⊕EPA ENVIRONMENTAL RESEARCH BRIEF

Surfactant-Enhanced DNAPL Remediation: Surfactant Selection, Hydraulic Efficiency, and Economic Factors

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INTRODUCTION

Chlorinated hydrocarbons are ubiquitous ground water contaminants due to their widespread use as organic solvents and cleaners/degreasers. The immiscibility of chlorinated organics with ground water causes them to exist as nonaqueous phase liquids (NAPLs); this results in their occurrence in the subsurface as residual and free phases. Having a density greater than water, they are often referred to as dense nonaqueous phase liquids (DNAPLs). Water solubilities of these chlorinated hydrocarbons are frequently several orders of magnitude above their drinking water standards, yet low enough to limit dissolution during pump-and-treat remediation. Remediation of residual DNAPL contamination can require hundreds to thousands of flushings of the ground water (pore volumes) using conventional pump-and-treat methods. Strongly sorbing (hydrophobic) compounds will experience a similar fate (e.g., PAHs, PCBs). The inefficiency of conventional pump-and-treat methods for these contaminants has recently been addressed, with surfactants being mentioned as a promising technology for enhancing conventional approaches (Haley, et al. 1991; Palmer and Fish, 1992).

Two obstacles to widespread implementation of surfactant-enhanced subsurface remediation are (1) gaining regulatory approval for the injection of surfactants, and (2) the economics as impacted by surfactant costs (suggesting minimization of hydraulic and physicochemical surfactant losses). The objective of this brief is to present research results addressing these two issues, as further delineated below. Of course, proper surfactant selection is imperative to successful enhancement of DNAPL extraction; factors affecting surfactant selection are discussed in this document. Gaining regulatory approval is an obstacle common to all chemical amendments being considered for subsurface remediation. Surfactants with U.S. Food and Drug Administration direct food additive status and which are commonly used in consumer products are the focus of this research. The economics of surfactant-enhanced remediation processes will potentially be limited by surfactant losses in the subsurface, including hydraulic losses to uncontaminated portions of the aquifer and physicochemical losses (e.g., sorption, precipitation). Hydraulic approaches for minimizing surfactant losses are presented, including discussion of vertical circulation wells. Finally, results of a preliminary economic analysis for surfactant-enhanced DNAPL remediation are presented, along with suggestions for optimizing the economics of this technology.

BACKGROUND

Surfactants (surface-active-agents) accumulate at surfaces or interfaces, a result of the dual nature of surfactant molecules. Surfactant molecules have hydrophobic (water disliking) and hydrophilic (water liking) moieties. Surfactants are commonly utilized in detergents and food products to alter the surface

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chemistry of the system in a desirable manner. Above a certain concentration surfactant molecules self-assemble into aqueous-phase spherical aggregates with the hydrophobic portions of the molecule in the interior of the aggregate and the hydrophilic portions at the exterior. This aggregate is referred to as a micelle and the surfactant concentration above which micelles form is referred to as the critical micelle concentration (CMC).

Surfactants can improve subsurface remediation by solubilization and mobilization. Solubilization significantly increases the aqueous concentration of the contaminant via micellar partitioning, thereby reducing the number of pore volumes which must be pumped to extract the DNAPL. Optimal mobilization utilizes ultra-low interfacial tensions (evidenced concomitant with formation of middle-phase microemulsions) to significantly reduce the capillary forces trapping the DNAPL, thereby allowing the oil to be readily extracted with the water.

Solubilization enhancement for neutral organic compounds results from the partitioning of the contaminant into the hydrophobic core (oil-like center) of the micelle. Two parameters that describe this process are the molar solubilization ratio (MSR) and the micellar-water partition coefficient (K_m). Given a graph of aqueous contaminant concentration versus surfactant concentration, the molar solubilization ratio (moles of contaminant per mole of surfactant) is the slope of the straight line portion of the plot above the CMC. The micellar-water partition coefficient (K_m) is the molar ratio of the contaminant in the micellar phase

divided by the molar ratio of the contaminant in the aqueous phase, and can be determined given values of MSR, contaminant water solubility, and the molar concentration of water (Shiau et al., 1994; Edwards et al., 1991).

