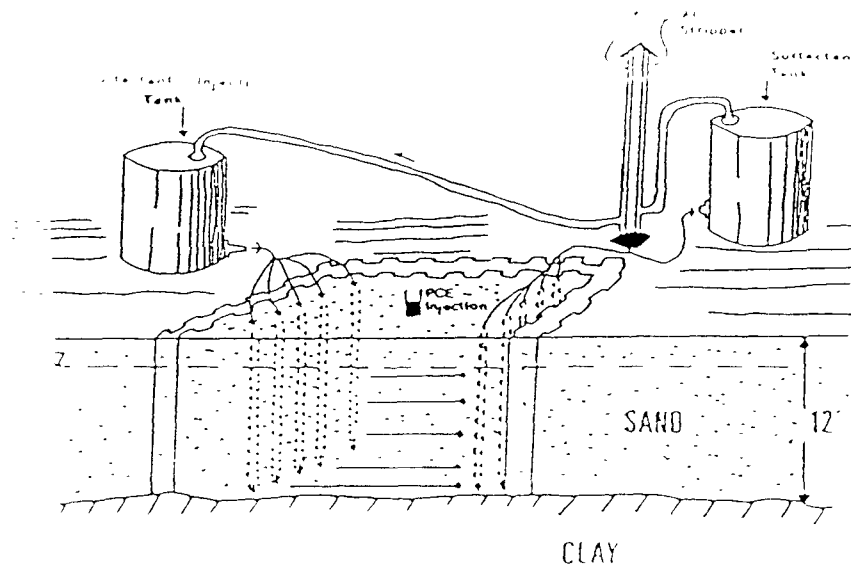


Figure 3.5.3.6 Schematic of field test using water and surfactant flooding for enhanced PCE recovery (Borden, Canada) [Fountain et al., 1990].

interfacial tension to 3.2 dynes/cm. The field test entailed the injection of approximately 14.4 pore volumes (1 PV=2400 gals) of surfactant over a 4 month period [Wunderlich et al., 1992]. Approximately 62 liters (27%) of PCE were recovered during the surfactant flood. The PCE concentrations in the effluent exceeded 4,000 ppm at its maximum, and dissolved PCE concentrations on the order of 12,000 ppm PCE were observed in the monitoring wells during flooding. Analysis of groundwater samples indicates that PCE concentrations have been reduced below 1 ppm over most of the cell [Fountain, in press]. Soil samples taken during flooding revealed that although some PCE had perched on fine soil lenses, this PCE was successfully removed. Other soil samples taken after surfactant flooding revealed that less than 10 liters of PCE remained within the test cell [Fountain, in press], or a total test recovery of 184 liters PCE (80%). Approximately 35-50 liters of PCE remain unaccounted for, and possible explanations for it include: volatilization of PCE; trapping of PCE near the edges of the test cell; and migration of PCE into fractures within the aquitard caused by the sheetpile driving [Fountain, in press]. While laboratory studies had indicated that rapid downward vertical migration of DNAPLs was possible when water-DNAPL interfacial tensions were lowered below 5 dynes/cm [Fountain et al., 1991], evidence indicates that this was not a problem during the pilot test [Fountain, in press].

Poly-chlorinated biphenyl (PCB) contaminated soils were the focus of a recent soil washing test in vadose soils [Abdul et al., 1992]. The test was conducted in a sandy fill material having a hydraulic conductivity on the order of 1×10^{-3} cm/s which extended to depths of 13 to 15 ft. The initial water table was at a depth of 4 ft. Soil cores revealed PCB and carrier oil concentrations up to 6,223 and 67,000 ppm, respectively. Estimates based on soil analyses indicated that approximately 15.3 kg of PCBs and 157.1 kg of carrier oil were present within the test cell. The 10 ft diameter test cell extended to a depth of 5 ft. Surface application of the surfactants required construction of a small berm. A 4-inch schedule 80 PVC extraction well was constructed in the center of the test cell with a screened interval at depths between 5.75 and 13.25 ft. Four 2-inch schedule 60 PVC monitoring wells were installed along the perimeter of the test cell. To measure the saturation response of the vadose soils, two sets of tensiometers and moisture measuring devices were installed within the test cell. The surfactant, a 0.75 wt% nonionic ethoxylated alcohol (Witconol SN70, Witco), was applied to the test cell at an average daily rate of 77 gal/day for a period of 70 days (5,375 gal total). Ground water containing leachates was extracted at an average daily rate of 157 gal/day (10,981 gal total). During the testing period, a total of 1.6 kg PCBs (10.5 wt%) and 16.9 kg (10.7 wt%) carrier oil were recovered.

A surfactant flood is currently being conducted at an industrial facility in Corpus Christi, Texas, where ground water has been contaminated with carbon tetrachloride [Fountain, 1992a, in press; Wunderlich et al., 1992]. The contaminated aquifer at the site is 4 m thick and is underlain by a thick clay deposit. The aquifer has an organic matter content of 0.025 wt%. Analysis of cores revealed carbon tetrachloride concentrations above 1100 ppm in the upper meter of the aquifer. Since no containment system was installed, potential downward migration of carbon tetrachloride was of obvious concern. Therefore, Witconol 2722 (Witco), a polysorbate, which was not the best solubilizer of carbon tetrachloride, was selected since it produced a water-carbon tetrachloride interfacial tension of about 10 dynes/cm. This value of interfacial tension was sufficient to prevent vertical migration of the carbon tetrachloride at the site. Thus, high solubilization was traded for added protection from potential downward migration of carbon tetrachloride free product. No results are available at this time.

Applicability/Limitations--

Theoretically, in-situ surfactant soil washing can be applied to almost any immiscible hydrocarbon providing a surfactant can be selected such that the phase behavior and the resultant changes in bulk liquid properties are favorable. Water-DNAPL interfacial tension reductions below 5 dynes/cm have resulted in rapid downward vertical migration of DNAPLs in laboratory studies [Fountain et al., 1991]. DNAPL recovery by surfactants will be greatly affected by soil heterogeneities.

Surfactant flooding was originally developed in the petroleum industry. Deep reservoir conditions such as high NAPL saturations, high NAPL viscosity, salinity, geologic confinement, scale of application, and the attainment of ultra-low interfacial tensions favor the creation of concentrated and viscous middle-phase microemulsions and banks to promote good sweep efficiency. An approach of this kind may be favored at sites like the former wood treating facility in Laramie, Wyoming, at which large-scale DNAPL contamination exists. However, for most other DNAPL-contaminated sites, micellar solubilization of DNAPLs using lower surfactant concentrations (<1 wt%) which provide moderate interfacial tensions seems most fitting in light of environmental sensitivity and the relatively small scale of contamination. Ongoing research will provide further insights into the applicability of ultra-low interfacial tensions to environmental remediation.

Surfactants themselves often reduce the viscosity of water, which often promotes unfavorable mobility ratios. If a more displacement-like operation is preferred over solubilization, any combination of compounds such as alkaline agents, cosolvents, polymers (density enhancement) and viscosifiers may be added to the surfactant to ensure a more favorable mobility ratio. However, compatibility issues arise and a careful study of the interactions of the surfactant blend (including any cosolvents and alkalis) with the field soils and pore fluids is essential or pore clogging, surfactant precipitation and sorption may result. Anionic and non-ionic surfactants are generally not prone to sorb to aquifer solids (organic matter interactions excluded), whereas cationic surfactants are; and they have been intentionally used to lower aquifer permeabilities [Brown et al., 1992; Burris and Antworth, 1992; Westall et al., 1992]. Many surfactants are biodegradable and non-toxic, and the anaerobic degradation of surfactants has been observed to be extensive on the time scale of months [Fountain, 1992a]. Therefore, the condition of the aquifer after surfactant washing should be favorable for continued biodegradation of any remaining hydrocarbons.

With the exception of borings, in-situ surfactant soil washing is not likely to be intrusive; therefore, there are few limitations due to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The above ground hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

Cost and Availability--

The hardware and surfactants required for in-situ surfactant soil washing are readily available. Expertise in this area is increasing rapidly in the environmental community. Surfactant soil washing has been demonstrated on the full scale in petroleum applications, and environmental field applications of surfactant soil washing have been completed. Several more field applications are planned.

Surfactants are good candidates for aquifer remediation of DNAPLs when used in conjunction with alkalis, cosolvents and viscosifiers. Surfactants will have their largest impact on DNAPL source areas. Application within fine-grained soils is not likely to be successful.

No information on costs is available at this time. Major issues requiring consideration are surfactant costs, surfactant recyclability, tankage requirements, and the effect of field scale soil heterogeneity on displacement efficiency. Since the emulsions created can be very stable and quantity of extracted fluids can be large, management of produced fluids can be problematic.

3.5.4 Water Flooding and Ground-water Extraction

Theoretical Background--

Water flooding and/or ground-water extraction, often referred to as pump-and-treat, is a process in which ground-water injection or reinjection and pumping is used for contaminant removal. The primary mechanisms are: increased recovery of the DNAPL as it responds to pumping stress in the aqueous phase

[Villaume, 1985; Wisniewski et al., 1985; Sale et al., 1989]; dissolution of the DNAPL components into the aqueous phase; and containment of the dissolved plumes. The first of these recovery mechanisms has been used alone and in conjunction with alkali and surfactant soil washing [Sale et al., 1989]. The response of a DNAPL under pumping stress is discussed here owing to its applicability as a remedial step at sites having widespread DNAPL contamination.

At extensively contaminated sites, that is, where sufficient separate phase is present, DNAPL flow to recovery wells may be induced simply by gravity or by the application of ground-water (hydraulic) gradients. However, the capillary pressure phenomena and considerations described in Sections 2, and 3.5.1 through 3.5.3 still apply. A related mechanism is the upconing of the interface between a dense fluid phase (i.e., saltwater, DNAPL) and ground water in response to pumping of the overlying ground water. Upconing of a dense fluid phase is initiated by total head reduction in each fluid phase in the vicinity of an extraction well [Muskat, 1982], as illustrated in Figure 3.5.4.1. When the fluids are miscible, as in the case of fresh and saltwater, the behavior of the interface can be described by a simple hydrostatic balance, i.e., the Ghyben-Herzberg approximation [Bear, 1972].

However, interfacial and viscous effects between water and DNAPLs may preclude the use of such a simplified approach, although it is often used as a first order approximation. DNAPL recovery is seen to be a function of the thickness of the DNAPL pool, capillary pressure, and the buoyant density and viscosity separate phase [McWhorter et al., 1992]. Based on theoretical calculations [McWhorter and Sunada, 1990], it is anticipated that DNAPL recovery can be maximized by utilizing small pumping rates [McWhorter et al., 1992].

Field Implementation--

Depending on the properties of the NAPL, conventional injection and extraction well construction equipment can be used for in-situ water flushing; and both horizontal and vertical well configurations have been used [Villaume et al., 1983; Villaume, 1985; Sale et al., 1988]. Well placement strategy depends on the nature and extent of contamination, soil heterogeneities, and anticipated flow behavior once water pumping commences.

For brevity, only the horizontal dual "drain line" approach is described here [Sale et al., 1988, 1989]. This vertically nested well configuration is shown in Figure 3.5.4.2a. By installing DNAPL recovery wells as close to the bottom of a DNAPL pool as possible; i.e., near stratigraphic depressions in underlying aquitards or bedrock, the DNAPL elevation head is maximized for recovery [Villaume, 1985]. Water recovery wells are nested directly above the DNAPL recovery wells at an elevation which accommodates upconing of the DNAPL interface.

Although pumping strategies are tailored to site specific needs, water recovery wells are usually pumped continuously. Once DNAPL is detected in the water recovery well, DNAPL recovery is initiated as illustrated in Figure 3.5.4.2b [Villaume et al., 1983; Sale et al., 1988]. DNAPL pumping is either intermittent, or continuous, but at a lesser rate than the water recovery well. Overpumping of the DNAPL well can decrease DNAPL recovery because DNAPL influx to the well is "pinched-off" when the cone of depression in the DNAPL phase is large and water influx results [Sale et al., 1988; McWhorter et al., 1992; USEPA, 1992a].

Level of Demonstration and Performance--

There are at least two documented instances in which the response of a DNAPL to pumping stresses in overlying ground-water has been used advantageously as an enhanced DNAPL recovery technique [Villaume, 1985; Sale et al., 1988].

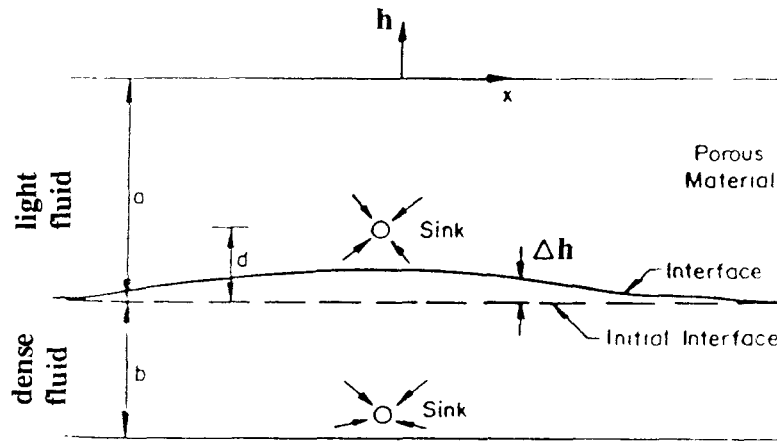


Figure 3.5.4.1 Schematic illustrating the upconing phenomena of a dense fluid phase to pumping stress in the overlying fluid phase [Wisniewski et al., 1985].

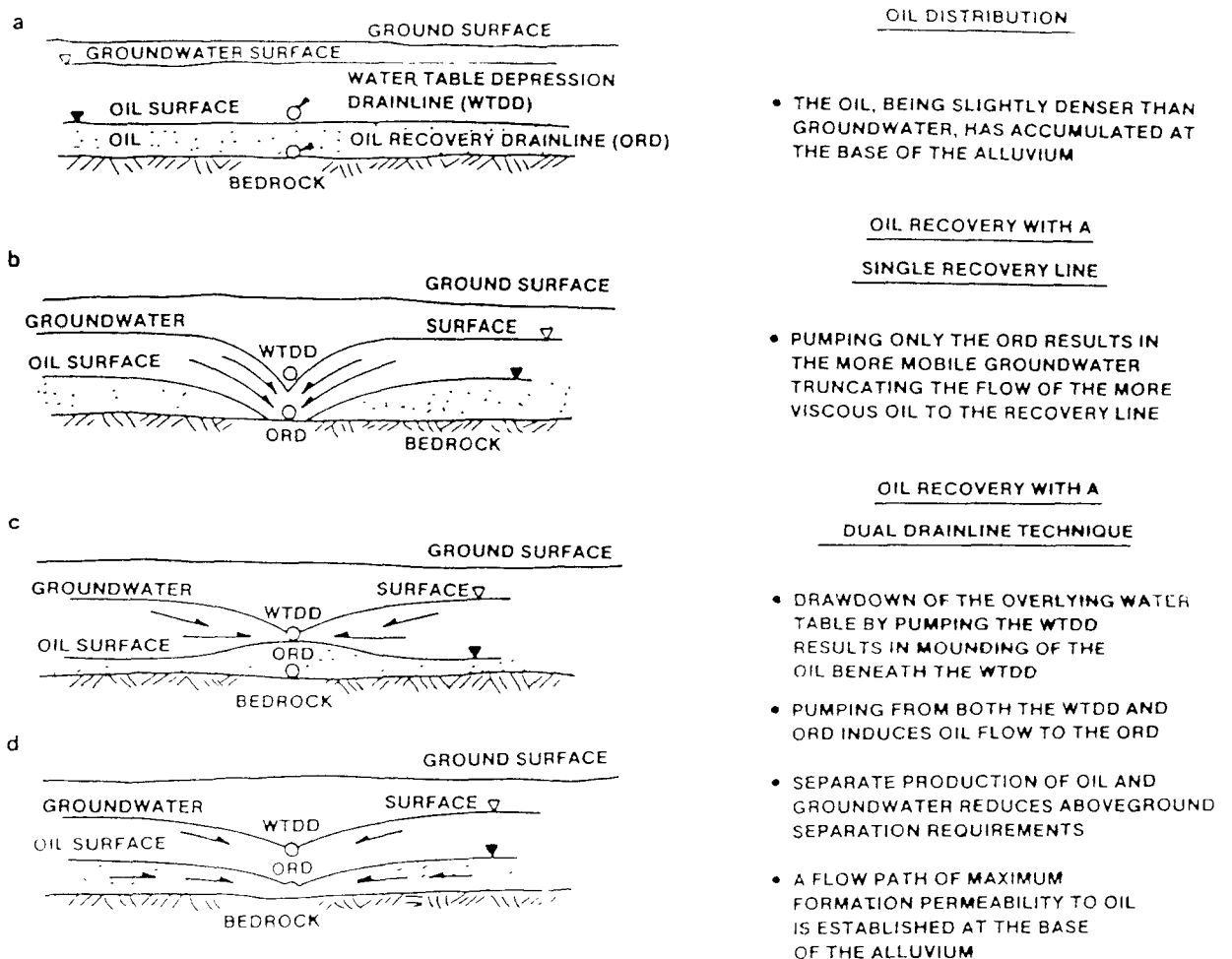


Figure 3.5.4.2 Schematic of dual drain line system for pumping of both light and dense fluid phase to enhance the recovery of the underlying, denser phase [Sale et al., 1988].

In the early 1980's, enhanced recovery of DNAPLs by water pumping was undertaken at a former coal gasification facility in East Stroudsburg, Pennsylvania [Villaume et al., 1983; Villaume, 1985]. The hydraulic conductivity of the near surface aquifer (clean sands and gravels) was approximately 5.3×10^{-3} cm/s. The aquifer, with a thickness of approximately 5 to 40 ft, is underlain by a silty sand stratum. This stratum behaved as an aquitard because its penetration by the pure phase coal tar was prevented by large capillary pressures. Approximate depths to ground water and natural hydraulic gradient were 10 ft and 0.015 ft/ft, respectively [Villaume et al., 1983]. In one area of the site, approximately 35,000 gal of coal tar (SG=1.02, μ =19 cp) was pooled in a stratigraphic depression on the underlying silty sand formation. The estimated thickness of the coal tar pool was 3-10 ft. The pure phase coal tar contamination was essentially confined to the sand and gravel aquifer because of capillary pressures.

One 4-inch and four 6-inch PVC wells were installed within a 30-inch gravel packed borehole to a depth of approximately 40 ft in the stratigraphic depression [Villaume et al., 1983]. Initially, only coal tar was pumped at a slow rate and approximately 100 gal/d of coal tar was recovered, but this recovery decreased rapidly owing to oil depletion in the vicinity of the well. At an elevation situated considerably above the static DNAPL surface, a packer was then installed in the central 4-inch well. Water removal then commenced at a slow rate, and extracted water was re-injected 65 ft upgradient. Using this approach, more than 8,000 gallons of coal tar having a water content of less than 1 wt% were recovered in nine months of operation.

In 1988, waterflooding was conducted at a former wood treating facility in Laramie, Wyoming [Sale et al., 1988] as a precursor to in-situ surfactant/alkali soil washing (see section 3.5.3). Sheetpiling was used to create a 27x27 ft test cell in alluvial soils to a depth of 12 ft where bedrock (shale) was encountered. The cell had an estimated pore volume (PV) of 5,000 to 5,500 gallons. Spent wood treating oils (SG=1.04, μ =54 cp) saturated the lower 3 ft of the alluvium. Contaminant concentrations in the soil within the test cell were estimated to be approximately 93,000 ppm. A 4-inch injection line and vertically nested dual drain line were placed in parallel, spaced 15 ft apart. The test cell is schematically depicted in Figure 3.5.3.5. The waterflood (140,000 gal) recovered 1,600 gal of oil. Residual oil concentrations of 15,500 ppm were estimated from soil core analyses. This constitutes a reduction of approximately 83 wt%.

Applicability/Limitations--

Waterflooding can be applied to enhance recovery from DNAPL pools; however, depending on the DNAPL, significant problems may be encountered as a result of chemical attack on downhole equipment [Villaume et al., 1983; Villaume 1985]. Thus far, only relatively light DNAPLs (SG<1.1) are known to have been recovered by this technique. Also, this treatment is suitable only as a precursor to other in-situ cleanup measures, since the residual concentrations of DNAPL will remain significant (approx 5-20 wt%) [Wilson and Conrad, 1984].

Simultaneous pumping of fluids from the water and DNAPL horizons can minimize ex-situ liquid separations requirements and increase DNAPL recycle [Villaume et al., 1983]. Since a large volume of fluids may be produced, water re-injection is often used.

With the exception of borings, in-situ soil washing is not intrusive and, therefore, there are few limitations due to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The above ground hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

Cost and Availability--

There are at least two published accounts which emphasize the use of upconing and pumping response strategies to enhance DNAPL recovery. Recovery of floating LNAPL product occurs by the same mechanism. The hardware required for in-situ waterflooding is readily available, and the requisite expertise

to design such systems exists within the environmental community.