Optimal mobilization requires alteration of the surfactant system to produce a middle-phase microemulsion; these systems have the potential to elute the residual saturation in several pore volumes due to significant reductions in interfacial tensions. Micellar systems transition from normal to swollen micelles (Winsor Type I), to middle-phase systems (Winsor Type III), and finally to reverse micelles (Winsor Type II system, surfactants reside in the oil phase) as properties of the surfactant system are varied. As the surfactant goes from the water phase (hydrophilic) to the oil phase (lipophilic), the hydrophilic-lipophilic balance (HLB) decreases. Thus, surfactants with high values of HLB are highly water soluble. As shown in Figure 1, for a very hydrophilic surfactant system (right side of figure), the surfactant resides in the water phase as micelles, and a portion of the oil phase partitions into the micellar phase. For a very lipophilic surfactant system (the left side of the figure), the surfactant resides in the oil phase as reverse micelles. Intermediate between these extremes, a third phase appears which consists of water, oil and surfactant; this is the middle-phase system (so designated by virtue of its intermediate density). As shown in Figure 1, these phase transitions can be achieved for ionic surfactants by adjusting the salinity or hardness of the aqueous phase (commonly utilized in surfactant-enhanced oil recovery -- Bourrel and
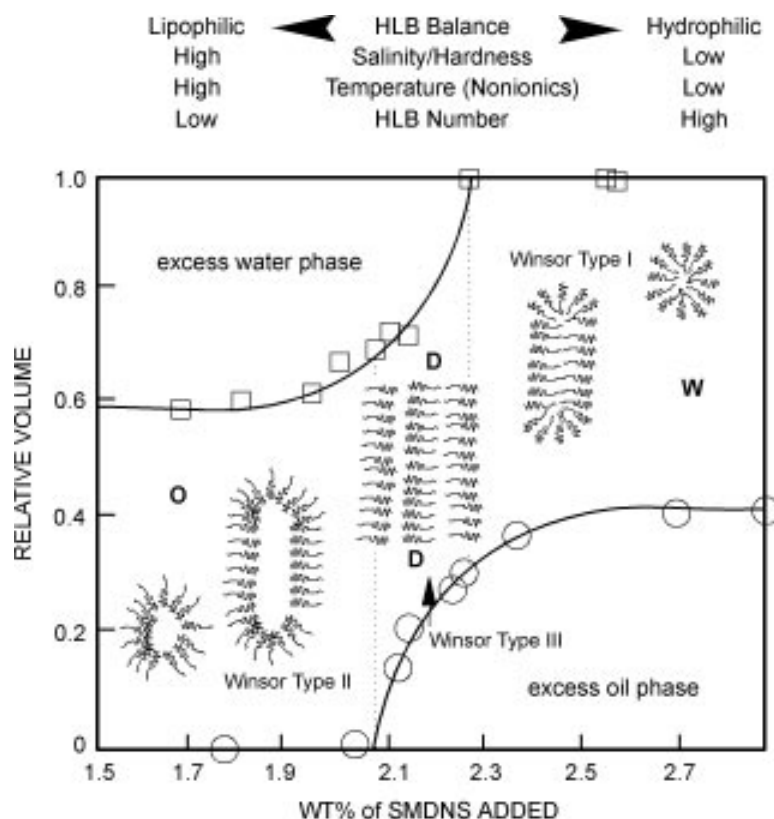

Figure 1: *Example Phase Diagram Showing Winsor Systems (1,2-DCE versus SMDNS Concentration @ 15°C and 0.5 wt% AOT), Adapted from Shiau et al., 1994. The Top Legend Refers to General Methods of Altering Phase Behavior, While the Bottom Legend Indicates the Specific Method Used for this Data (i.e., Salinity / Hardness and Temperature Were Not Varied in this Experiment).*

Schechter, 1988). However, introduction of high salt concentrations is not desirable in aquifer restoration as remediation of brine contamination is also a difficult problem. In this research, middle-phase systems are achieved by altering the HLB of a binary surfactant system.

Surfactant-enhanced environmental remediation research to date has evaluated a wide spectrum of issues (e.g., Valsaraj and Thibodeaux, 1989; Vignon and Rubin, 1989; Edwards et al., 1991; Smith and Jaffe, 1991; Jafvert and Heath, 1991; Peters et al., 1992; West, 1992; West and Harwell, 1992; Abdul et al., 1992; Fountain, 1992; Pennel et al., 1993; Baran et al., 1994; Sabatini et al., 1995). The objective of this document is to discuss the technical feasibility and limitations of using food grade surfactants for solubilization and mobilization of chlorinated solvents, describe physicochemical and hydraulic approaches that minimize surfactant losses while not compromising remediation enhancement, and present a preliminary evaluation of the economics of implementing surfactant-enhanced subsurface remediation. This document emphasizes the importance of proper design of the surfactant system and hydraulic regime for the technical and economical feasibility of surfactant-enhanced subsurface remediation.

MATERIALS AND METHODS

The chlorinated organics evaluated in this research were tetrachloroethylene (PCE), trichloroethylene (TCE), and trans-1,2-dichloroethylene (1,2-DCE). Table I summarizes characteristic parameters for these contaminants. These compounds were selected based on their ubiquitous occurrence as subsurface contaminants and their range in hydrophobicity (as noted by their relative K_{ow} values). The surfactants evaluated in this research were selected based on their status as FDA direct food additive compounds and their relative HLB values. The food grade surfactants are largely combinations of fatty acids and sugars. The S-MAZ surfactants and T-MAZ surfactants are sorbitan esters and ethyloxylated sorbitan esters, respectively (with ethylene oxide groups ranging from 0 to 80). Table II summarizes properties of select surfactants evaluated in this research. Surfactant solubilization, mobilization, precipitation and sorption studies were conducted according to standard procedures (as documented in Shiau et al., 1994, 1995a,b; 1996a,b; Rouse et al., 1993; 1995; 1996). Sorption assays were conducted utilizing the Canadian River alluvium (CRA) material which consists of 72% sand, and 27% silt and clay, and has an organic carbon content of 0.07%.

SURFACTANT SELECTION FOR OPTIMIZING SUBSURFACE REMEDIATION

Solubilization of chlorocarbons was evaluated using single surfactant systems (SDS and three of the T-MAZ surfactants). Solubilization curves for the three chlorinated organics (PCE, TCE, 1,2-DCE) with T-MAZ 60 are presented in Figure 2. The aqueous phase concentration of the chlorinated organics increases linearly above the CMC. However, at higher surfactant concentrations (exceeding the surfactant solubility limit) negative deviations from this linear trend are observed (Shiau et al., 1994). These results illustrate several points: (1) below the CMC, surfactant addition has little to no effect on the solubility of these contaminants, and (2) the higher the surfactant concentration is above the CMC the greater is the chlorocarbon solubility enhancement due to the increased number of micelles

(i.e., operate well above the CMC to achieve maximum enhancement, but below the surfactant's solubility limit). From Figure 2 the 1,2-DCE solubility enhancement is approximately two-fold at 10 mM T-MAZ 60 and approximately eight-fold at 50 mM T-MAZ 60; the enhancement approaches two orders of magnitude for PCE. The salinity of these systems was less than 30 mg/L and the hardness was 16 mg/L (this is true throughout this section unless noted otherwise).