Total operating and maintenance costs for the coal tar recovery were on the order of \$1,000/month, including repairs associated with chemical attack [Villaume et al., 1983]. Recovered coal tar (17,500 Btu/lb) was sold as a fuel supplement. Installation costs should be comparable to pump-and-treat.

3.6 AIR STRIPPING

Introduction--

In-situ air stripping processes generally rely on the air circulation through the subsurface to remove volatile DNAPLs from the subsurface. The applications considered herein, in-situ air sparging and vacuum extraction (section 3.6.1) and vacuum vaporizer wells (section 3.6.2), differ from conventional air stripping and soil vapor extraction in the vadose zone in that they operate in both the saturated and unsaturated zones.

Air sparging and vacuum extraction entail the injection of clean air directly into the saturated zone. Stripping occurs within the porous medium and volatilized contaminants are recovered by vapor extraction wells nested in the vadose zone. Vacuum vaporizer wells, or UVBs, create water recirculation cells within the porous media. Stripping is performed "in-well" and contaminant laden vapors are collected at the top of the well, while water is recycled back into the aquifer. UVBs can also simultaneously recover soil vapors from the vadose zone.

Both processes are diffusion limited, and apply to the recovery of volatile and semi-volatile DNAPLs only. Sparging may also result in uncontrolled migration of DNAPL out of the treatment zone. Enhanced biostimulation may be a beneficial by-product of both processes. Both technologies are commercially available and used.

3.6.1 Air Sparging and Vacuum Extraction

Theoretical Background--

Air sparging and vacuum extraction (ASP/VE) relies on the air stripping mechanism to remove volatile contaminants from the saturated zone. The injection, or "sparging," of clean air into the saturated zone is coupled with vacuum extraction to recover volatile contaminants within the vadose zone. While analogous to in-situ air stripping and vacuum extraction, the fundamental kinetics of ASP/VE have yet to be clearly elucidated. The ASP/VE design is empirically based [Marley et al., 1992a], and the design strategy revolves around the limitations imposed by subsurface geology, contaminant volatility, and the nature and areal extent of contamination.

As clean air is injected into liquid saturated, homogeneous, isotropic porous media, the region affected by a properly pressurized air sparger is assumed to be conical in shape, having some radius of influence, r_{inf} , as shown in Figure 3.6.1.1. The actual flow regime of the sparged air through the porous media is not clearly understood at this time. One theory suggests that air flows through the porous media as discontinuous spherical micro-bubbles, thus possessing a large surface area to volume ratio which favors partitioning of gases across the air-liquid interface [Loden and Fan, 1992; Sellers and Schreiber, 1992]. A second theory suggests that the air flows continuously in discrete and stable channels through pores which represent the paths of least resistance [Loden and Fan, 1992; Marley et al., 1992a]. While micro-bubbles can be generated using an in-situ diffuser to promote micro-bubble percolation, it is more likely that the actual flow regime is more channelized, owing to the coalescing of micro-bubbles under the operating injection rates.

Figures 3.6.1.2a and 3.6.1.2b schematically illustrate the influence that heterogeneities can have on the success of ASP/VE [Marley et al., 1992a; Martin et al., 1992; Loden and Fan, 1992]. Depending on the type and distribution of heterogeneities and the areal extent of subsurface contamination, different injection strategies may be required such as those pictured in Figure 3.6.1.3. The air spargers should be installed below the heavily contaminated soil zone, as shown in Figure 3.6.1.2, to permit the sparged air to contact and hence vaporize aqueous and separate phase volatile NAPLs, as well as to promote their desorption.

Vertical placement of injection wells is favored in coarser soils because they possess a low air entry pressure making a large r_{inf} possible, all other factors being equal. While the air entry pressure governs the lowest possible air injection pressure, the maximum injection pressure must be less than the soil fracturing pressure to prevent fracturing and the subsequent short-circuiting of air flow [Marley et al., 1992a]. However, a large r_{inf} may result in by-passing of contaminated soil zones due to sparger over-pressurization, as shown in Figure 3.6.1.4, or due to subsurface heterogeneities, Figure 3.6.1.2b.

The effective r_{inf} of an individual sparger (or system) can be gauged by: pressure response (>0.1 inches H_2O) of vadose zone to the applied vacuum; rise in water table elevation; increases in volatile contaminant vapor concentrations in the neighboring extraction wells; and increases in the dissolved concentration of oxygen in neighboring monitoring wells. R_{inf} on the order of 5 to 20 feet has been observed in coarse soils [Marley et al., 1992a,b], while r_{inf} in stratified environments has been observed on the order of 40 to 60 ft. [Marley et al., 1992a,b,c; Martin et al., 1992]. Other studies report that r_{inf} of 50 to 150 ft is possible [Gudemann and Hiller, 1988; Brown and Fraxedas, 1991; Brown et al., 1991], and r_{inf} has been reported to potentially extend up to 300 ft under sealed surfaces such as geosynthetics, paved areas, and buildings [Gudemann and Hiller, 1988].

Recovery of volatile NAPLs requires that vacuum extraction be continuous. Air sparging can be continuous, but in normal practice it is often pulsed. The combination of sparging in the saturated zone and reduced air pressures in the vadose zone often leads to increases in the ground water table elevation which can be on the order of several feet.

Aerobic in-situ biodegradation of NAPLs may result as a secondary benefit of ASP/VE. In fact, air sparging is often used as a means of oxygen delivery for in-situ aerobic processes (section 3.2.1). The stimulation of microorganisms as a result of oxygenation is often referred to as bioventing, and its contribution to overall removal is often reported, but is usually not accurately quantifiable. In one year-long air sparging and vapor extraction experiment, 23% mass reduction of gasoline was attributed to in-situ biodegradation [Johnson et al., 1992].

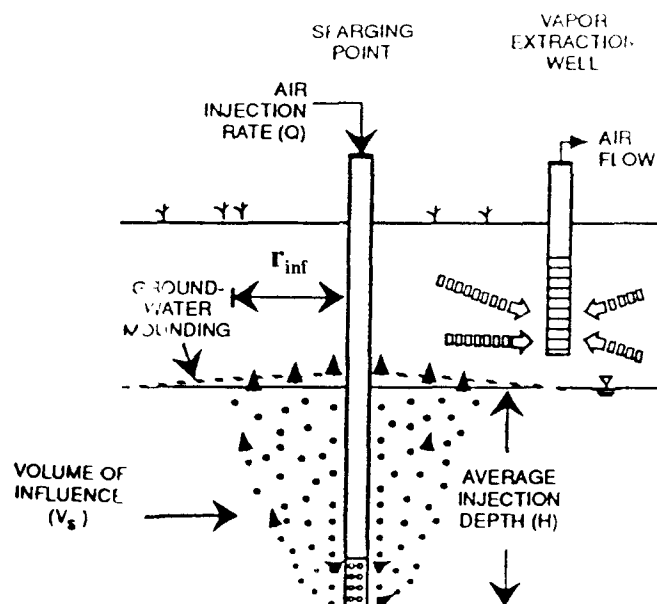
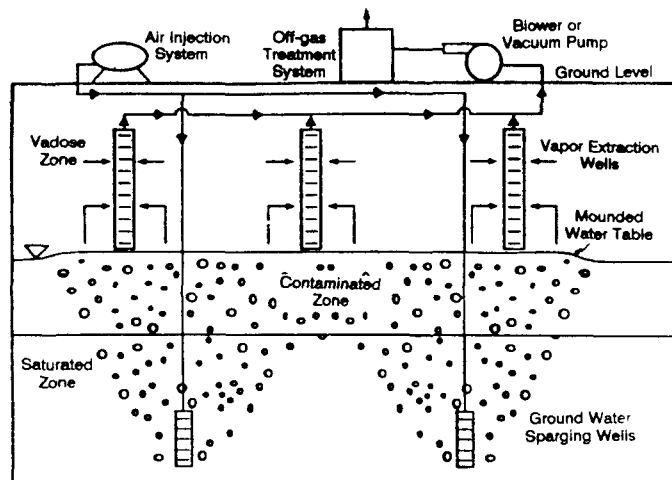
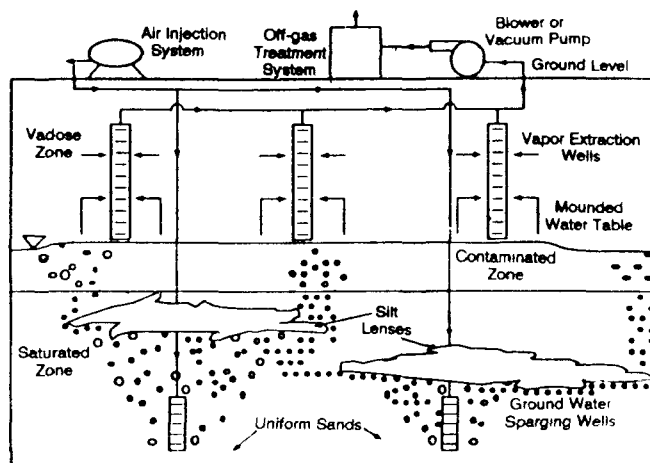


Figure 3.6.1.1 Schematic of air sparging/vacuum extraction system [Sellers and Schreiber, 1992].



(a)



(b)

Figure 3.6.1.2 Schematic of (a) typical air sparging system configuration and (b) the effect of subsurface heterogeneities on gas channeling [Marley et al., 1992a].

Field Implementation--

A good summary of the design of soil vapor extraction systems is presented in the Environmental Protection Agency's "Soil Vapor Extraction Technology: Reference Handbook" [1991d]. Construction of air sparging systems is essentially identical, with a few minor changes [Marley et al., 1992a; Martin et al., 1992]. The injection and vacuum well risers have often been constructed of 1- to 1.5-inch diameter PVC (schedule 40-80) or galvanized steel. Stainless steel construction allows for the heating of the injected air as well as operation in corrosive environments. Compatible well point screens have been fitted using threaded 10-slot or 20-slot PVC screen sections.

Screened intervals in injection wells are usually limited to 1 to 3 ft. Longer screen lengths are unwarranted because the air enters the porous media at the top of the screened interval; i.e., the point of lowest hydrostatic head. Vertical nesting of injection wells has been implemented, and header type manifolds are used to accommodate different injection pressures [Marley et al., 1992a; Loden and Fan, 1992]. Dual injection/extraction wells are common [Kresge and Dacey, 1991; Loden and Fan, 1992]. Extraction wells are fully screened in the vadose zone to within several feet of the capillary fringe to accommodate the water table mounding. The screened and riser zone backfill consist of coarse silica sand and bentonite, respectively.

Level of Demonstration and Performance--

Numerous sites in North America and Europe containing dense hydrophobic organic compounds are reported to have been remediated by ASP/VE to concentrations in the range of 10 to 1000 ppb [Brown, 1992; Loden and Fan, 1992]. Sites contaminated with PCE, TCE, TCA, 1,2-DCE, BTEX compounds, and petroleum compounds in sandy and silty soils are among those reported to have been successfully treated by ASP/VE [Marley et al., 1992a; Loden and Fan, 1992, Brown and Fraxedas, 1991]. A recent ASP/VE technology review highlights 21 ASP/VE applications, nine of which include DNAPLs [Loden and Fan, 1992]. Several other case studies are also available [Marley et al., 1992a; Martin et al., 1992; Middleton and Hiller, 1990, Brown and Fraxedas, 1991; Kresge and Dacey, 1991; Brown et al., 1991]. Table 3.6.1.1 highlights several applications at DNAPL contaminated sites, three of which are described below.

In Connecticut, a 4-week pilot study was conducted at a spill site in a 2,000 sq ft test cell with a depth of 40 ft [Marley et al., 1992a; Martin et al., 1992]. The subsurface consisted of stratified fine sands and silts. Initially, the water table was located at a depth of 20 ft. Ground-water TCE concentrations within the test cell ranged from 0.76 mg/l to 11 mg/l. Seven spargers were installed at depths of 27 to 40 ft. Intermittent pairs of air spargers were pulsed at injection rates of 3 to 10 scfm and pressures of 15 to 60 psi on a 4/2 hr or 3/3 hr (on/off) cycle because of problems encountered (see next paragraph). Two extraction wells were nested in the vadose zone. The extraction wells operated continuously at 70 scfm (combined) at vacuums of 15 to 20 inches H₂O. Four pounds of VOCs (primarily TCE) were recovered. Two weeks after shutdown, VOC concentrations were reported to have returned to background levels.

One finding of this study was that ground-water mounding was evident approximately 60 ft outside of the test cell. This mounding, and the consequent lateral migration of aqueous phase VOCs, resulted from the preferential horizontal air flow caused by soil stratification. Stratification also promoted short circuiting of air flow from spargers into monitoring wells nested at depths of 19 to 28 ft both inside and outside of the test cell. In these monitoring wells, the VOC vapor concentrations were as high as 150 ppm. To mitigate these effects, pulsed injection rather than continuous injection was practiced.

Full-scale ASP/VE was used at a site in Germany with a subsurface characterized as quaternary sands and gravels to a depth of 110 ft [Gudemann and Hiller, 1988]. The water table was situated at a depth of 27 ft, and a silty sand layer was located at depths of 44 to 47 ft. The unsaturated and saturated zones were contaminated with TCE and PCE. The soil was vented for 100 days using two extraction units capable of 475 scfm flow. Venting alone recovered 5100 lbs of solvents (combined TCE and PCE). Sparging then commenced using six-injectors at depths of 37 ft with flow rates of 6 scfm. Ground-water concentrations decreased from an initial 33 ppm to 0.027 ppm in 3 months. ASP/VE treatment removed a total of 8900 lbs of solvents in 8 months of application.

In the United States, full-scale ASP/VE was used at a site underlain by coarse sands which had been contaminated by PCE, TCE, TCA, 1,2-DCE, and petroleum hydrocarbons (TPH) [Brown et al., 1991]. The water table was located at a depth of 11 to 14 ft., and subsurface contamination appeared to be concentrated in the intervals of 3 to 9 ft and 15 to 18+ ft, below the ground surface. Initial readings in ten ground-water monitoring wells included: a high of 41,000 ppb total VOCs (excluding TPH); two below

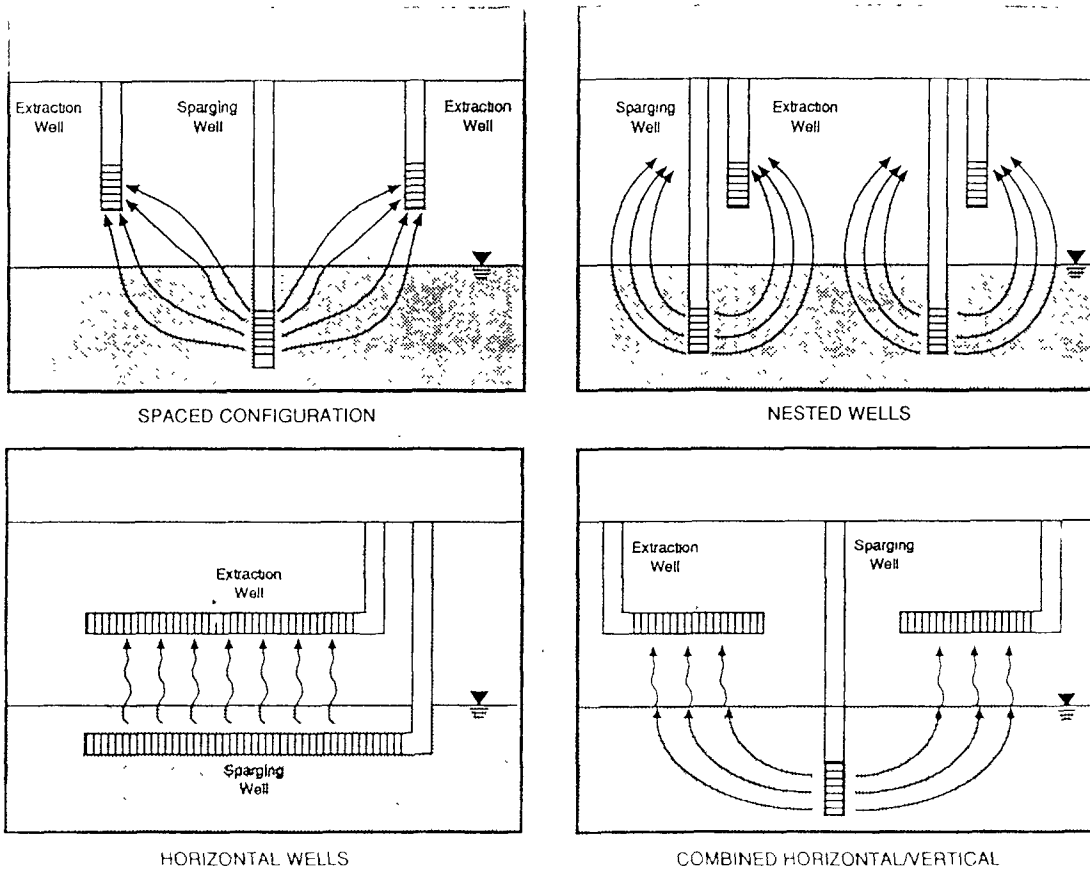


Figure 3.6.1.3 Possible air sparging well configurations [Loden and Fan, 1992].

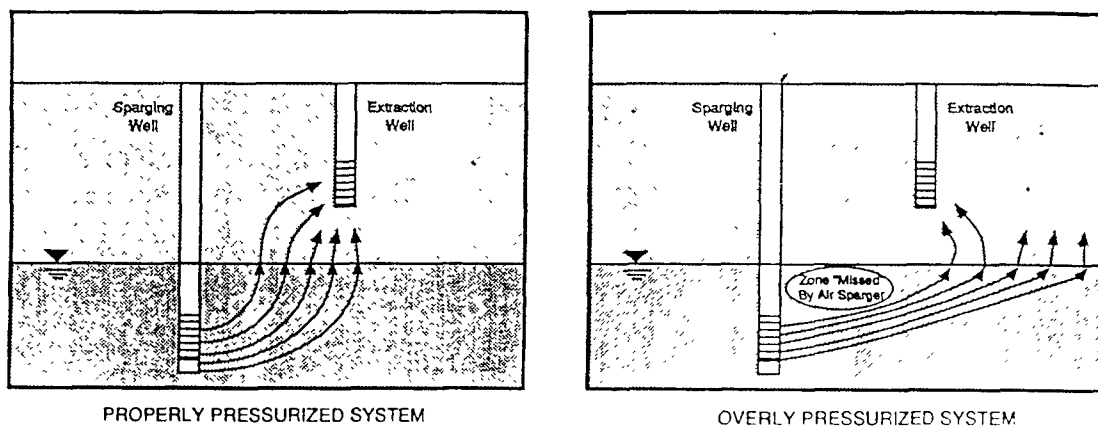


Figure 3.6.1.4 Effect of gas injection pressure on air sparging system [Loden and Fan, 1992].

detection levels (BDLs); a ten well average of 5685 ppb; and, a median of 1137 ppb. The ASP/VE system consisted of seven spargers, seven dual sparger/extraction wells, and one extraction well. The dual wells were installed to depths of approximately 33 ft, and the seven spargers were installed to 7 to 9 ft below the water table.

First, a vacuum (20-30 inches H₂O) was applied by the 8 extraction wells at a combined flow of 450 scfm. Sparging then commenced in the dual wells using a blower capable of delivering 270 scfm at 10 psi (specific operating parameters not provided). The remaining spargers were then engaged. After 125 days of ASP/VE treatment and one week of shutdown, VOC concentrations in the ten monitoring wells averaged 130 ppb, had a median of 13.5 ppb, a high of 897 ppb, and two BDLs. ASP/VE removed approximately 900 lbs of PCE and TCE from the subsurface.

Information on the long term efficacy of ASP/VE is lacking. In one full-scale implementation of ASP/VE at a site contaminated with up to 10,000 ppb total BTEX compounds, ground-water concentrations were reduced to approximately 600 ppb BTEX and less than 0.5 ppb benzene and remained stable for a period of 6 months after sparging was shut down [Marley et al., 1992a].

Applicability/Limitations--

Sites contaminated with dissolved volatile and semi-volatile hydrocarbons possessing Henry's constants greater than 10^5 atm-m³/mole are good candidates for ASP/VE treatment, depending on subsurface conditions. To obtain sufficient in-situ air flow in the saturated zone, a minimum soil hydraulic conductivity of 0.001 cm/sec is required [Middleton and Hiller, 1990]. While sites underlain by gravel, fill, sand, and sandy and silty lenses have been treated by ASP/VE, the process is strongly controlled by stratigraphic heterogeneities; and therefore, careful well placement and a site specific clean-up strategy is required. In addition, to mitigate potential lateral spreading of contaminants, peripheral containment or extraction wells may be required [Marley et al., 1992a,c; Martin et al., 1992].

Many authors state that the intended use of ASP/VE is to remediate contaminants in the aqueous phase and sorbed on the soil [Felten et al., 1992; Loden and Fan 1992; Marley et al., 1992a,b,c; Sellers and Schreiber, 1992; Leonard and Brown, 1992]; but considering that sparging occurs below the zone(s) of contamination and the relatively low sorption potential of coarse soils, it is likely that NAPL lenses are affected by spargers. Since air sparging changes the pressure regime within the vicinity of the sparger, NAPLs may be potentially mobilized laterally beyond the treatment zone, or vertically downward below the sparger.

The question of the presence of sparged air as discrete micro-bubbles or stabilized air channels has very different implications in terms of mass transfer limitations and potential mobilization of NAPLs. Sellers and Schreiber (1992) developed a simple air sparging model which estimates clean-up times and ground-water concentrations. Sparged air is modeled as discrete micro-bubbles, and the model suggests that contaminant removal is diffusion limited. In two simulations using published field data, the results of the Sellers and Schreiber model compared favorably with the field observations of Marley et al. (1990, 1992c), but not those of Brown et al. (1991).

A 3-D air sparging model using Darcy's Law for multiphase flow compared well with two sets of actual field data [Marley et al., 1992b]. This model compares predicted and measured air pressure distributions and flow velocities in the subsurface. It is not clear whether the sparged air is treated as discrete micro-bubbles or as stable channels. However, the actual flow regime, whether pulsed or continuous, may have important consequences. If air flow occurs as stable channels, the removal process will be mass transfer limited. Subsurface contamination by semi- and non-volatile DNAPLs may be potentially exacerbated by the preponderance of stable channels in the saturated zone. The spreading behavior of certain DNAPLs may permit them to migrate as films along the air-water interfaces (see section

TABLE 3.6.1.1 SUMMARY OF DATA PUBLISHED ON AIR SPARGING SITES [adapted from Loden and Fan, 1992].

SITE, CITATION	SOIL TYPE	COMPOUNDS	CLEANUP TIME* (MONTHS)	INITIAL GW CONCENTRATION (PPM)	FINAL GW CONCENTRATION (PPM)	DEPTH TO GW TABLE (FEET)	NO OF SPARGERS, EXT WELLS	SCREEN DEPTH (FT)	INJ. PRESSURE/ FLOW RATE (IN H ₂ O)/(CFM)	OTHER
Berlin Harsco Geotechnics, 1989	Sand, silt lenses Aquitard-clay	c-1,2-DCE, TCE, PCE	24	c-1,2-DCE > 2	c-1,2-DCE < 0.440	15-18	3, 1	--	--, --	
Bielefeld Northern-Westfalen Harsco Geotechnics, 1989	Fill, sand, silt Aquitard-Siltstone	PCE, TCE, TCA	11	PCE 27, TCE 4.3, TCA 0.7	Total VOCs - 1.207	2-8	5, 2	--	--, --	
Munich, Bavaria Harsco Geotechnics, 1989	Fill, gravel, sand Aquitard-clayey silt	PCE, TCE, TCA	4	PCE 2.2, TCE 0.4, TCA 0.15	PCE 0.539, TCE: 0.012 TCA 0.002	15	7, 1	--	--, --	
Plüderhausen, Baden-Württemberg Harsco Geotechnics, 1989	Fill, silt, gravel Aquitard-clay	TCE	2	1.20	0.023	11	5, 1	--	--, --	
Solvent Spill Middleton and Hiller, 1990	Quaternary sand & gravel	TCE, PCE	3	Total VOCs - 33	Total VOCs - 0.27	27	5, 2	--	--, 30	Extraction flow rate - 475 cfm
Solvent leak at Degreasing Facility Middleton and Hiller, 1990	Fill, sandy and clayey silts	TCE	2	0.200 - 12	< 0.010 - 0.023	18 - 20	5, 1	--	--, --	
Chemical Manufacturer Middleton, et al., 1990	Sandy gravel Aquitard-clay	halogenated hydrocarbons	9	THH - 1.9 - 5.417	THH - 0.185 - 0.320	8	8, 4	--	--, --	
Dry Cleaning Facility Brown, et al., 1991	Coarse sand Natural clay barrier	PCE, TCE, DCE TPH	4	Total VOCs - 41	Total VOCs - 0.897	13	7, 1 7 nested sparge/vacu m	2' sparge 8 vacuum	277, 225	40 in H ₂ O vacuum Extraction flow rate - 500 cfm (2) 1800 lbs GAC vapor treatment
Mannheim - Kaefertal Herrling, et al., 1991	Sand	PCE, chlorinated hydrocarbons	--	--	--	33	1 w/gw recirc and extract	--	--, --	19.7 in H ₂ O vacuum Extraction flow rate - 300 cfm Activated Carbon vapor treatment
Savannah River Site Looney, et al., 1991	Sand, silt & clay	TCE, PCE	3	TCE 0.5 - 1.81 PCE 0.085 - 0.104	TCE 0.010 - 1.031 PCE 0.003 - 0.124	135	1, 1 (horz)	-300 (sparge) 205 (vacuum)	10-15, 165-185	130-145 in H ₂ O vacuum Extraction flow rate 0 - 935 - 1020 cfm
Pilot-Scale (CT) Marley et al., 1992a Martin et al., 1992	Fine sands, silts	Mainly TCE PCE, DCA, TCA	1	TCE 0.96 - 11	Background	15 - 20	7, 2	2' sparge	-5, -15-30 psi	Extraction flow rate 70 cfm @ 15 - 20 in H ₂ O
Pilot-Scale (NY) Leonard & Brown, 1992	Sandy fill Alluvial sands	TCE, PCE, TCA, DCE, DCA, VC, Toluene	--	Chlorinated VOCs 0.35 - 71	-	6	1, 1	2 sparge	4-8 psi, --	
Case 2, Germany Gudemann and Hiller, 1988	Sands, silts gravels	TCE	3	6.9 - 20	0.023	--	9, 6	--	--, 6	
Case 3, Germany Gudemann and Hiller, 1988	Sandy gravels	halogenated solvents	9	1.9 - 5.4	185 - 32	8	8, --	- 1' sparge	--, -	Extraction flow 165 cfm

* Cleanup time indicates the time interval between the initial and final ground-water concentrations reported in this table. Total site remediation may be longer.

2.2.4). Under these conditions, potential downward migration of DNAPL out of the treatment zone may result.

With the exception of borings, ASP/VE is not intrusive; and therefore, few limitations are present with respect to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The above ground hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment [USEPA, 1991d]. Some of these systems can be automated, monitored and operated from remote locations.

ASP/VE may stimulate in-situ biological degradation through oxygenation of the subsurface which may lead to biological fouling. Precipitation of metal carbonates and oxides may clog the aquifer [Felten et al., 1992]. Despite its empirical nature and its drawbacks, ASP/VE has been very successful in attaining negotiated cleanup goals relatively quickly-- on the order of several months in many cases.

Cost and Availability--

ASP/VE was developed specifically as a physical-chemical treatment technology in Germany in the mid-1980's [Gudemann and Hiller, 1988]. However, earlier incorporation of ASP/VE as an oxygen delivery system as part of in-situ biological treatment in the saturated zone occurred in the late-1970's to early 1980's in the US [Marley et al., 1992a]. Regardless of its actual origin, Loden and Fan (1992), in a recent technology review report that hundreds of sites (presumably contaminated with volatile hydrocarbons including DNAPLs) within the US and Europe have been remediated by ASP/VE. See Table 3.6.1.1 for data specific to dense hydrophobic organic compounds. The hardware for ASP/VE is readily available as is the expertise.

ASP/VE is a good candidate for remediating dissolved phase plumes of volatile hydrocarbons in aquifer media. Hot-air injection is likely to enhance stripping. The potential mobilization of the separate phase makes its application to spreading DNAPLs questionable.

Costs are site specific, and reporting of ASP/VE costs has been poor. The pilot study which recovered 4 lbs of VOCs (primarily TCE) cost approximately \$140,000. Using an estimated test cell volume of 80,000 cu ft, this cost translates to approximately \$50/yd³. Using soil vapor extraction alone as a benchmark of approximately \$50/yd³, full scale ASP/VE is estimated to be approximately \$75-\$125/yd³ [Fan, 1992]. Discharged vapors are normally treated by granular activated carbon units.

3.6.2 Vacuum Vaporizer Wells (UVB)

Theoretical Background--

Vacuum-Vaporizer-Wells (UVB, in German: Unterdruck Verdampfer Brunnen) rely on the air stripping mechanism to recover volatile DNAPLs. In-situ air stripping is achieved in two ways: actively, by direct "in-well" stripping of volatile NAPLs from the ground water; and, passively, by soil vapor extraction in the vadose zone which may recover volatile compounds emanating from dissolved plumes [Herrling et al., 1992a,b]. Since the emphasis of this document is on the saturated zone applications, soil vapor extraction is not formally addressed here. However, a good summary of soil vapor extraction systems is available [USEPA, 1991d].

The effectiveness of the UVB to remediate a contaminated aquifer depends on compound solubility and volatility, and the ability of the UVB to recirculate treated ground water within the aquifer. The essential components of the UVB design include the circulation system, sphere of influence, and capture zone of an individual UVB or UVB field [Herrling et al., 1991, 1992a; Herrling and Stamm, 1992a]. UVB differs from traditional ground-water wells in that the generated radial flow regime is not strictly horizontal: non-negligible vertical components of ground-water velocity exist. In quiescent ground-water environments, the

three-dimensional flow field can be represented by a simple two-dimensional (2-D) streamline analysis [Herrling et al., 1991, 1992a].

Figure 3.6.2.1a depicts the symmetric vertical recirculation pattern and streamlines created by a UVB. Figures 3.6.2.1b,c are cross sections taken through the UVB normal to the flow direction which illustrate the general effect of the overall ground water flow regime on the recirculation pattern. However, the actual radial flow pattern generated by the UVB is asymmetric in three dimensions. Therefore, analyses using curved separating stream surfaces and particle tracking methods are often used to delineate UVB capture zones [Herrling and Buermann, 1990; Herrling et al., 1991]. Anisotropic effects can be incorporated as well. Figure 3.6.2.2 schematically shows the 3-D capture zone of the contaminated ground water. The recycling of treated water in the upgradient direction depresses the flow lines along the path of the contaminated water to the UVBs, thus making the capture zone within the aquifer wider at the bottom than at the top. By overlapping capture zones, dissolved plumes of volatile DNAPLs can be effectively treated. UVBs can also be placed in parallel, that is, a second UVB is placed immediately downstream of the first UVB to provide additional stripping [Herrling et al., 1992b].

Field Implementation--

Three configurations of the UVB apparatus are illustrated in Figure 3.6.2.3. The well configuration shown in Figure 3.6.2.3a has a separation plate dividing the UVB into two distinct regions: an "extraction" region in which ground-water extraction occurs; and a "stripping" region in which air stripping, vapor extraction, and ground water recirculation occurs [Herrling et al., 1992a]. Contaminated ground water enters the well via the lower well screen and exits via the upper well screen after being air stripped. Clean air, drawn from outside the well, enters the water column through an adjustable "pinhole plate" apparatus. The pinhole plate is situated at an elevation in the water column corresponding to sub-atmospheric pressure. The upward flow of the bubbles creates an "in well" stripping region, and due to the efficiency of mixing, an air/water ratio of 10:1 is achieved [Herrling et al., 1991]. Contaminant laden vapors from stripping, and soil gas vapors from the vadose zone which entered the UVB through the unsaturated portion of the upper well screen, are exhausted to the off-gas treatment system.

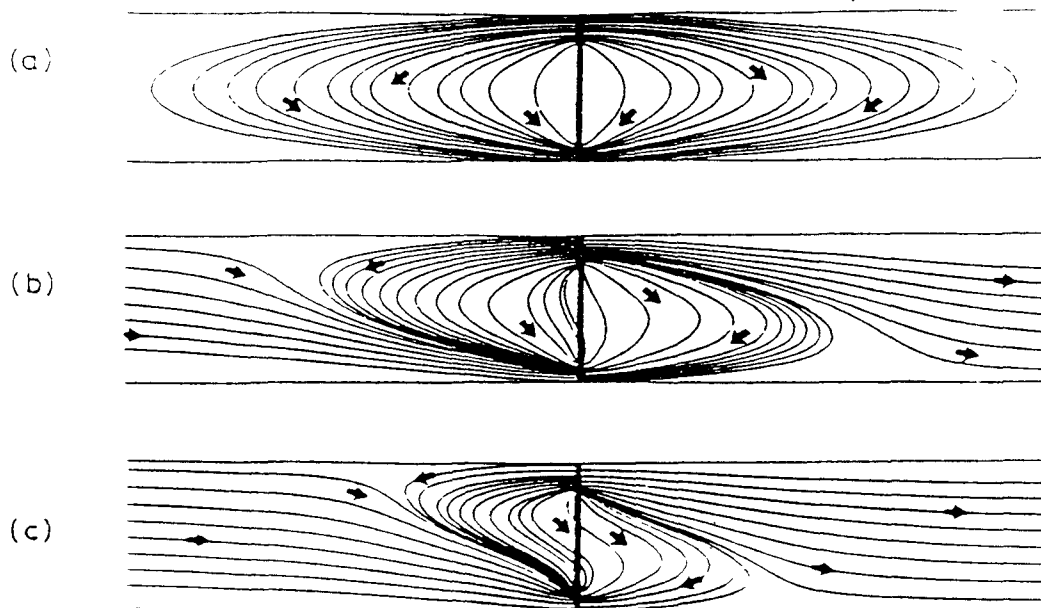


Figure 3.6.2.1 Streamlines for longitudinal vertical recirculation patterns for several ground-water flow velocities: (a) 0 m/d; (b) 0.3 m/d; (c) 1.0 m/d [Herrling et al., 1991].

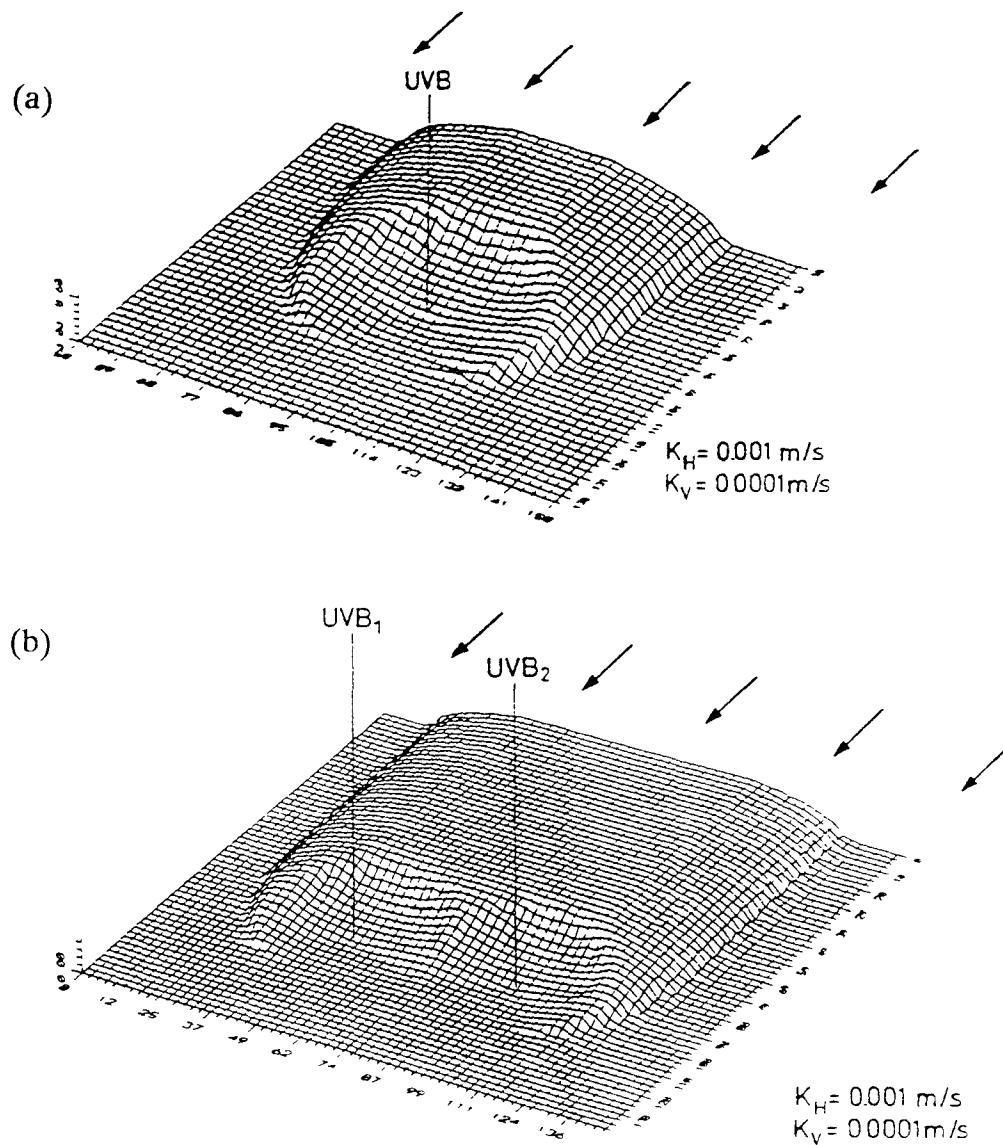


Figure 3.6.2.2 Schematic of three-dimensional capture zone for anisotropic soil conditions using (a) single and (b) dual UVBs. Effect of recirculation cell on incoming flow is indicated by the depressed areas [Herrling et al., 1991].

Sub-atmospheric pressures in the stripping region are maintained by a ventilation system. The applied vacuum concurrently induces a rise in the ground-water table elevation in the UVB, inflow of clean air bubbles into the well via the pinhole plate, and vapor inflow from the surrounding vadose soils into the well. Air bubbles strip compounds from the ground water. All collected vapors exit the top portion of the well and are routed to the off-gas treatment system. Rising air bubbles induce upward convective flow within the well which is usually sufficient to draw more contaminated ground water into the lower well screen. In certain cases, additional ground-water pumping may be necessary. Hence, the use of partially penetrating well screens in the lower and upper well regions and the adjustable separation plate facilitates the ground-water circulation within the aquifer

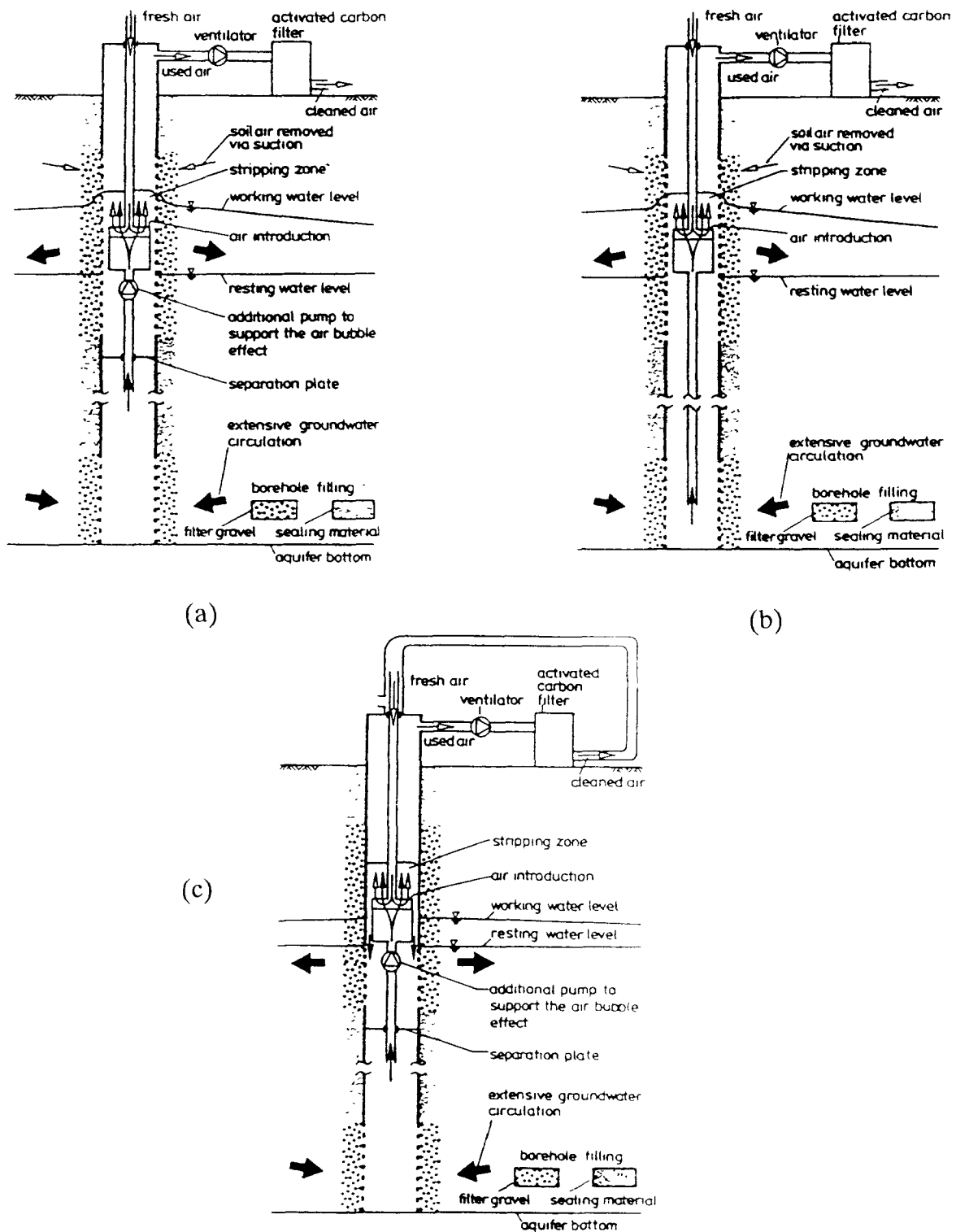


Figure 3.6.2.3 Schematic of vacuum vaporizer well (UVB) configured with (a) separation plate and vacuum extraction; (b) no separating plate and vacuum extraction; and, (c) separation plate and closed air recirculation. [Herrling et al, 1992a].