Solubilization parameters (MSR and K_m, on a molar basis) are summarized in Table III for SDS, T-MAZ 28, T-MAZ 20, and T-MAZ 60. The data in Table III demonstrate that more hydrophobic compounds (e.g., PCE) will realize the greatest enhancement (higher K_m indicates greater contaminant partitioning into micelles). K_m is observed to vary more between contaminants for any surfactant than between surfactants for a given contaminant. Thus, for the solubilization mechanism, surfactant selection is relatively independent of the contaminant(s) and will most likely be made based on factors such as cost, susceptibility to losses, toxicity. At the same time, when estimating (extrapolating) K_m values or when modeling the solubilization process, it should be recognized that micellar solubilization (and thus K_m) varies as a function of contaminant type (nonpolar versus polar/ionic) and aqueous contaminant concentrations below their water solubility (Nayyar et al., 1994; Rouse et al., 1995). Aqueous contaminant concentrations below water solubility may be experienced due to nonequilibrium solubilization, mixed NAPL phases, etc. (Pennell et al., 1993; Rouse et al., 1995; Pennel et al., 1994; Soerens, 1995).
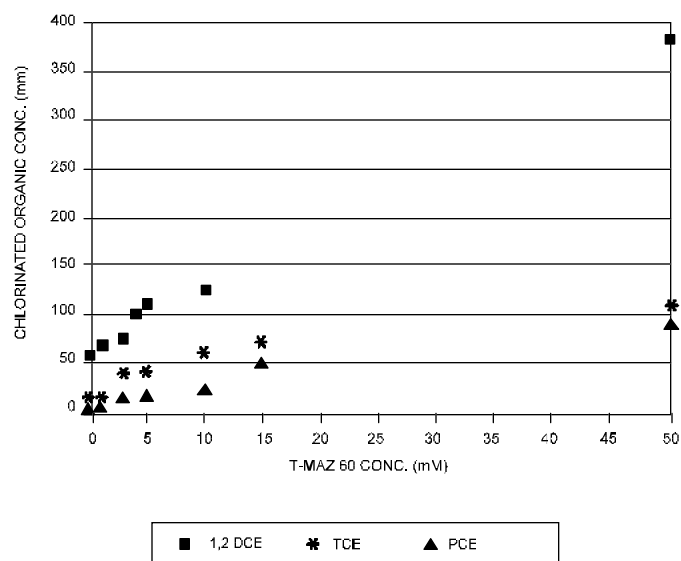

Figure 2: Solubilization of DNAPLs (PCE, TCE, 1,2-DCE) in T-MAZ 60 @ 15°C, After Shiau et al., 1994a. T MAZ 60 CMC = 0.02 mM. Molecular Weight: PCE, 166 mg/mM; TCE, 131 mg/mM; DCE, 97 mg/mM; and T-MAZ 60, 1310 mg/mM. Data Shown is Average of Replicates, Errors within Size of Symbols.

Table I: Contaminant Properties

Chemical	Molecular Formula	Molecular Weight	Aqueous Solubility (mg/L)	log K_{ow} [a]
Tetrachloroethylene (PCE)	C_2Cl_4	166	200	2.6
Trichloroethylene (TCE)	C_2HCl_3	131	1100	2.38
Trans-1,2-Dichloroethylene (DCE)	$C_2H_2Cl_2$	97	6300	0.48

[a] K_{ow} = octanol-water partition coefficient
After Shiau et al. (1994)

Table II: Surfactant Properties

Surfactant	MW[a]	Type[b]	HLB[c]
SMDNS[d]	260	A	>40
Sodium Dodecyl Sulfate (SDS)	288	A	40
POE (80)[e] sorbitan monolaurate (T-MAZ 28)	3866	N	19.2
POE (20)[e] sorbitan monolaurate (T-MAZ 20)	1266	N	16.7
POE (20)[e] sorbitan monostearate (T-MAZ 60)	1310	N	14.9
Aersol OT[f] (AOT)	445	A	NA[g]
POE (20)[e] sorbitan tristearate	1842	N	10.5
Sodium stearoyl-2-lactylate	450	A	10
Sorbitan monooleate	428	N	4.6
Sorbitan trioleate (S-MAZ 85K)	956	N	2.1

[a] MW = molecular weight
[b] A = anionic, N = nonionic
[c] HLB = hydrophilic-lipophilic balance
[d] SMDNS = Sodium mono and dimethyl naphthalene sulfonate
[e] ( ) = number of ethylene oxides
[f] Bis-2-ethylhexyl sodium sulfosuccinate
[g] NA = not available, but included in table in order of HLB (i.e., between 14.9 and 10.5)
After Shiau et al., 1994