At many sites, the configuration without a separation plate depicted in Figure 3.6.2.3b is used [Herrling et al., 1992a]. While it would appear that the lack of a separation plate should result in excessive short circuiting of fluid flow within the well, density differences between the untreated and treated ground water can result in net fluid flow in either the upward or downward direction. Ground water may either be heated or cooled as a result of heat transfer with the fresh air: heated (less dense) and cooled (more dense) water will exit through the upper and lower screens, respectively. In this way, water circulation patterns are reversible, and both have been observed in the field [Herrling et al., 1992a].

Both configurations shown in Figures 3.6.2.3a and 3.6.2.3b are susceptible to clogging as a result of iron, manganese and calcium precipitation [Herrling et al., 1992a]. Treated air recirculation and water re-introduction below the working phreatic surface can mitigate these effects. After air is recycled a few times and air-water equilibrium is re-established, precipitation of insoluble salts should cease or be reduced. The incorporation of separation plates and additional water pumps, and the potential for extended ground-water circulation within the aquifer, make the configurations shown in Figures 3.6.2.3a and 3.6.2.3c the most preferred configurations [Herrling et al., 1992a].

UVBs have been installed to depths of 40 meters [Herrling et al., 1991, 1992a]. Multiple screened intervals, nested ground-water sampling ports, separation plates and additional water pumps can be installed to selectively create recirculation cells within any vertical portion of an aquifer [Herrling et al., 1991]. Screened intervals have been in the range of 2 to 5 meters. Reported volumetric flow rates of UVB ventilation systems are as high as 500 m³/hr [Herrling et al., 1991; 1992a]. Fresh air and soil gas vapor inflows to UVBs have been reported as high as 180 and 320 m³/hr, respectively [Herrling et al., 1992a].

Depending on the well configuration, UVBs may stimulate in-situ biological degradation of organic compounds through oxygenation of the subsurface [Herrling and Stamm, 1992a,b]. This observation has led to the development of Groundwater Circulation Wells (GZB, in German: Grundwasser Zirkulations Brunnen). GZBs facilitate continuous or pulsed introduction of aqueous phase compounds for physical or biological treatment of ground water using the same ground-water circulation strategy as UVBs [Herrling et al., 1992b; Herrling and Stamm, 1992a,b].

Level of Demonstration and Performance--

Numerous sites (60+) within Europe containing immiscible compounds are reported to have been remediated to concentrations in the range of 10 to 1000 ppb [Herrling et al., 1991, 1992a,b]. Sites contaminated with PCE, TCE, TCA, 1,2-DCE, DCM, and BTEX compounds in sandy to silty soils are among those reported to have been successfully treated by UVB [Herrling et al., 1991, 1992a,b]. Two European applications are summarized here.

In 1988-91, UVB was applied at a former steel processing plant in Rhine-Ruhr region of Germany to clean up TCE contaminated ground water. The site was underlain by approximately 40 meters of *interbedded fine to medium sands and gravels with occasional silt lenses* [Herrling et al., 1991]. The ground-water table was located at a depth of 6 m, situated just below an upper layer composed of artificial fill. Pump tests indicated hydraulic conductivity coefficients on the order of 10⁻³ to 5x10⁻⁴ m/s. UVB1 was installed to a depth of 12.5 m with a screened interval of 4 to 12.5 m using the configuration without a separation plate shown in Figure 3.6.2.3b. About 20 m from, and somewhat downgradient of, UVB1, UVB2 was installed to a depth of approximately 40 m with three screened intervals: 6-8.2 m; 20-25 m; and, 35-40 m. A separation plate was installed between each screen. TCE was detected up to a maximum concentration of 5 ppm and other organic compounds were detected at much lower concentrations. Before pumping commenced, the concentration profile in the UVB2 sampling ports were 1.26, 1.22, 1.64 ppm at depths of 11, 24, and 38 meters, respectively.

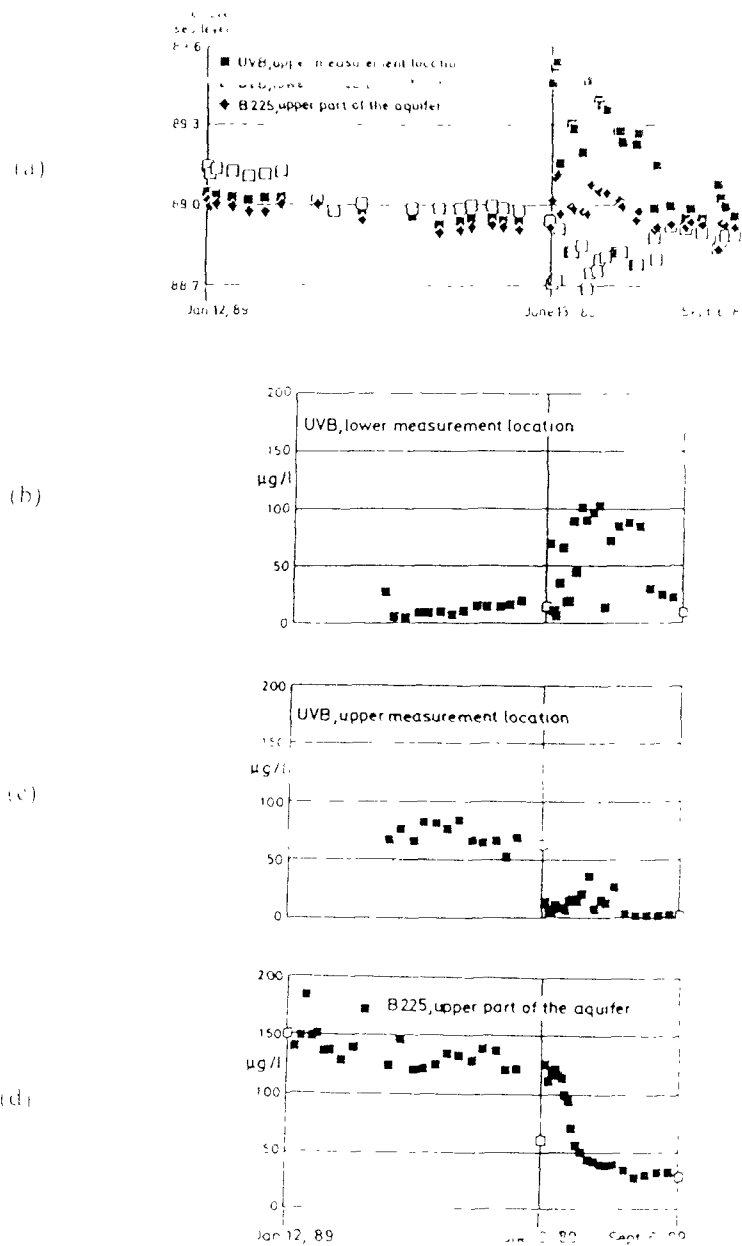


Figure 3.6.2.4 Field data obtained from Mannheim-Kaefertal site (Germany). Measured hydraulic heads (a) indicate vertical flow patterns in aquifer. Downflow in well occurs until 6/13/89, upflow thereafter. Corresponding PCE concentrations in ground-water monitoring locations in the lower UVB (b), upper UVB (c), and in a downgradient well (d) which is screened in the upper portion of the aquifer illustrate the importance of upflow in the UVB well on PCE recovery [Herrling et al., 1992a].

In terms of recovery, vapor concentrations exiting UVB1 fluctuated between 120-300 mg/m³, and average daily removal rates were approximately 2.0 kg/d. Approximately 1500 kg of VOCs were recovered from the unsaturated and saturated zones in 15,000 hours of operation. After one month of operation, vapor concentrations in the sampling ports of UVB2 decreased to 0.1 ppm of VOCs and remained at this level. UVB2 commenced pumping some 800 days after UVB1. Daily vapor recovery rates at UVB2 were initially 375 g/d and decreased to 20 g/d. In 4,000 hours of operation, UVB2 recovered 50 kg of VOCs.

Dissolved organic compound concentrations in a monitoring well situated 60 meters upstream of UVB1 and just beyond the estimated location of the upstream stagnation point of the recirculated water steadily decreased from approximately 1.5 ppm to 0.3 ppm. Within the recirculation zone, concentrations decreased from 1.5 ppm to 0.2 ppm in a well situated 10 m from UVB1. Wells located downstream from UVB1,2 showed a decrease in concentrations of volatile NAPL from initial readings of 2-5 ppm to 0.4-0.8 ppm. However, ground-water concentrations in a monitoring well located approximately 150 meters upgradient from UVB1 fluctuated between 0.46 and 5.08 ppm and showed an unexplained increasing trend with time. While some dilution may have occurred and another NAPL hotspot may have been located, recovery of dissolved contaminants, primarily TCE, was continuous and considerable.

In 1989, field experiments were conducted at a site in the Mannheim-Kaferetal area (Germany) [Herrling et al., 1992a]. In these experiments, the effect of flow reversal in the UVB on efficacy of cleanup was investigated. The stratified subsoils consisted of interbedded sands and gravel to a depth of approximately 38.7 m where a clay aquitard was encountered. A discontinuous lens of clay appeared at a depth of 16.5 to 18.3 m. One UVB was installed to a depth of 40.0 m with upper and lower screened intervals of 8.5-14.0 m and 35.5-38.5 m, respectively. The configuration without the separating plate shown in Figure 3.6.2.3b was used for the first six months of operation, and then was modified to include a separation plate and a water pump. One monitoring well, situated 15 m downgradient of the UVB, was installed only in the upper portion of the aquifer.

Chlorinated hydrocarbons (including PCE) were detected at concentrations between 0.1-0.2 ppm. Figure 3.6.3.4a presents total hydraulic head data from the two sampling ports within the UVB. Concentration data obtained during the period when no separation plate was used (Phase 1: 1/89-6/89) indicate that downflow was occurring in the well and that the water flow in the surrounding aquifer was opposite of that depicted in Figure 3.6.2.1a. After separation plate installation (Phase 2: after 6/89), the flow direction in the well was reversed to the upflow direction making aquifer flow consistent with that shown in Figure 3.6.2.1a. The effect of flow reversal on the PCE concentration data taken from the UVB sampling ports is shown in Figure 3.6.2.4b,c. For example, significant PCE concentration reductions were observed in the downgradient well after the beginning of Phase 2.

Since treated water was cycled to the top of the aquifer and the downgradient well was only screened in this interval, the flushing effect of the treated water on this well is manifested by PCE reductions. The PCE reduction occurring at this location are consistent with what is expected from the aquifer recirculation pattern shown in Figures 3.6.2.1b,c.

Applicability/Limitations--

UVBs can be applied to sites contaminated with aqueous phase volatile and semi-volatile organic compounds having Henry's constants greater than approximately 10^5 atm-m³/mole. It is not known whether the separate phase liquids will be mobilized: most likely they will not be mobilized and the solubilization process will be diffusion limited.

Good site characterization is required to avoid cross-contamination of unconfined and confined aquifers. Sites underlain by gravel, fill, sand, and sandy to clayey lenses have been treated by UVBs [Herrling et al., 1991; 1992a,b]. The hydraulic conductivities of subsurface soils at treated sites have been

in the range of 10^{-3} m/s to approximately 10^{-6} m/s [Herrling et al., 1991; 1992a]. Ambient ground-water velocities that have been accommodated are reported as high as 1 m/d.

With the exception of the UVB itself, this process is not intrusive; therefore, there are few limitations due to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem.

There is no ground-water extraction to the ground surface and no overall lowering of the phreatic surface; that is, pronounced cone of depression is not formed [Herrling et al., 1992b]. The only ex-situ process is the treatment of the extracted gas phase. For UVB configurations which do not recirculate air (Figures 3.6.2.3a,b), oxygenation of the ground water may potentially lead to biological fouling and precipitation of metal carbonates and oxides in both the UVB and aquifer. Hot-air injection is likely to enhance stripping.

Cost and Availability--

The technology is commercially available and has been implemented on the full-scale in Europe. The UVB and GZB have been patented by IEG mbH (Reutlingen, Germany). Their US affiliate is IEG Technologies Corp. (Charlotte, North Carolina).

UVB technology is a good candidate for remediating dissolved plumes of VOCs in aquifer media. However, because solubilization of the separate phase is diffusion limited, application of UVBs to DNAPL cleanup is limited.

The application in the Rhine-Ruhr area (Germany) in which approximately 1550 kg of volatile NAPLs (primarily TCE) cost \$352,000 which includes site investigations planning etc. (21.8%), monitoring and field work (21.5%), analytical work (8.2%), borings and UVB installation (15.3%), granular activated carbon treatment and NAPL disposal (24.1%), and energy cost (9.1%) [Herrling et al., 1991]. Average monthly operating costs were \$4,000. These costs are somewhat inflated by technology development and specific costs associated with conducting business in Germany (insurance, patents, regulations). Because it is composed of elements common to ASP/VE, soil vapor extraction, and pump-and-treat, UVB is likely to cost about \$50-100/yd³.

3.7 THERMAL PROCESSES

Introduction--

Thermal and thermally enhanced processes rely on various means for the delivery of thermal energy into the subsurface: the CROW® process (see below) utilizes hot water and/or low quality steam injection; in-situ steam enhanced extraction (SEE) relies on high quality steam injection; and radio frequency heating and in-situ vitrification facilitate heating using microwave and electrical arrays, respectively. During these processes, steam and hot water progress through cool porous media and they heat the interstitial fluids and porous media. These fluid-fluid displacement processes are analogous to liquid-liquid displacement processes (see section 3.5) with the added complexity of heat transfer. The contaminants can be recovered as vaporized gases, and as dissolved- and separate-phase liquids.

The effectiveness of the CROW® process (section 3.7.1) and steam enhanced extraction (section 3.7.2) is controlled by the thermodynamics and hydrodynamics of hot-water and steam displacement in porous media. Thus, the thermal properties of both the porous media and the pore fluids become important. The orientation and shape of the propagating steam fronts are governed by the matrix *heterogeneities, geometry of the aquifer, initial moisture and boundary conditions, steam quality, injection rates, and most importantly, the ratio of buoyancy to viscous forces.* In saturated homogeneous isotropic porous media, the ratio of buoyancy to viscous forces is important in terms of gravity override and effective sweep-out [Basel and Udell, 1989]. The same principles hold for condensation fronts propagating through layered media, but the temperature profiles and fronts will be curved at layer interfaces owing to intrinsic permeability differences [Udell and Stewart, 1989]. When gravity effects are negligible, the behavior of propagating fronts can be readily predicted and controlled [Buckley and Leverett, 1942; Udell and Stewart, 1989].

Radio frequency heating (section 3.7.3) achieves subsurface heating by using an electrode array system to transmit electromagnetic waves through the porous media. In-situ moisture is converted to a steam front which propagates through porous media thus displacing other pore fluids, including DNAPLs, in a manner similar to that described above.

In-situ vitrification (ISV, section 3.7.4) also employs an electrode array system, but for the purposes of current flow. Large current flows cause electrical resistance (joule) heating of the soil to the melting point. During this process, DNAPLs can be volatilized and pyrolyzed.

The CROW® process, SEE and radio frequency heating processes have their origins in the enhanced oil recovery business. ISV was developed for the stabilization/solidification of wastes containing radionuclides. All of these technologies have been demonstrated at the pilot scale, but only CROW® and SEE have been successfully demonstrated in the saturated zone. A full-scale demonstration of SEE is in progress.

3.7.1 Contained Recovery of Oily Wastes (CROW®)

Theoretical Background--

The Contained Recovery of Oily Wastes (CROW®) process uses low-quality steam and hot-water injection to enhance contaminant removal from the subsurface. The primary mechanisms are: the flotation of NAPL contaminants by temperature induced viscosity reduction and buoyancy; and by displacement of dissolved contaminants and NAPL by a propagating hot-water front. Secondary mechanisms include solubility enhancement of the targeted compounds which assists in their recovery, and enhanced in-situ biological degradation (see Section 3.2) [Western Research Institute, 1992; Johnson and Suddeth, 1989]. This process is in many ways identical to enhanced oil recovery methods utilizing steam, solvent, surfactant or caustic floods [Shah, 1981; Janssen-van Rosmalen and Hesselink, 1981].

As low-quality steam and/or hot water enter and progress through cool porous media, they heat the interstitial fluids and porous media. Unlike steam enhanced extraction (SEE, section 3.7.2) which relies on steam front propagation for contaminant displacement, the low-quality steam employed by the CROW® process results in a hot water front which immiscibly displaces NAPL contaminants. By utilizing hot water as the displacing fluid, the viscosity, buoyancy, and capillary pressures of DNAPLs can be favorably affected. The relative permeability of the porous media to water (k_{rw}) is also increased.

The viscosity reduction of several petroleum-derived DNAPLs is shown in Figure 3.7.1.1a. If the viscosity reduction is not sufficient, surfactants and viscosifiers can be added to the hot water to improve mobility ratios. The addition of surfactants enhances DNAPL solubilization and interfacial tension reduction [Fountain et al., 1991]. Capillary pressure-saturation relationships and parameters for Brooks-Corey or van Genuchten equations as a function of temperature are necessary to model the displacement process. Depending on the actual compound and applied temperature, a DNAPL may be effectively transformed to a LNAPL, which aids in flotation and thus free product recovery. The temperature dependence of density is shown for several petroleum-derived DNAPLs in Figure 3.7.1.1b.

Field Implementation--

A schematic of the field implementation is shown in Figure 3.7.1.2. Horizontal well configurations are also possible [Johnson, 1992]. A specially designed injection well has the capacity to simultaneously inject three different fluids (low-quality steam, hot, and cool water) at three separate elevations. Production (extraction) wells recover aqueous and pure phase DNAPL which is pumped to the ground surface for treatment and/or recycle. Hot and cool water may be re-injected after treatment.

The objective of the CROW® process is to upwardly displace, or float, DNAPLs toward the water table and extraction wells by reducing separate phase density, viscosity, and interfacial tension. The strategy implemented to accomplish DNAPL mobilization is summarized below.

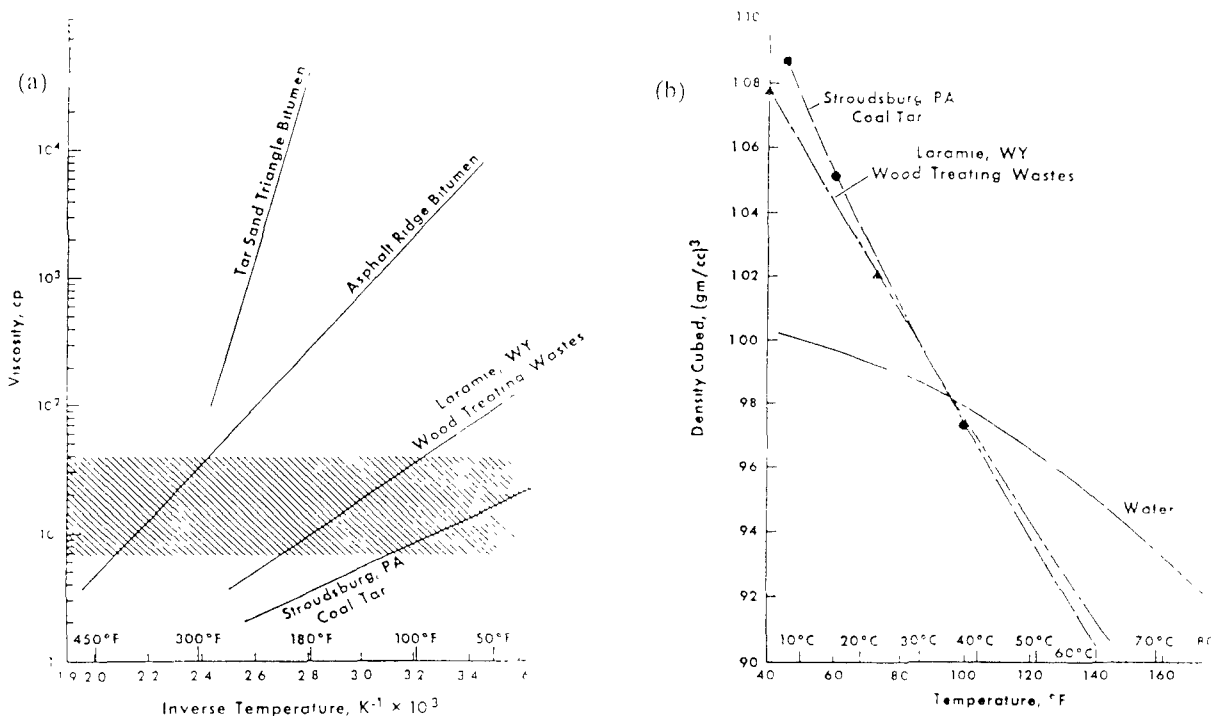


Figure 3.7.1.1 Influence of temperature on fluid viscosity (a) and density (b) for several DNAPLs [Johnson and Suddeth, 1989].

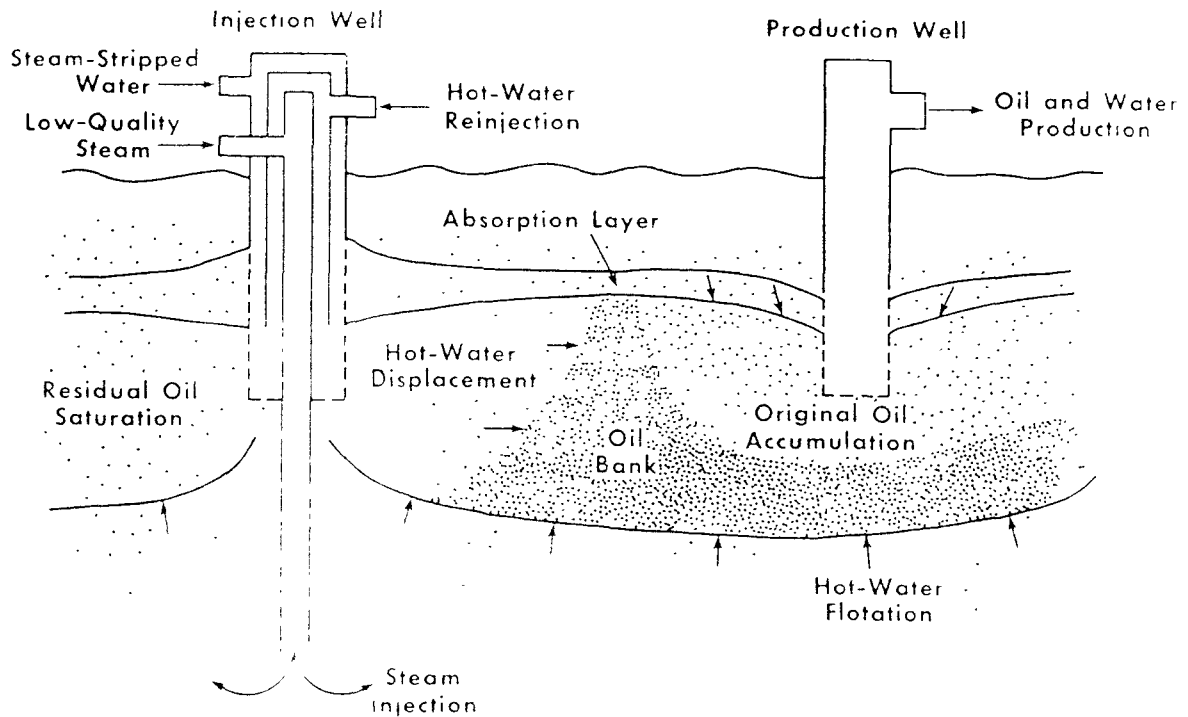


Figure 3.7.1.2 Conceptual schematic of the CROW® process [Johnson and Suddeth, 1989].

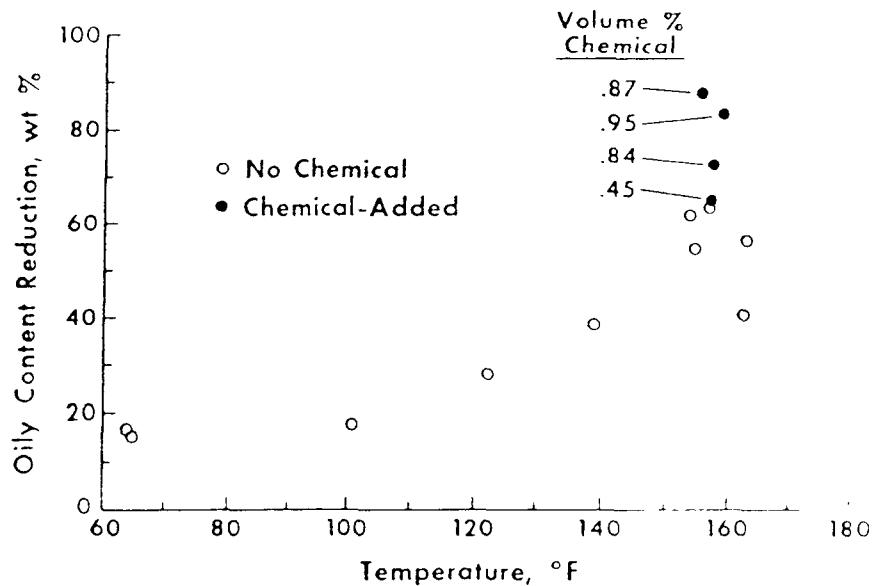


Figure 3.7.1.3 Temperature dependence of DNAPL recovery using hot water and surfactant solutions in one-dimensional column tests by CROW® process [Johnson and Leuschner, 1992].

Low-quality steam is injected below the contaminated soil zone which results in heating of the porous media and pore fluids. DNAPL is mobilized upward providing it becomes less dense than water under the applied temperatures, and a favorable ratio of buoyancy to viscous forces is maintained. As DNAPL migrates upwards, a concentrated NAPL bank (dark stippled area in Figure 3.7.1.2) may form ahead of the propagating hot-water front. Displacement of this kind can result in a lower residual saturation (S_{or}) of NAPL and an associated increase in k_{rw} in the swept-out zone. Also, enhanced DNAPL solubilization can occur at elevated temperatures in the zone swept by hot water.

Simultaneous injection of hot water along the periphery of the contaminated zone serves the dual purpose of lateral containment and displacement of DNAPL toward the extraction well. The lateral displacement occurs analogously to the upward displacement, although the frontal stability condition is somewhat different owing to the orientation of forces. DNAPL solubilization occurs at elevated levels in the zone swept by the continual passing of hot-water.

An "absorption layer" [Johnson, 1989] or cold water cap is created above the contaminated zone by cool-water injection. The purpose of this layer is to provide vertical containment of the rising pore fluids, and to condense any vapors emanating from the heated contaminated soil zone situated directly below. This may not be necessary when dealing with non-volatile DNAPLs.

Any combination of compounds such as alkaline agents, surfactants, polymers (density enhancement) and viscosifiers may be added to the injectates to ensure a more favorable mobility ratio between the hot water and the DNAPL or to enhance compound solubilities. After the quantity of residual DNAPL is reduced by the hot-water front, nutrients and electron acceptors (primarily hydrogen peroxide) may be added to the hot water to enhance biodegradation of residual DNAPL.

Level of Demonstration and Performance--

One-dimensional studies in 3.75-in. dia. and 36-inch long packed columns using former wood treatment plant contaminated soils containing creosote, pentachlorophenol (PCP) and petroleum products, and manufactured gas plant contaminated soils containing oily residues have shown that the residual saturations of DNAPLs could be significantly lowered depending on the waste type, applied hot-water temperatures and surfactant addition [Leuschner and Johnson, 1990; Johnson and Leuschner, 1992].

Two test samples of wood treating plant soil contained 2.9 wt% and 7.4 wt% hydrocarbons and PCP concentrations of 1,500 ppm and 3,200 ppm, respectively. Using a flow rate approximately twice that of natural ground-water velocity and hot-water temperatures of 120°F (49°C) and 140°F (60°C), 0.5 wt% hydrocarbon concentrations and PCP concentrations below 2.5 ppm were obtained for both samples. This constitutes hydrocarbon reductions of 84% and 94% for the two soils, respectively.

Testing on the manufacturing gas plant soils was somewhat more extensive using soils that contained 0.13 wt% to 3 wt% organics. Initially, the extremes were tested. Using a flow rate approximately twice that of natural ground-water velocity and ambient water temperatures of 64°F (18°C), hydrocarbon reductions of only 15% and 21% were obtained for the two soils, respectively. Injection of hot water at 100°F (38°C), 120°F (49°C), and 140°F (60°C) showed organic concentration reductions of 23, 30, and 42 wt%, respectively for the 3 wt% soil.

One-dimensional experiments using hot-water temperatures between 155°F (68°C) and 165°F (74°C) were then completed on samples having up to 2.8 wt% hydrocarbon. Reductions were on the order of 55 to 63 wt% with the optimum removal occurring near 155°F (68°C), as shown by the open circles in Figure 3.7.1.3. One sample, initially having 0.13 wt% hydrocarbon was reduced by 61 wt% compared to the 15 wt% obtained previously at 18°C. At 155°F (68°C), NAPL reductions were improved to between 64 and 84 wt% by using 0.45 to 0.95 vol% Igepal CA-750 surfactant solutions, as shown in Figure 3.7.1.3.

These results are consistent with 1-D displacements performed in reservoir sands which showed that hot caustic floods outperformed hot-water floods by 16-18% on a pore volume basis [Janssen-van Rosmalen and Hesselink, 1981].

Next, two three-dimensional tests using hot- and cool-water injection were also completed on the manufactured gas plant soils in a reaction box (3x3x7 ft) fitted with 80 thermocouples and injection/extraction ports situated on the long axis. The soils were layered to simulate site stratigraphy: 1 ft impervious base; 0.5 ft of very saturated oily sand; 0.5 ft of lightly saturated oily sand; and, 1 ft cap of clean sand. Both tests were run at flow rate approximately twice that of natural ground-water velocity. The cool water was injected into the clean sand and hot water was injected at 155°F (68°C) into the oily sands, see Figure 3.7.1.4. In both tests, the temperature profiles show that a cooler adsorption layer could be maintained over the treated soil zone.

The duration of the first test was 100 hours using hot water only. The second test used hot water and 1.0 vol% Igepal CA-750 (surfactant) addition and lasted only 50 hours due to clogging caused by migration of fines. Comparison of the nearly coincident 60 wt% saturation reduction and 140°F profiles in Figure 3.7.1.4a reveals that removal efficiency exceeds that of the 1-D tests, Figure 3.7.1.3. One possible explanation for this may be the larger sample may permit the formation of a larger oil bank [Johnson and Leuschner, 1992].

One pilot study has been completed at a former wood treatment plant site [Fahy et al., 1992]. The main purpose of this test was to demonstrate hydraulic control of the hot-water front as it propagated in the subsurface. The hot-water front was successfully kept within the capture zone of the extraction well throughout the pilot test. Creosote and pentachlorophenol (PCP) in a fuel carrier oil comprised the subsurface contamination. The pilot test was conducted in a 23-47 ft thick aquifer consisting of uniform silty, fine to medium gravel and sands. The water table was situated between 10 to 20 ft below the ground surface across the site. The aquifer was underlain by a 96 ft thick till layer having a hydraulic conductivity of approximately 10^{-7} cm/s.

The pilot test utilized one injection well, one extraction well, four monitoring wells, and three piezometers. The injection well was screened from the top of the till layer and extended to within 5 ft below the ground surface. The extraction well (previously installed) was located 50 ft from the injection well. The monitoring wells were constructed of 2-inch I.D., 0.01 inch continuous slot stainless steel screen and solid casing risers. The screened interval extended from the top of the till layer to approximately 13 to 16 ft below the ground surface. The monitoring wells and piezometers were each fitted with thermocouples situated at 18, 23, 28, and 33 ft, and, 22, 32, and 37 ft below the ground surface, respectively.

The extraction well was pumped continuously for one week prior to start-up of the injection well, and continued until the end of the test, Day 41. Injection commenced on Day 7 and continued until Day 37. The injection and extraction wells were pumped at an average rate of 4.5 and 6.5 gpm, respectively. No surfactant addition or pH adjustment of the hot water was employed.

The initial injection temperature of the hot water was 147°F (64°C), but on Day 9 it was elevated to 203°F (95°C) for the remainder of the test. As shown in Figure 3.7.1.5, uniform heating of the subsurface was achieved by Day 35 in the treatment zone at monitoring well BP-24 (located near midpoint between injection and extraction wells). The injection pressure gradually increased from 6 to 14 psig. NAPL arrival (floating product) at the extraction well was detected on Day 21, and the hot water broke through on Day 27. Hot-water injection totaled 193,000 gallons. Extraction totaled 390,000 gallons with an estimated NAPL recovery of 2,000 gallons. Polynuclear aromatic hydrocarbons such as 2-methylnaphthalene, acenaphthalene, dibenzofuran, naphthalene and phenanthrene were also present in the effluent.

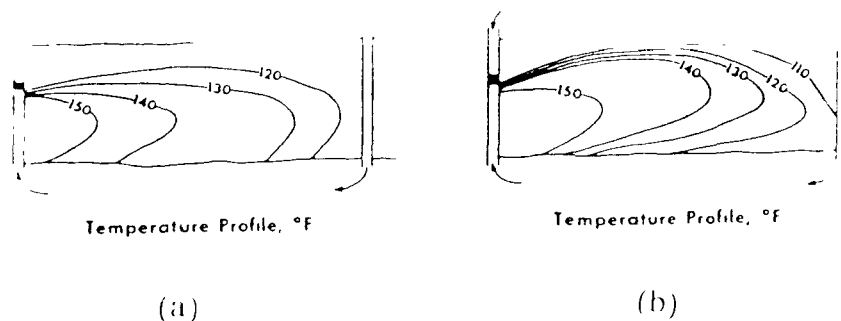


Figure 3.7.1.4 DNAPL removal and corresponding temperature isotherms using hot (a) water and (b) surfactant solutions in 3-D tests by CROW® [Johnson and Leuschner, 1992]

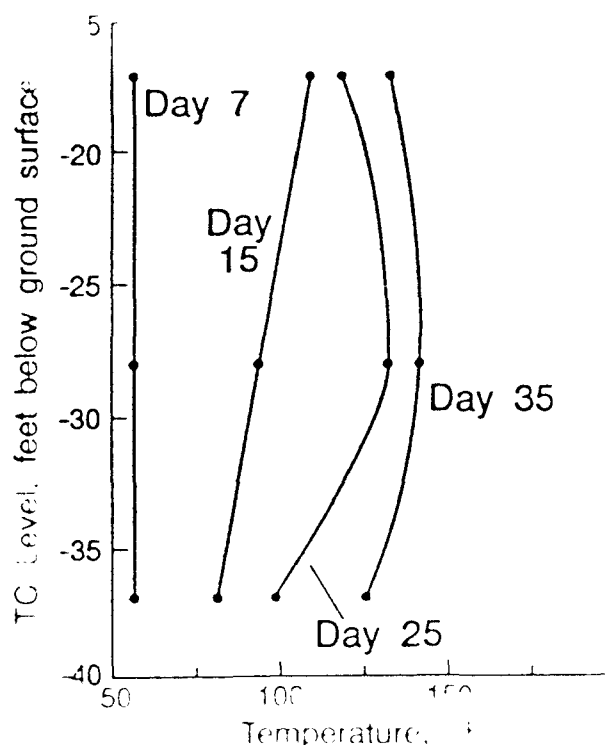


Figure 3.7.1.5 Temperature profiles at well location BP24 during CROW® pilot test (MN) [Fahy et al., 1992].

Soil samples CT1 and CT2 were taken after completion of the pilot test at 4 and 10 ft from the injection well, respectively. Figure 3.7.1.6 shows the hydrocarbon reductions achieved as a function of depth and radial distance from the injection well. In particular, hot water displaced approximately 80 wt% of hydrocarbon at CT1 within 20 pore volumes of flushing, and the PCP concentrations at CT1 were reduced from 2,100 to approximately 3.6 ppm

Applicability/Limitations--

CROW® can be applied to sites contaminated by LNAPLs and DNAPLs such as coal tar and its derivatives, pentachlorophenol solutions, creosote, and petroleum by-products [USEPA, 1991a]. Organic compounds of this type usually have densities within 10-15% of water at 20°C and are therefore very amenable to flotation by temperature-induced density gradient reversal, as shown in Figure 3.7.1.1b. WRI

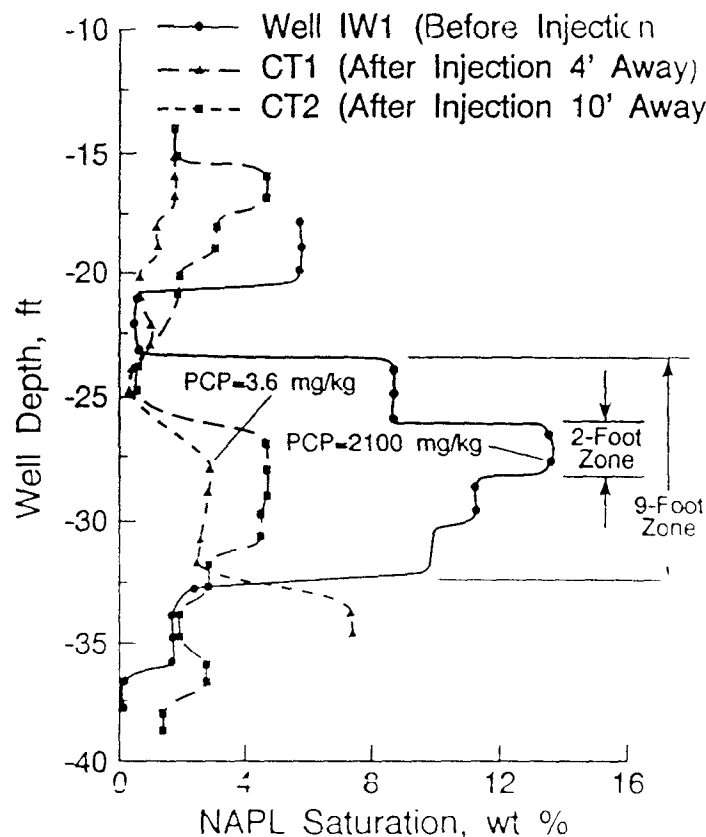


Figure 3.7.1.6 NAPL saturation profiles in soil samples (CT1,CT2) taken in vicinity of injection well (IW1) after CROW® pilot test [Fahy et al., 1992].

is currently investigating the application of CROW® to sites contaminated with much denser DNAPLs such as TCE and PCE.

Residual saturations (S_{or}) of DNAPL are controlled by the N_B and N_C (see section 2.0), and a reduced residual saturation of DNAPL (S_{or}) on the order of 0.1-5 wt% may persist even after treatment by the CROW® process, as indicated by the 1-D, 3-D and pilot study findings. The CROW® process must therefore be augmented with other forms of in-situ treatment. The significant S_{or} reductions, toxicity reduction, better mixing (increased k_{iw}), compatibility of equipment, and easily facilitated oxygenation and nutrient addition make CROW® an attractive precursor to in-situ biological treatment. However, to date, in-situ biological treatment has not been used in conjunction with the CROW® process.

With the exception of borings, CROW® is not intrusive, and there are few limitations due to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The ex-situ hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

Depth of application and soil type will dictate allowable steam and hot-water injection pressures, well spacing and thus cost [USEPA, 1991a]. Capital cost will depend on the well spacing per unit area and depth of application basis because the boring and well construction are the major cost items.

Cost and Availability--

One pilot study at the site of a former wood treatment plant in Minnesota has been completed [Johnson, 1992]. Other treatability studies are being conducted. US Patent No. 4,484,460 has been assigned to the Western Research Institute, Laramie, Wyoming, for CROW® [Johnson and Suddeth, 1989]. Design of two full-scale CROW® applications are currently underway [Johnson, 1992]. One application is proposed as part of the USEPA SITE Demonstration Program, at the Pennsylvania Power and Light (PP&L) Brodhead Creek site, Stroudsburg, Pennsylvania [USEPA, 1991a]. Approximately one-half acre of contaminated soils will be treated to a depth of 20 ft [Johnson, 1993]. A second full scale application is planned for the former wood treatment plant site, where the pilot study was completed [USEPA, 1991a]. Approximately 2.7 acres of contaminated soil will be treated to a depth of 20 ft [Johnson, 1993].

CROW® appears to be a viable candidate for cleanup of DNAPL contamination in aquifer media. CROW® will have its largest impact on DNAPL source areas. However, it is not clear that the injection of hot water and low quality steam by the CROW® process represents a distinct thermal advantage over the high quality steam injection of SEE.

A soil treatability study requiring a minimum of 120 lbs (two 5 gal. containers) of soil costs approximately \$20,000 [Johnson, 1993]. This estimate excludes modifications made to the hot water such as pH adjustment or surfactant addition. The total cost of the pilot study at the site of the former wood treatment plant in Minnesota was approximately \$300,000 and the full-scale application is anticipated to cost \$2.2 million [Johnson, 1993]. The SITE program demonstration at the Stroudsburg, Pennsylvania, site is anticipated to cost \$1.2 million [Johnson, 1993]. All of these applications will be sampling and monitoring intensive.

These estimates exclude in-situ biological treatment. In-situ biological treatment can operate using the CROW® hardware with minor modifications and tankage conversions. Unless additional borings are required, operating and maintenance costs for in-situ biological treatment are anticipated to be on the order of \$50-60,000/year depending on site conditions [Leuschner, 1993].