Table III: Solubilization Parameters for Chlorinated Organics

Chlorinated Organic	Surfactant	MSR	Log K_m
PCE	SDS	0.39	4.5
	T-MAZ 28	0.45	4.55
	T-MAZ 20	2.27	4.9
	T-MAZ 60	3.15	4.94
TCE	SDS	0.34	3.27
	T-MAZ 28	1.68	3.66
	T-MAZ 20	3.29	3.75
	T-MAZ 60	3.95	3.77
1,2-DCE	SDS	1.37	2.76
	T-MAZ 28	2.46	2.85
	T-MAZ 20	7.49	2.95
	T-MAZ 60	6.91	2.94

After Shiau et al., 1994

Initial efforts to achieve middle-phase systems, without consideration of surfactant structure, were unsuccessful. The HLB of the surfactant systems was varied from 2.1 to 40. Although phase inversion was observed in this HLB range (Type II to Type I), a clear middle-phase was not achieved in the transition (instead a mesophase was realized). Using the branched surfactant Aerosol OT (AOT) and sodium mono- and di-methyl naphthalene sulfonate (SMDNS), a middle-phase microemulsion was realized in the transition region. Thus, it is observed that surfactant selection (structure) is critical to achieving middle-phase systems.

Mobilization with AOT and SMDNS was achieved by varying the SMDNS concentration while holding the AOT concentration constant. Figure 1 shows a phase diagram for 1,2-DCE using AOT and SMDNS as the surfactant system. At low SMDNS concentrations a Type II system is realized (surfactant has partitioned into the oil phase). Increasing the SMDNS concentration diminishes the potential for AOT to partition into the oil, thereby allowing it to accumulate at the interface and produce a middle-phase system. At yet higher SMDNS concentrations, the system is over-optimized and the surfactants reside in the water phase (Type I system). Middle-phase systems were achieved via this approach for PCE, TCE, and 1,2-DCE individually (Shiau et al., 1994) and in binary and ternary mixtures of these chlorocarbons (Shiau et al., 1996a).

Salinity and hardness can affect the formation of middle-phase systems. Potential impacts of naturally occurring hardness on middle-phase systems are illustrated in Figure 3 (TCE middle-phase systems at two levels of calcium (hardness)). Higher hardness levels required more SMDNS to maintain the surfactant balance and achieve a middle-phase system (the optimal SMDNS concentration is higher). The increased calcium concentration

will tend to drive the ionic AOT into the oil phase, thus requiring additional SMDNS to achieve the middle-phase microemulsion. Similarly, lower temperatures increased the SMDNS concentrations necessary to obtain middle-phase systems (Shiau et al., 1994). As expected, surfactant systems capable of achieving middle-phase systems are a function of the DNAPL (for single component) or DNAPL composition (for multicomponent oils). For example, the optimal SMDNS concentration for 0.5% AOT with PCE, TCE, and 1,2-DCE is 1.40, 2.43 and 2.19 wt%, respectively (Shiau et al., 1994).