3.7.2 Steam Enhanced Extraction (SEE)

Theoretical Background--

The Steam Enhanced Extraction (SEE) process relies on several mechanisms of contaminant removal from the subsurface. The primary mechanisms are: vaporization of low boiling point (b.p.<100°C) contaminants at the steam condensation front; enhancement of evaporation rates of higher boiling point (b.p.>100°C) contaminants at the condensation front and within the steam zone; displacement of dissolved contaminants and NAPLs by a steam condensation front and by steam within the steam zone; and desorption from solids.

As steam progresses through cool porous media, the steam condenses and transfers its latent heat of vaporization to the interstitial fluids and porous media. Fig. 3.7.2.1 schematically shows that continuous steam injection results in the development of three distinct thermodynamic zones: a hot isothermal (steam) zone at the steam temperature; a relatively sharp thermal transition zone of several centimeters thickness; and a cool isothermal zone which represents the porous media and interstitial fluids at their ambient temperature [Udell and Stewart, 1992]. Steam temperature depends on injection pressure, which is governed by the depth of the injection interval, while ambient temperatures may vary between sites. The steam condenses at the interface between the steam zone and the thermal transition zone, creating a "steam condensation front." The growth rate of the steam zone is directly related to the injected steam enthalpy flux if the thermal transition zone does not grow in length [Hunt et al., 1988c; Stewart and Udell, 1988].

When gravitational forces are negligible, in unsaturated porous media, for example, results of laboratory experiments and theoretical analyses show that in a homogeneous isotropic medium, the orientation of the propagating condensation front will remain essentially perpendicular to the direction of steam flow [Basel and Udell, 1989]. The same is essentially true for layered soil systems having relatively homogeneous layers of different permeabilities. For example, the temperature profiles for a propagating steam condensation front through layered media is illustrated in Fig. 3.7.2.2. After breakthrough of all propagating fronts, a steady state isothermal condition is achieved; that is, a steam zone is created between the injection and extraction wells.

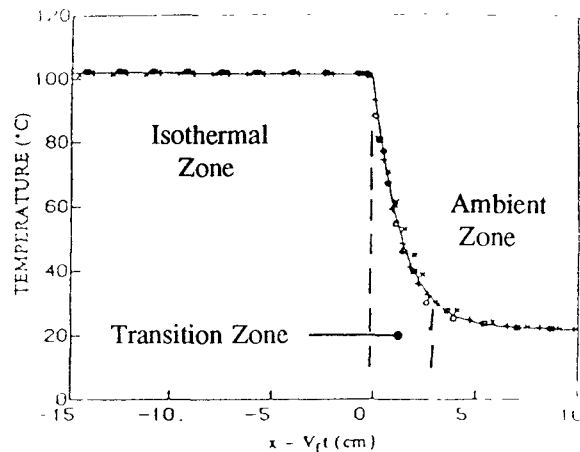


Figure 3.7.2.1 Temperature distribution near steam condensation front [adapted from Udell and Stewart, 1989]

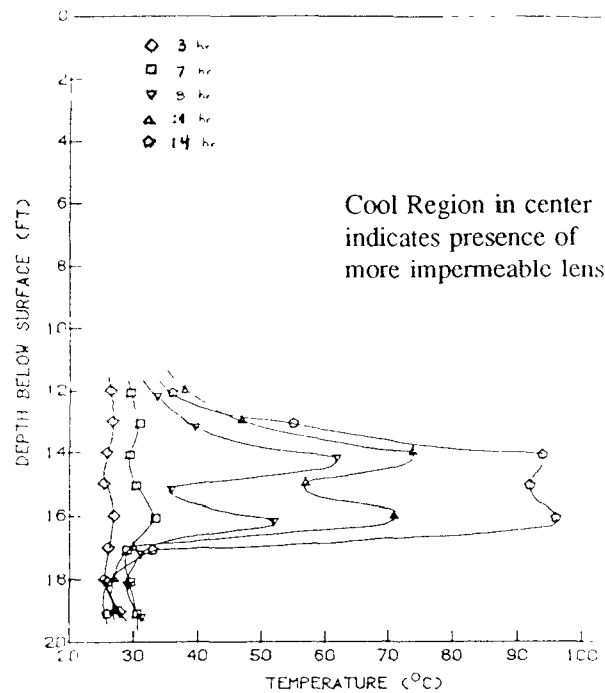


Figure 3.7.2.2 Effect of soil heterogeneity on steam front advancement [adapted from Udell and Stewart, 1989].

NAPLs with low boiling points that are contacted by steam vaporize and are completely removed from the steam zone [Udell and Stewart, 1992]. They migrate ahead of the steam zone to the leading edge of the thermal transition zone where they recondense to a separate phase liquid. A saturated front or "bank" of NAPL forms [Hunt et al, 1988c] and it is displaced to the extraction point. Figure 3.7.2.3 shows the results of a one-dimensional laboratory experiment in which gasoline was displaced from a water saturated sand column [Hunt et al, 1988c]. As can be seen, the NAPL compounds were removed from the column just ahead of the steam front.

NAPLs with a high boiling point that are contacted by steam undergo enhanced volatilization. This enhanced volatilization is proportional to the ratio of NAPL vapor pressures at the steam temperature (100°C or more depending on pressure) and 20°C and the NAPL mole fraction in the remaining multicomponent liquid phase in the pore space. NAPL vapors also migrate to, and coalesce with, the multicomponent NAPL bank ahead of condensation front. After steam breakthrough at the extraction point (well), contaminant vapors are recovered in the gaseous form. This recovery mechanism has been successfully modeled using numerical simulations [Falta et al., 1992a,b], as illustrated in Figure 3.7.2.4.

Desorption of contaminants from solids is enhanced because sufficient energy is added to the aquifer media by steam condensation to overcome the latent heat of adsorption of many organic contaminants and inorganics [Udell and Stewart, 1992]. Hence, partitioning to the aqueous phase is made favorable, and subsequent vaporization of NAPLs and water and/or their displacement out of the soil matrix lead to a net reduction of sorbed contaminants.

Another significant aspect of the process is the potential for removal of interstitial water and low boiling point fluids in dead-end or otherwise remote (uncontacted) micro- and macropores [Udell and Stewart, 1992]. The boiling of these fluids is achieved by vacuum drying the aquifer media after the steam front has broken through and steam injection is discontinued [Udell et al., 1991]. As the soil matrix cools adiabatically under vacuum, it transfers its energy to the remaining pore fluids (held by capillarity) which boil under the applied vacuum. A net vapor flux from the remote pores towards the main flow channels in the porous media is thus realized.

Field Implementation--

A schematic of the field implementation of SEE is presented in Figure 3.7 2.5. Once the treatment zone (vadose and/or phreatic zone) and its areal extent is defined, a system of steam injection and vapor and liquid condensate extraction wells is installed. In experiments to date, steam injection and extraction wells have been constructed of low carbon steel to accommodate the operating temperatures and pressures. Borings up to 18-inches in diameter have been used to accommodate the necessary hardware [Udell and Stewart, 1989]. Insulation is necessary in the non-screened intervals to minimize heat losses. The extraction well must be capable of recovering both vapors and condensed liquids. Backfill for injection and extraction wells has consisted of pea gravel and cement in the screened and non-screened intervals, respectively. temperature monitoring wells constructed of steel pipe which house thermocouples or other devices have been used to monitor the progression of the steam condensation front through the subsurface.

Normal operating practice requires that the steam be slightly supersaturated to account for thermal losses in the manifold prior to wellhead entry. As such, one hundred percent (100%) quality steam reaches the wellhead and is injected into subsurface soils which are initially at their ambient temperatures, usually 20°C-25°C, although other temperatures are easily accommodated [Udell and Stewart, 1989]. The steam temperature depends on the allowable injection steam pressures. Steam injection pressures must be selected sufficiently below the fracturing pressure of the porous media which is related to depth of application. Near surface (up to 20 ft. depth) steam injection pressures of 6 psig. have been used at one site resulting in steam temperatures near 100°C [Udell and Stewart, 1989].

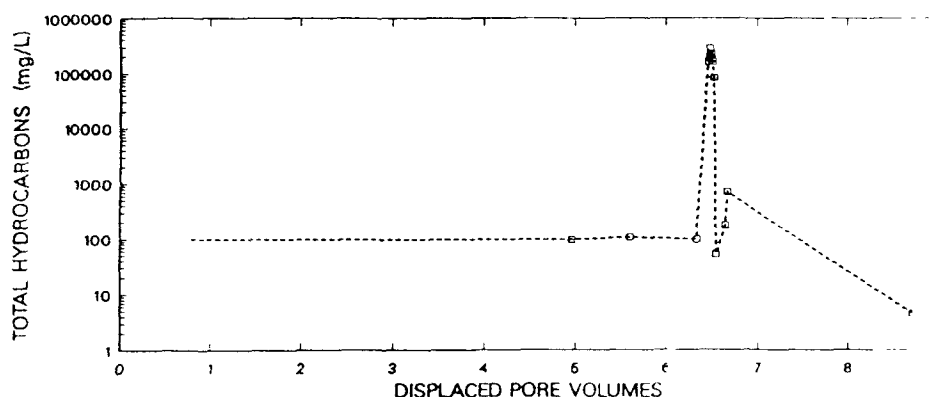


Figure 3.7.2.3 Total hydrocarbon concentration measured in column effluent reported per liter of displaced fluid. Concentration spike indicates presence of NAPL "bank" [Hunt et al., 1988c].

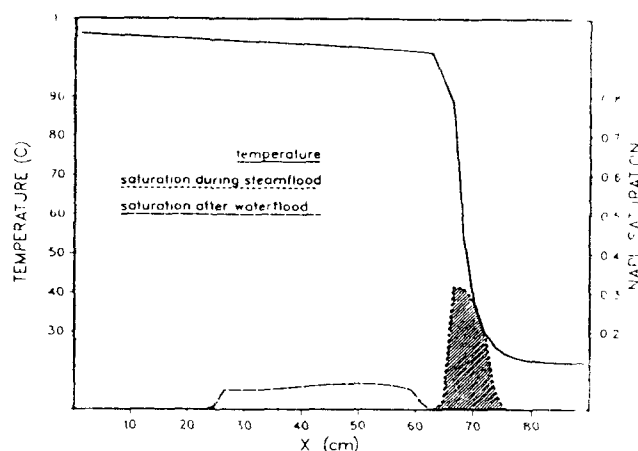


Figure 3.7.2.4 Temperature profile and calculated separate phase o-xylene saturation before (residual water flood saturation) and after steam flood commencement ($t=5000s$). O-xylene "bank" situated ahead of steam front [Falta et al., 1992b].

Level of Demonstration and Performance--

In one-dimensional laboratory studies, the complete removal of xylene, toluene, and gasolines has been documented [Hunt et al., 1988c]. In two separate experiments, gasoline and JP-5 contaminated sand columns have been reduced from 3,000 mg/kg to 1.5 mg/kg and from 49,000 mg/kg to 59 mg/kg, respectively. Similar experiments in a silty clay with gravel revealed that diesel soil concentrations were reduced from 1,500 mg/kg to 19 mg/kg. Bench scale experiments utilizing burn pit ash soils containing solvents and hydrocarbons were treated from 4,200 mg/kg to 220 mg/kg total fuel hydrocarbons and gasoline. The last work represents the treatability study performed by Udell Technologies for the proposed SITE program demonstration at McClellan AFB near Sacramento, California [Udell Technologies, 1991].

A pilot study ($\sim 60 \text{ yd}^3$) was completed in the unsaturated zone at a site in San Jose, California. At this site, silty sands between depths of 9 to 17 feet below ground surface were contaminated with a mixture of solvents which included volatile and semi-volatile LNAPLs and DNAPLs [Udell and Stewart, 1989]. Depth to ground water was approximately 20 ft. The major contaminants (conc. > 1 ppm) were: BTEX compounds (19,000 ppm), 1,2-DCB (2,900 ppm), 1,1,1-TCA (1,700 ppm), acetone (1,650 ppm), TCE (1,600 ppm), PCE (1,400 ppm), Freon 112 (480 ppm), 2-butanone (450 ppm), methylene chloride (97 ppm), 4-methyl-2-pentanone (4.6 ppm), and cis 1,2-DCE (2.5 ppm). Soil concentrations were reduced from 2,065

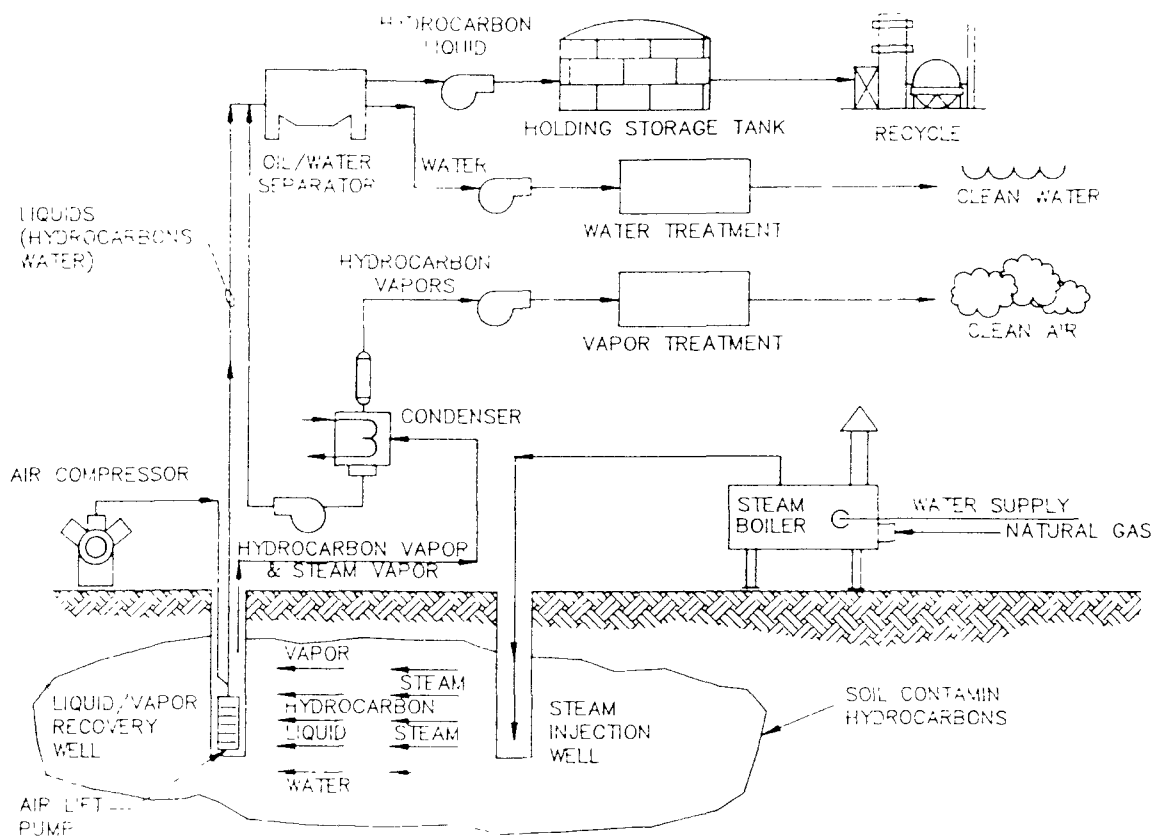


Figure 3.7.2.5 Schematic of in-situ steam enhanced extraction process [USEPA, 1992d].

mg/kg to 12 mg/kg total contaminant concentrations [Udell Technologies, 1991].

The well hardware for the pilot study was installed in 18-inch borings. A cylindrical treatment cell with an injection well encircled by six injection wells at a 5-ft. radius was employed. The injection wells were constructed of 1-inch diameter steel pipe (for steam delivery from the manifold) which was insulated and encased within a 6-inch diameter low carbon steel casing. The screened sections for the injection and extraction wells were constructed of 6-inch diameter low carbon schedule 40 slot wire wrap screen. The in-situ temperatures were monitored using 3/4-inch diameter schedule 80 steel pipe which housed thermocouples spaced at approximately 1-foot vertical intervals.

Utilizing this design, approximately 763 lbs of contaminants were removed following 140 hours of steam injection cycled with vacuum extraction [Udell and Stewart, 1989]. No vapors were observed escaping from the treatment cell. Vacuum extraction alone was responsible for 29% removal, while the total contribution resulting from steam injection was 71%. The pilot study operational parameters were: steam injection of approximately 250 lb/hr at injection pressures of 6 psig, vacuum rates of approximately 25 scfm, and a well spacing of 5 feet [Udell and Stewart, 1989].

Full-scale Steam Enhanced Recovery Process (SERP) is currently under way in Huntington Beach, California. Recovery of 135,000 gallons of diesel is being attempted at depths of 40 ft [USEPA, 1991b]. Thirty-seven steam injection wells and 39 dual vacuum extraction (vapor/liquid) wells were employed to

remediate approximately two acres of subsurface below a truck unloading facility. Vapor flow of the extraction system was 1200 cfm. In five months of operation, 4400 gallons of free product condensate and vapors amounting to 14,000 gallons of product have been recovered, effectively reducing the plume to 20-30% of its original volume [van Sickle, 1992]. No offsite migration of vapors or liquids was detected, and surface activities were not interrupted. Ex-situ treatment of recovered liquids and vapors included thermal oxidation and waste water treatment, respectively [van Sickle, 1992].

A full-scale attempt at cleanup of a gasoline contaminated aquifer is currently in operation at Lawrence Livermore National Laboratory in Livermore, California, at depths of 137 feet [USEPA, 1991a]. The estimated gasoline spill size was on the order of 6200 gallons. Steam was periodically injected for approximately two months. To date, over 7400 gallons of petroleum hydrocarbons were removed [Udell, 1993]. Three weeks after shutdown of the steam injectors, contaminant removal from the aquifer remained on the order of 50-100 gallons/day. Preliminary estimates indicate that the contaminant removal attained by combined steam injection/vacuum extraction is approximately forty times greater than that attainable by conventional soil vapor extraction and ground-water pumping [Udell, 1993].

Applicability/Limitations--

SEE has successfully mobilized volatile and semi-volatile NAPLs, as well as certain inorganics, from both the unsaturated and saturated zones through steam injection coupled with vapor and condensate extraction in a controlled manner [Hunt et al., 1988c; Udell and Stewart, 1989, 1992]. The successful removal of halogenated semi-volatiles such as dichlorobenzene (DCB, all isomers) is possible, and dioxins can be mobilized by the condensation front [Udell Technologies, 1991]. Treatability and pilot studies have documented the efficacy of SEE on multicomponent mixtures of petroleum hydrocarbons and solvents [Hunt et al., 1988c; Udell and Stewart, 1989, 1992] in a variety of saturated and unsaturated media: sand, ash, and silty clays with gravels.

Types of media which can be treated include in situ soils and sludges both saturated and unsaturated. Efficacy is site specific; and in general, sites dominated by silts and clays present problems, as is the case for all in situ technologies. Hence, impermeable layers may not be remediated to the targeted cleanup levels. However, contaminant reduction by SEE can be expected in these areas and heterogeneous regions by the vacuum drying mechanism [Udell and Stewart, 1992]. Because SEE utilizes both heat and mass transfer for remediation, successful treatment is less susceptible to heterogeneities than with other in situ technologies. One-dimensional soil column treatability studies are recommended. To date, no applications of SEE performed in fractured rock are known to exist.

It is expected that shallow applications of SEE will not result in the sterilization of aquifer media and that microorganisms will persist in a dormant state [Alvarez-Cohen, 1993b]. Upon cooling of the porous media, they are expected to flourish: thus, thermally enhanced in-situ biodegradation is anticipated as a secondary benefit of SEE. However, deeper applications of SEE which require greater injection pressures may result in the complete sterilization of aquifer media, and in-situ biodegradation is only anticipated to occur after re-acclimation and repopulation [Alvarez-Cohen, 1992]. Therefore, no biofouling is expected. Also, clogging of porous media is not likely to result from precipitation of inorganic compounds, as described earlier.

With the exception of borings, SEE is not intrusive; and, there are few limitations due to interference from ground structures, overhead or buried utilities, and other subsurface obstructions. Site grading is not a problem. The ex-situ hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

Depth of application and soil type will dictate allowable steam injection pressures, well spacing, and thus cost [USEPA, 1991b]. Capital cost will depend on well spacing per unit area and depth of application.

basis because the boring and well construction are the major cost items. For these reasons, SEE is very attractive for use in the most contaminated hot spots for rapid pure product recovery.

Cost and Availability--

US Patent No. 5,018,576, has been awarded to the University of California for SEE [Udell et al., 1991], and US Patent No. 5,009,266 for a similar technology is held by USPCI, a subsidiary of the Union Pacific Corporation.

One pilot study involving dense immiscible hydrocarbons in the vadose zone has been completed [Udell and Stewart, 1989]. Pilot-scale treatability studies require a minimum of 50 yd³ of soil [Udell Technologies, 1991]. A demonstration of SEE is proposed as part of the SITE Demonstration Program at McClellan AFB near Sacramento, California [USEPA, 1991a,b]. Two full-scale SEE applications for remediation of gasoline contaminated soils are currently under way [USEPA, 1991a,b]. No other domestic full-scale applications are known to exist at this time.

SEE can operate both above and below the water table therefore making it a good candidate for cleanup of both LNAPLs and DNAPLs. It will have its biggest impact on NAPL source areas. Studies show that it can enhance contaminant removal from low permeability zones. It has not been applied to fractured media at this time.

SEE is anticipated to cost about \$50-125/yd³ depending on site characteristics [Udell Technologies, 1991]. Included in this estimate is the treatment of the waste streams emanating from the recovery wells: condensible and non-condensable gases, and extraction pump liquids. Condensible gases and extraction pump liquids are concentrated for recycling or destruction by separations equipment. Non-condensable gases are collected and treated by granular activated carbon units.

The factors cited to most influence the overall treatment cost are: areal extent of treatment, depth of contamination, waste quantity and targeted cleanup goal, site preparation, ongoing surface activities and waste handling [Udell Technologies, 1991].

3.7.3 Radio Frequency Heating

Theoretical Background--

Radio Frequency (RF) heating is an enhanced oil recovery process which uses electromagnetic energy to accomplish subsurface heating, thereby enhancing contaminant removal. The primary removal mechanisms, which depend on the actual heating strategy, are: vaporization of low boiling point (b.p.<100°C) organic compounds and water; enhancement of evaporation rates of higher boiling point (b.p.>100°C) organic compounds; partial or complete displacement of heated pore fluids by a propagating steam condensation front partial or complete displacement of all contactable NAPLs by the propagating steam front, and/or enhanced pore liquid mobilization resulting from liquid density and viscosity alterations (increased capillary numbers). The flexibility of applied temperatures and geometries allows this technology to potentially operate analogously to either CROW® or SEE (section 3.7.1 and 3.7.2, respectively), or it may be used in conjunction with, or as a precursor to, soil washing processes (section 3.5)

The focus here is on the actual heating mechanisms; ohmic and dielectric heating of pore fluids [Dev et al., 1988]. Wave frequencies in the range of 6.78 MHz to 2.45 GHz are used to achieve bulk volumetric heating of the pore fluids and porous media [Dev et al., 1987]. Ohmic heating results from ionic or conduction current flow through the porous media. Dielectric heating refers to the mechanism by which electromagnetic energy is converted into thermal energy. In this process, agitation and physical distortion of the molecular structure of polar compounds (i.e., water), initiated by an applied alternating AC electric field, result in increased kinetic activity and thus heating. Important parameters governing the success of

dielectric heating are the relative dielectric constant of the porous medium and its loss-tangent, where the loss tangent is defined as the ratio of the apparent conductivity to the frequency, relative dielectric constant, and permittivity of a vacuum [Dev et al. 1988]. The dielectric properties of porous media decrease with increasing applied frequencies [von Hippel, 1954].

The amount of RF power adsorbed is directly proportional to the frequency of the applied electric field, the square of the amplitude, the relative dielectric constant, and the loss tangent [Dev et al., 1988]. Medium breakdown, corona discharge and ohmic heating result with increased power and thereby limit the useful transmitter output [Smith and Hinchee, 1993]. The effective penetration depth, or "skin depth," of the electromagnetic energy is defined as the distance at which the wave amplitude decreases to 37% of its initial value [Dev et al., 1987]. The skin depth decreases with increasing loss tangent, relative dielectric constant (ϵ_r) and apparent conductivity [Morey, 1974; Johnson and Sitar, 1986]. The ϵ_r for dry soils varies between 2 and 10, and typical values for different materials are available [von Hippel, 1954; Morey, 1974; Okrasinski et al., 1979]. Since $\epsilon_{\text{water}} \sim 80$ is very high, RF adsorption in highly water saturated porous media is large, making the penetration depth small. Thus, water immediately adjacent to the RF electrodes is converted to steam which may assist in NAPL recovery, and in this way a steam front can be generated.

The impact of water on ϵ_r and the loss tangent, even at low saturations, can be seen in Figure 3.7.3.1 which shows the relationship between loss tangent, relative dielectric constant and soil temperature for a sample of Utah tar sand. Although the water content of the tar sand was not reported, ϵ_r s between 4 and 8 suggest that it must be very low, considering ϵ_{NAPL} (see Table 2.1) is usually below 5 and ϵ_{water} is about 80. In Figure 3.7.3.1, ϵ_r increases from an initial value of 6 to a peak value of 8. As water is boiled off ($T \sim 100^\circ\text{C}$), ϵ_r and the loss tangent are abruptly reduced to a final value of 4 and 0.1, respectively. Thus, as water is boiled off near the RF electrode, the corresponding decrease in loss tangent indicates that the skin depth effectively increases. However, the drop in loss tangent affects the efficiency of coupling between the RF field and porous media. This represents a major challenge in RF system design. Coupling may be maintained by changing transmission frequency and/or electrical properties of the network [Smith and Hinchee, 1993].

Field Implementation--

A schematic of a field implementation is shown in Figure 3.7.3.2. Horizontal well configurations are also possible [Sresty et al., 1986]. Since the generated EM waves used for soil heating can interfere with communications and navigation equipment as well as pose a human health threat, any RF application must be designed to effectively contain the EM radiation within the specified soil treatment zone. Triplate line and fringing-field transmission line arrays are therefore employed [Dev et al., 1988]. The triplate line array system, as shown in Figure 3.7.3.2, will be described here since it has been used in an enhanced oil recovery and environmental application. The fringing-field transmission line configuration is described elsewhere [Dev et al., 1987].

The triplate line configuration is an electromagnetic analogy to a central conductor enclosed between two parallel plates. Tubular electrodes are arranged in three parallel rows. Whereas the frequency of operation is governed by the dielectric properties of the porous media and treatment zone size, the geometry and spacing between rows is governed by the thickness of the treatment zone (or deposit), heating rate and final heating temperature. In enhanced oil recovery applications, the spacing between rows has been taken to be less than the deposit thickness [Sresty et al., 1986]. The spacing of electrodes in each row is generally somewhat smaller than the row spacing. Electrodes can be constructed of thin-walled pipe, copper, steel or aluminum tubing which can be perforated to accommodate vapor flow [Sresty et al., 1992a]. In large applications, use of low cost materials such as aluminum permits electrode abandonment.

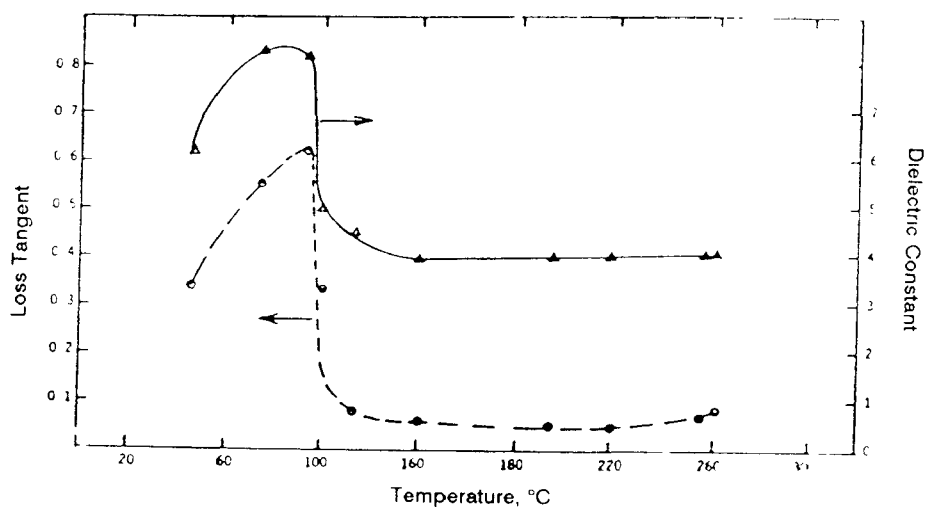


Figure 3.7.3.1 Loss tangent and dielectric constant of tar sand samples [Vernon et al., 1986].

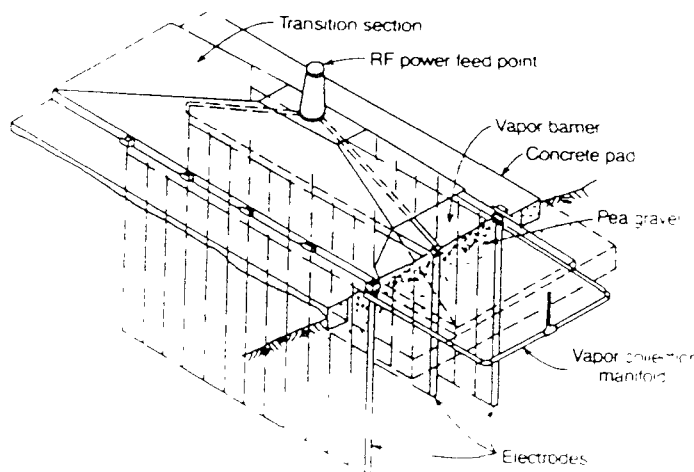


Figure 3.7.3.2 Schematic of radio-frequency soil heating process showing electromagnetic electrode array and vacuum hood [Dev and Downey, 1988].

As the subsurface is heated, water and contaminant vapors flow to the ground surface or the nearest perforated electrode. For applications installed at the ground surface, Halon® tracer experiments have confirmed that the induced vapor flow produces a draft into the soil treatment zone from the adjacent porous media [Dev and Downey, 1988; Dev et al., 1988]. Depending on the initial water content and soil temperature, steam and/or distilled vapor fronts can be established in-situ which aid in recovery (see section 3.7.2 for details on steam recovery mechanisms). Vapors are recovered by a vapor collection manifold/impermeable barrier system situated at the ground surface. Subsurface heating also promotes gravity segregation of pore fluids because of density and viscosity alterations. In fact, gravity drainage of viscous bitumen from tar sands is economically favorable [Sresty et al., 1986].

When the soil temperature is below 100°C, hot-water displacement of NAPLs may assist in NAPL recovery. Any combination of compounds such as alkaline agents, surfactant, polymers (density

enhancement) and viscosifiers may be introduced into the treatment zone to ensure a more favorable mobility ratio between the hot water and the NAPL or to enhance compound solubilities.

Level of Demonstration and Performance--

Recovery of bitumen from a tar sand deposit was conducted in small-scale field experiments at the Asphalt Ridge deposit near Vernal, Utah [Sresty et al., 1986]. On a surface outcrop, an RF electrode array was installed vertically into the tar sand deposit. Mobilized bitumen was allowed to drain by gravity into a collection gallery within a pre-existing mine shaft situated directly below the RF array. Approximately 33 cu yd (25 m³) of tar sands were heated by 20 ft long electrodes arranged in a triplate geometry. The daily power input varied from 40 to 75 kW, and soil temperatures were increased to approximately 200°C. RF power was terminated after 20 days. Total bitumen production from this experiment was approximately 336 gals, or 35% recovery. Redistribution of bitumen as a result of gravity drainage was clearly evident, even though bitumen viscosity at 100-150°C was on the order of 20-50 cp [Sresty et al., 1986].

The fire training pit area at the Volk Field Air National Guard Base in Wisconsin is the site of the only known environmental application of RF heating [Dev and Downey 1988; Dev et al., 1988; Sresty et al., 1992a]. The sandy subsurface soils have been contaminated with numerous waste oils, fuels and solvents yielding hydrocarbon concentrations up to 4,000 ppm. Depth to the water table is approximately 12 ft. The moisture content profile for the vadose zone was not provided.

A triplate electrode array using perforated electrodes was installed within a 6 x 12 ft test cell area. Each row consisted of 13 electrodes using a 1 ft spacing for a total row length of 12 ft. Spacing between adjacent rows was 3 ft. The center and outer rows were installed in the vadose zone to depths of 6 and 8 ft, respectively. Thermocouples were attached to the inner sides of the electrodes to monitor soil heating. Fluid-filled thermowells were installed to measure soil temperatures between electrode rows. At the ground surface, a concrete frame was constructed around the test cell area and an impermeable silicon rubber sheet was bonded to it to form the vapor barrier. Below the vapor barrier, two perforated vapor extraction tubes were installed at the ground surface through which a low vacuum equivalent to 6 in H₂O was applied.

A daily power input of 35 kW, at 6.78 MHz, was used for the first four days of the test to vaporize the porewater. This input was reduced to 20 kW for the remainder of the test. Soil temperatures exceeded 100°C within two days of soil heating. After day 8, the soil temperatures reached 150-160°C in the center of the test cell, and were maintained at that temperature for four days. Soil temperatures along the test cell periphery averaged about 100°C owing to heat conduction losses to the surrounding porous media. The test duration was 12.5 days. Since effluent concentrations were not measured and contaminant influxes into the test were not estimated, a mass balance calculation was precluded. Contaminant removal was based on soil samples.

Soil samples were taken after the test was shut down for 17 days, at which time the soil had cooled to 50-60°C [Dev et al., 1988]. Soil analyses revealed that the removal rate for volatiles (b.p.<120°C) was 99.6% and 99.3% for aromatic and aliphatics, respectively. The removal rate for semi-volatiles (120°C<b.p.<300°C) was somewhat less: 99.1% and 94.3% for aromatics and aliphatics, respectively. Contaminant removal increased with depth, and this trend was thought to be caused by two factors: hydrocarbon condensation near the ground surface resulting from lower near surface temperatures along the edges of the test cell; and hydrocarbon condensation within the test cell near the ground surface that may have occurred from shutting down the vapor extraction system 24 hrs after heating was terminated.

Applicability/Limitations--

RF heating technology is applicable to soils contaminated by low and high boiling point organic compounds. For applications with temperatures occurring below the boiling point of a given compound, enhanced volatilization is likely to be the dominant removal mechanism.

The soil water content greatly affects the viability of RF heating because of the large dielectric constant of water. The initial water contents of the samples tested were on the order of 5 to 12 wt%. It is therefore difficult to ascertain whether RF heating is a viable technology for environmental applications in the saturated zone: and if it is, what are its possible advantages over SEE are (section 3.7.2). Radio frequency heating equipment requires a high degree of sophistication to implement and operate [Smith and Hinchee, 1993].

Bench and pilot treatability studies simulating in-situ heating (nitrogen/steam injection) have indicated that the presence of clay minerals did not significantly affect contaminant removal [Sresty et al., 1992a]. Although the RF process was not used, this result seems surprising in light of the low permeability of clays and their high moisture contents. Furthermore, field scale stratigraphy with low permeability lenses has been observed to not only affect steam front propagation, but also contaminant removal [Udell and Stewart, 1989, 1992; Ho and Udell, 1992]. The affect of soil stratigraphy on the actual RF heating process has yet to be evaluated. The high temperatures employed by RF heating may inhibit and destroy indigenous microorganisms, and could have an adverse impact on the humic matter in soil [Smith and Hinchee, 1993]

With the exception of borings, the RF heating process is not intrusive; therefore, there are few limitations with respect to interference from ground structures and overhead utilities. Site grading is not a problem. Subsurface obstructions such as buried utilities, abandoned foundations, etc., appearing within the RF treatment zone may reduce the effectiveness of the process or potentially cause leakage of EM energy. Leakage of EM energy is a concern because of its interference with communications and navigation equipment and human health. The ex-situ hardware can be trailer-mounted and constructed of readily available materials and standard unit operations equipment.

Cost and Availability--

This technology is commercially available through the Illinois Institute of Technology Research Institute (IITRI). The process is reported to have been patented by IITRI, and is exclusively licensed to Roy F. Weston, Inc. [Roy F. Weston, Inc., 1989]. Two field scale studies have been completed, and others are planned [Sresty et al., 1992b]. However, no application has been completed in the saturated zone or specifically on DNAPLs.

Radio frequency heating technology appears to hold promise for cleanup of dissolved contaminants and DNAPLs, but many issues are unresolved at this time. Radio frequency heating is anticipated to have its biggest impact on DNAPL source areas. However, since the objective is to heat the subsurface and to generate a sweep front, it is not clear whether RF heating has any distinct advantage over steam injection.

The cost of RF heating is estimated to be on the order of \$40-100/ton of soil depending on soil moisture content, and final treatment temperature [Sresty et al, 1992a]. This estimate is based on a maximum soil moisture content of approximately 20%. Residuals produced by this process include vapors, and steam and vapor condensates. Gas vapors can undergo cooling to condense out low boiling point NAPLs which can be followed by carbon treatment polishing. Condensed liquids can be reclaimed/recycled.

3.7.4 Vitrification

Theoretical Background--

In-situ vitrification (ISV) is a process that relies on joule resistance heating and consequent melting of the contaminated zone to enhance organic contaminant removal. The primary mechanisms are: accelerated chemical reactions in the soil surrounding the melt and the pyrolysis zone (thermal zone

adjacent to the melt); recovery of organic vapors in a vacuum hood situated above the soil treatment zone; pyrolysis of DNAPLs in the melt and pyrolysis zones; and pyrolysis of combustible vapors in the vacuum hood [Dragun, 1991].

Joule resistance heating of the soil results from electric current flow through the porous media [Fitzpatrick et al., 1984]. Since the soil becomes more conductive upon melting, the voltage and current requirements must be adjusted to maintain the same power delivery. To initiate the soil melt, a conductive mixture of graphite and glass frit is placed on the ground surface between the electrodes to serve as an initial conductive (starter) path, see Figure 3.7.4.1 [Hansen and Fitzpatrick, 1991]. An electric potential is applied, and the high current flowing through the graphite and glass frit causes them to melt. Heat is transferred by conduction from the molten mass to the surrounding soils which causes boiling of pore fluids and, ultimately, melting of the soil. Soil temperatures of 1,600 to 2,000 °C can be achieved [Hansen and Fitzpatrick, 1991]. Upon melting, the adjacent soils become electrically conductive. In this way, the process is continued beyond startup and the molten mass grows vertically downward at an approximate rate of 1-2 in/hr to the desired treatment depth [Fitzpatrick et al., 1984]. The chemical reactions and processes which are thought to occur within the soil melt and the adjacent soils are depicted in Figure 3.7.4.2.

The propagating soil-melt interface is preceded by a transition zone, dry zone, and pyrolysis zone, respectively. The total combined thickness of these zones is approximately 9-12 inches [Hansen, 1993]. Within the transition zone (~25-100°C), enhanced vaporization of soil moisture and DNAPLs occurs. When soil moisture and low boiling point (b.p.<100°C) DNAPLs are reached by the propagating 100°C isotherm, they are boiled in-situ. Enhanced volatilization of high boiling point (b.p.>100°C) DNAPLs occurs in the transition zone and dry zone (~100-400°C) until the soil temperature reaches the boiling point of the compound. The dry zone is narrow and is reported to have temperature gradients on the order of 150-250°C/in [Hansen and Fitzpatrick, 1991]. Since the liquid saturation of the dry zone is low and its gas permeability is high, the dry zone is thought to serve as a conduit for water and organic vapor flow to the ground surface. Other vapors may reach the ground surface through the perforated electrodes. Within the oxygen-deficient pyrolysis zone and reducing environment of the high temperature melt zone, any remaining high boiling point compounds are thermally decomposed. Convective currents within the molten soils mass cause it to have a uniform chemical composition [USEPA, 1988; Dragun, 1991]. Because of convective mixing, pyrolysis byproducts can also reach the ground surface. As vapor, gases and other organic pyrolysis products escape from the treatment zone at the ground surface, they are captured in the vacuum hood. Flammable pyrolysis products encounter oxygen in the vacuum hood and are combusted. All emissions are treated by an off-gas treatment system.

Elevated temperatures accelerate a variety of reactions between the organic compounds, soil moisture, and mineral surfaces of the porous media. Dragun (1991) enumerates that hydrolysis, substitution, oxidation, reduction, and surface-catalyzed reaction rates may be increased in the affected soil zones.

Upon cooling, the vitrified soil mass resembles obsidian. This amorphous material has a strength 5-10 times that of concrete, high leach resistance [Buelt and Westsik, undated], and its durability is similar to that of granite [EPRI, 1988].

Field Implementation--

A schematic of a typical field implementation of ISV is shown in Figure 3.7.4.1. The objective of the ISV process scheme is to create a molten soil mass in which heavy metals and radionuclides are stabilized and DNAPLs are pyrolyzed. The strategy implemented to accomplish in-situ heating is summarized below.

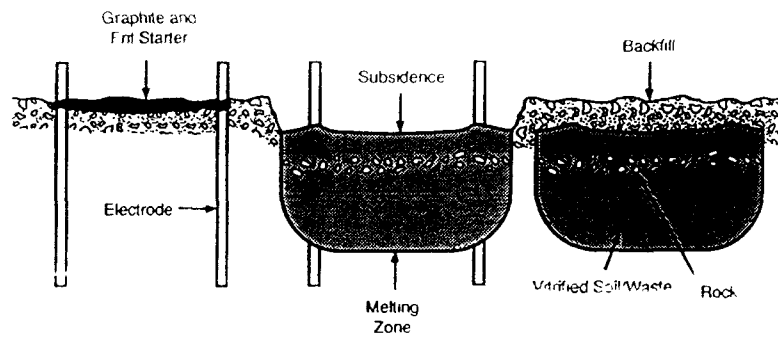


Figure 3.7.4.1 Schematic illustrating the in-situ vitrification (ISV) process [Smith and Hincsee, 1993].

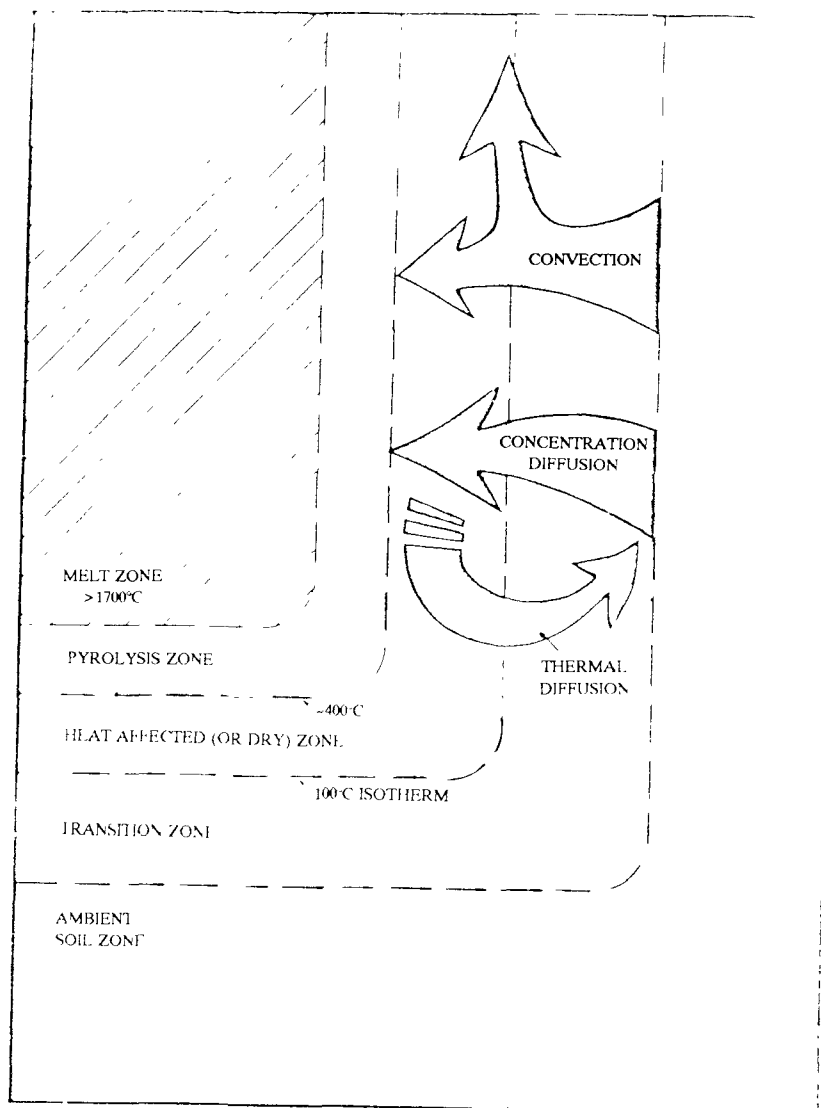


Figure 3.7.4.2 Chemical processes and reactions occurring within and near the soil melt zone [Dragun, 1991].

Electrodes have been constructed of molybdenum cores and perforated graphite collars [Hansen and Fitzpatrick, 1991]. Electrodes can either be fixed, that is, installed to a specified depth, or can be moveable, which allows them to be lowered as the soil melt progresses downwards. A 50 ft diameter vacuum hood is placed over an electrode array to capture fugitive emissions emanating from the heated soil zone. Under the hood, square electrode arrays having a maximum width of 35 ft are possible. Electrode installation depths have exceeded 19 ft, and depths as great as 25 ft are considered possible [USEPA, 1992d]. Soil has been treated to a depth of 24 ft [Smith and Hincsee, 1993]. The applied vacuum of the off-gas treatment system is on the order of 0.5 to 1.0 in H₂O.

After treatment is complete, subsidence occurring at the ground surface can be back-filled. The process can be sequentially applied and adjacent melts can be fused together [Hansen and Fitzpatrick, 1991]. Mobilization between treatment zone locations requires approximately 16 hours [Dragun, 1991].

Level of Demonstration and Performance--

Since 1980, 20 pilot-scale and 6 large-scale ISV tests processing 10-50 and 400-800 tons of contaminated soil, respectively, have been completed using metals and simulated radionuclides [Dragun, 1991]. ISV has been tested at several private, Superfund, and U.S. Department of Energy (DOE) sites [USEPA, 1992d]. None of these applications have included organic compounds. Testing with NAPLs has occurred on the engineering test-scale using soil quantities of 1 ton or less [Hansen, 1993]. Table 3.7.4.1 illustrates typical removal efficiencies for porous media containing several organic compounds.

Applicability/Limitations--

The ISV process was originally developed for sites contaminated with heavy metals and radionuclides [USEPA, 1988] where there are very few options for treatment and the treatment costs are enormous. The ISV process can theoretically destroy DNAPLs by pyrolysis and it has been demonstrated in small-scale tests [Hansen and Fitzpatrick, 1989, 1991]. Therefore, ISV is a potentially attractive treatment alternative for sites containing mixed inorganic and organic wastes.

A limitation of the technology is that ground-water recharge in permeable soils with hydraulic conductivities greater than 10^{-4} cm/s will stop the progress of the melt [USEPA, 1988; Hansen 1993]. This makes the ISV process essentially applicable to treatment of vadose soils only, unless dewatering, containment, or other hydraulic controls are engaged to minimize ground-water recharge into the treatment zone [Hansen and Fitzpatrick, 1989]. While the process may be applicable to fine grained saturated soils such as clays because of their low hydraulic conductivity [Hansen, 1992] and higher relative electrical conductivity than coarse soils [McElroy, 1993], the amount of DNAPL contained within clay soils is likely to be low compared to that of coarser media.

Subsurface obstructions and features can interfere with the operational efficiency of the ISV process. While ISV can accommodate a very heterogeneous subsurface, several rule-of-thumb limitations apply: general metals concentration of 5-16 wt%; no continuous metal traversing a distance greater than 90% of the electrode spacing; combustible organic concentrations limits of 5-10 wt%; rubble limit of 20 wt%; must have sufficient glass forming minerals (usually not a problem for soils); and individual void volumes less than 150 ft³ [Hansen and Fitzpatrick, 1989, 1991; USEPA, 1992d; Smith and Hincsee, 1993]. Buried drums, crates and cartons containing wastes may pose additional problems [Hansen and Fitzpatrick, 1991]. High concentrations of iron or other dense metals may result in its pooling near the bottom of the melt and current short circuiting [Hansen and Fitzpatrick, 1989]. Concentrated vapor loading of pyrolyzed organics from DNAPL pools may potentially overload the off-gas treatment system.

The ISV process produces a solidified soil mass, and the subsurface is essentially unusable once the process is complete. However, the vitrified mass can be broken and moved. Light structures or vegetation may be supported on the backfill materials, but there is usually little incentive to reuse land

contaminated by mixed wastes containing radionuclides [Hansen, 1993]. Since vitrification results in the collapse of the pore volume and removal of combustible organic materials, soil volume reduction on the

TABLE 3.7.4.1 TYPICAL ORGANIC DESTRUCTION/REMOVAL EFFICIENCIES BY ISV [Hansen and Fitzpatrick, 1991].

Contaminant	Concentration (ppb)	Percent Destruction	Percent Removal (1)	Total DRE (%)
PESTICIDES	*****	*****	*****	*****
4, 4 DDD/DDE/DDT	21-240,000	99.9-99.99	>99.9	99.9999
Aldrin	113	>97	>99.9	99.99
Chlordane	535,000	99.95	>99.9	99.9999
Dieldrin	24,000	98-99.9	>99.9	99.99
Heptachlor	61	98.7	>99.9	99.99
VOLATILES	*****	*****	*****	*****
Fuel Oil	230-110,000	>99	>99.9	99.999
MEK	6,000 (2)	>99	>99.9	99.999
Toluene	203,000	99.996	>99.9	99.99999
Trichloroethane	106,000	99.995	>99.9	99.99999
Xylenes	3,533,000	99.998	>99.9	99.99999
SEMI-VOLATILES	*****	*****	*****	*****
PCP	>4,000,000	99.995	>99.9	99.99999
NON-VOLATILES	*****	*****	*****	*****
Glycol	8,000 (3)	>98	>99.9	99.99
PCBs	19,400,000	99.9-99.99	>99.9	99.9999
Dioxins	>47,000	99.9-99.99	>99.9	99.9999
Furans	>9,400	99.9-99.99	>99.9	99.9999

- (1) Percent removed from off-gas after destruction; percentages are additive for the total DRE.
- (2) 98% MEK in container, yielding 6,000 ppm in layer of container thickness
- (3) 50% ethylene glycol in container, yielding 8,000 ppm in layer of container thickness

order of 25-45% is possible. In one application, 4 ft of subsidence was observed [Geosafe Corp., 1992]. The vacuum hood requires a side clearance of 15-20 ft [Hansen and Fitzpatrick, 1991].

The ex-situ hardware is trailer-mounted. The large ISV equipment can treat soil at a rate of approximately 10,000 lbs/hr [Hansen and Fitzpatrick, 1989]. Since typical soil applications require 0.35-0.4 kilowatt hrs/lb, 4,000 kilowatts per application are required. This is comparable to the daily energy consumption of an average-size hotel in a major city [Hansen and Fitzpatrick, 1989]. However, because of the efficiency of soil heating, ISV consumes less than one-third the energy of an incinerator [Hansen, 1993].

Cost and Availability--

No field- or full-scale ISV applications exist involving DNAPLs situated below the water table. The U.S. Department of Energy has been awarded the patent (Patent No. 4,376,598) for the ISV process

[Fitzpatrick et al., 1984]. DOE has licensed the technology to Battelle, which created the Geosafe Corporation (Kirkland, Washington) and has exclusively sublicensed the ISV technology to Geosafe for commercialization purposes [Hansen and Fitzpatrick, 1989]. Geosafe is participating in the SITE Program; and the Parsons/ETM site in Grand Ledge, Michigan, has been selected for the demonstration [USEPA, 1992d]. The ISV process has been selected as a preferred technology at ten other sites (private, Superfund and DOE sites) [USEPA, 1992d].

The ISV process is not a viable candidate for in-situ cleanup of DNAPLs below the water table because the presence of water will stop the progression of the melt unless ground-water recharge is cut-off. Other methods should therefore be sought. However, for mixed wastes containing radionuclides and DNAPLs, few remedial alternatives exist and dewatering or impermeable barrier construction may be warranted.

The cost of a treatability study to determine the viability of ISV is on the order of \$35-40,000, and could be more depending on unusual analytical requirements [Hansen and Fitzpatrick, 1989]. Process cost estimates which exclude mobilization costs (\$125-200,000) and sampling costs (\$50-80,000) have been provided [Fitzpatrick et al., 1984; Hansen and Fitzpatrick, 1991]. Major factors affecting the process cost of ISV include: cost of electrical power; initial moisture content of soil and recharged water to be removed during the ISV process; depth of treatment; and analytical requirements associated with process control and permit compliance [Hansen and Fitzpatrick, 1991]. The dependency of process cost on moisture content and electrical rates using 1982 dollars is shown in Figure 3.7.4.3. For a vadose soil containing 25% moisture, Figure 3.7.4.3 predicts that the maximum total cost will approach approximately \$450/yd³ [Fitzpatrick et al., 1984]. More current estimates place typical ISV process costs at \$300-400/ton using a non-specific moisture content basis [Hansen and Fitzpatrick, 1991].

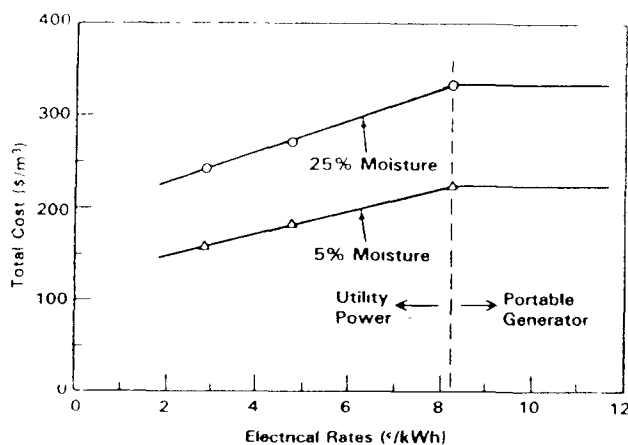


Figure 3.7.4.3 Effect of soil moisture on cost of in-situ vitrification [Fitzpatrick et al., 1984]

SECTION 4.0

IN-SITU TECHNOLOGY COMPARISONS

4.1 INTRODUCTION

In the previous sections of this report, the factors controlling the fate and transport of DNAPLs have been reviewed, and the various technologies with a potential for application in remediation of DNAPL contamination have been described. The purpose of this section is to provide side-by-side comparisons and an overview of the technologies reviewed in the report. To facilitate the overview, Table 4.1.1. lists the major characteristic features of each technology. The entries in the table are based on the essential features of each technology, and on judgement and interpretations made on the basis of the available information.

4.2 EXPLANATION OF TERMS

The main factors used to rate each technology are as follows: Design Basis; Operational Mechanism; Applicability; Scale of Demonstration; Expected Efficiency, Commercial Availability; and Approximate Cost Range.

Design Basis--

This aspect of the technology is classified as either theoretical or empirical. The distinction is made on the basis of how well the specific application is researched and elucidated, and how much of the implementation is theoretically based versus common sense and field experience. Though a technology is designated as "theoretical," this does not imply that its implementation will be more successful than an "empirical" one, even if designed by qualified professionals, because of site specific considerations.

Operation Mechanism--

This heading relates to the intended use and purpose of the technology and is defined as either: treatment (i.e., degradation, destruction); recovery (i.e., enhanced solubility, mobilization, volatilization, coupled with recovery); or containment (i.e., immobilization, isolation). Some technologies have multiple capabilities, but the major emphasis is indicated.

Applicability--

Applicability refers to the type of contamination for which the technology is suitable, and the terms used in Table 4.1.1 are self explanatory. For limitations and problems associated with each specific technology, the reader is referred to the specific technology descriptions (section 3.0). These issues could not be conveniently and briefly summarized within Table 4.1.1.

Scale of Demonstration--

This indicates the most current testing or demonstration level of the technology as it specifically pertains to environmental applications. For example, electro-osmosis has been implemented on the full-scale in geotechnical engineering applications for several

decades, but specific environmental applications are still at the pilot scale. Similarly, soil washing (flooding) using alkalis, cosolvents and surfactants and combinations of these compounds has been demonstrated in the petroleum engineering field, yet specific applications to environmental problems and conditions are still at the emerging and pilot scales.

Expected Efficiency--

Under this heading the anticipated efficiency is rated at the full scale solely within the context of the technology's operational mechanisms and its applicability. By rating the expected efficiency of slurry walls as "high," the proper interpretation is that for their intended purpose, that is containment of the dissolved and separate phases, slurry walls usually perform extremely well. As an additional example, it is not implied that air sparging is capable of recovering separate phase DNAPLs efficiently.

Commercial Availability--

Degree of availability indicated. Many of the technologies and/or the components comprising and utilized by the technologies were formerly established in other disciplines and are presently available. A few technologies have completed pilot scale testing, and are ready for scale up to full scale and/or have been previously implemented in other disciplines (e.g., chemical flooding).

Approximate Cost Range--

Estimated costs in $\$/\text{yd}^3$ have been developed to provide a benchmark of anticipated costs and to provide relative comparisons between technologies. Where costs in section 3.0 were reported on a $\$/\text{ton}$ basis, a soil unit weight of $120 \text{ lb}/\text{ft}^3$ was used as a conversion factor. While technologies such as slurry walls and hydraulic gradient control can provide containment relatively inexpensively, it should be realized that the majority of the DNAPL remains in the subsurface.

4.3 PROMISING TECHNOLOGIES

As already indicated in Section 2.7, the remediation of DNAPLs faces a number of challenges posed by the site stratigraphy and heterogeneity, the distribution of the contamination, and the physical and chemical properties of the DNAPL. Thus, a successful technology has to be able to overcome the problems posed by the site complexity and be able to appropriately modify the properties of the DNAPL to facilitate recovery, immobilization, or degradation. In addition, the methodology has to be adaptable to different site conditions and has to be able to meet the regulatory goals. There are several ways in which to define a "promising technology." A promising technology for the purposes of this report is defined as a technology that is capable of effectively treating or recovering the DNAPL from the source areas, lenses and pools, and residually contaminated zones.

Because the thermally based technologies represent perhaps the largest thermodynamic perturbation to the subsurface system, they are among the most promising. Among thermal technologies, steam enhanced extraction (SEE) is probably the most promising candidate. The CROW® process relies on similar mechanisms, however, it is not clear whether the injection of hot water and low quality steam offers an advantage over SEE. Radio frequency heating, which relies on in-situ steam generation to be most effective, has only been tested in the vadose zone.

TABLE 4.1.1. IN-SITU TECHNOLOGY COMPARISONS

IN SITU TECHNOLOGY	DESIGN BASIS	OPERATIONAL MECHANISM	APPLICABILITY	SCALE OF DEMONSTRATION	EXPECTED EFFICIENCY	COMMERCIAL AVAILABILITY	APPROX. COST RANGE (\$/yd ³)
Aerobic Biodegradation	Theoretical	Treatment	Dissolved phase only	Pilot	Intermediate/High	Pilot/Available	15-60
Anaerobic Biodegradation	Theoretical	Treatment	Dissolved phase only	Pilot	Intermediate/High	Pilot/Available	15-60
Electro-Osmosis	Theoretical	Treatment/ Recovery	Dissolved phase only	Pilot	Low	Available	75-150
Electroacoustic Soil Decontamination	Empirical/ Theoretical	Treatment/ Recovery	Dissolved phase only	Laboratory	Low	Emerging	60-150
Slurry Walls	Empirical	Containment	Dissolved and separate phase	Full	High	Available	7-13/ft ²
Grouting	Empirical	Containment	Dissolved and separate phase	Full	Intermediate/High	Available	60-100
Hydraulic Gradient Control	Theoretical	Containment	Dissolved phase only	Full	Intermediate/High	Available	50-100
Stabilization/Solidification	Empirical	Containment	Dissolved and separate phase	Full	Intermediate/High	Available	SSM 26-65 DSM 130-260
Permeable Treatment Walls	Empirical/ Theoretical	Treatment	Dissolved phase only	Pilot	Intermediate/High	Pilot	50-100
Alkali Soil Washing	Theoretical	Recovery	Dissolved and separate phase	Pilot	Intermediate/High	Pilot/Available	75-125
Cosolvent Soil Washing	Theoretical	Recovery	Dissolved and separate phase	Laboratory	Intermediate	Emerging	75-125
Surfactant Soil Washing	Theoretical	Recovery	Dissolved and separate phase	Pilot	Intermediate/High	Pilot/Available	75-125
Water Flooding	Empirical/ Theoretical	Recovery	Dissolved and separate phase	Full	Low/Intermediate	Available	50-100
Air Sparging	Empirical	Recovery	Dissolved phase only	Full	Intermediate/High	Available	75-125
Vacuum Vaporizer Wells	Theoretical	Recovery	Dissolved phase only	Full	Intermediate	Available	50-100
CROW® Process	Theoretical	Recovery	Dissolved and separate phase	Pilot	Intermediate	Pilot	50-125
Steam Enhanced Extraction	Theoretical	Recovery	Dissolved and separate phase	Pilot	High	Pilot/Available	50-125
Radio Frequency Heating	Theoretical	Recovery	Dissolved and separate phase	Pilot (vadose zone)	Intermediate	Pilot	65-160
Vitrification	Empirical	Treatment/ Recovery	Vadose Zone only				400+

(see text for additional notes and explanations)

The next group of promising technologies are the soil washing technologies because they can manipulate chemical equilibria and reduce capillary forces. A blend of alkalis, cosolvents, and surfactants is probably the best combination for a soil washing application, and each is important for its own reasons: alkalis can saponify certain DNAPLs and affect wettability and sorption; cosolvents provide viscous stability, and enhance solubility and mass transfer between the aqueous phase and the DNAPL; and surfactants have the largest impacts on solubility and interfacial tension reduction. Water flooding is best applied in highly contaminated areas (source areas) as a precursor to these methods. Of course, the exact approach will depend on site specific conditions.

The thermal and soil washing technologies are best suited for areas that are highly contaminated with DNAPLs. However, even under the best conditions, these techniques by themselves still may not be able to achieve the currently mandated regulatory cleanup standards. Thus, consideration should be given to using these technologies in combination with the technologies suitable for long-term plume management. In particular, the bioremediation techniques and permeable treatment walls seem to hold the best promise, although any of the remaining technologies in Table 4.1.1 are capable of dissolved plume management, and each has its own niche, depending on site specific considerations.

A special problem is posed by mixed wastes, heavy metals and radionuclides mixed with DNAPLs, since recovery at the ground surface may not be desirable in many instances. In such instances, stabilization/solidification and vitrification currently appear to be the most viable in-situ technologies. Excluding radionuclides, in-situ S/S is the most promising candidate because of its broadly demonstrated effectiveness, cost, and applicability to the saturated zone.

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TABLES

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