For multicomponent residual phases, the optimal surfactant concentration is a function of the mole fraction of each phase in the mixed waste and the optimal SMDNS concentration for each individual phase. Figure 4 illustrates this by considering a ternary DNAPL system with a constant mole fraction of 1,2-DCE (0.5050) and a variable mole fraction of PCE and TCE (the mole fraction of PCE is shown on the ordinate and the mole fraction of TCE is equal to 0.4950 minus the PCE mole fraction). Thus, an ordinate value of 0 corresponds to a binary system of TCE and 1,2-DCE while an ordinate value of 0.4950 corresponds to a binary system of PCE and 1,2-DCE. The abscissa corresponds to the average equivalent weight of the surfactant system ([SMDNS]* plus AOT, where AOT is constant at 0.5 wt%; these units are utilized to facilitate the regular solution analysis). The ideal solution analysis is based on ideal mixing while the regular solution plot accounts for nonidealities (parameters for the ternary regular solution predictions were determined independently in three binary systems). As can be seen in Figure 4, regular solution theory is better able to predict phase behavior in the ternary system than ideal solution theory (Shiau et al., 1996a). It is especially encouraging that, given analyses from binary systems, one can better predict results for ternary systems of variable DNAPL composition.
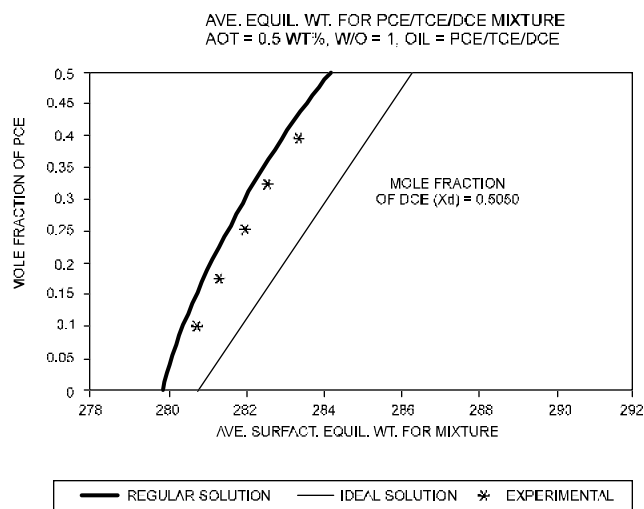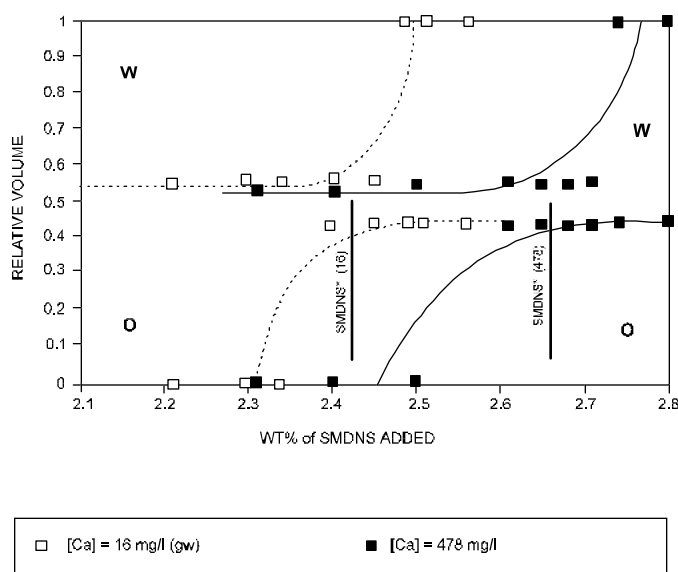

Figure 3: Phase Diagram for TCE at 15°C for AOT and SMDNS for Two Calcium Values (SMDNS* Optimal Concentration at Each Calcium Level), Adapted from Shiau et al., 1994.

Figure 4: Phase Diagram for Ternary DNAPL System for Constant Mole Fraction of 1,2-DCE and Varying Mole Ratio of PCE and TCE.

These results illustrate the sensitivity of middle-phase systems to aquifer conditions (temperature, hardness, etc.), contaminant composition, and surfactant structure, and should alert users to potential problems if proper surfactant selection and design efforts are not utilized when implementing mobilization via middle-phase microemulsions. Also, vertical migration of released residual may be realized depending on aquifer conditions and the hydraulics of the extraction system. This again illustrates the care that must be taken in utilizing mobilization. Despite these limitations, mobilization has the potential to be significantly more efficient than solubilization and should not be prematurely dismissed as a viable technology. In fact, vertical circulation wells can potentially mitigate and even take advantage of any tendencies for vertical migration. Both of these issues are discussed below in more detail.

In comparing the efficiency of the solubilization and mobilization mechanisms, Table IV documents the enhancements resulting from these two mechanisms for a similar weight percent of surfactant (via solubilization with T-MAZ 60 and mobilization with Aerosol OT and SMDNS). As observed in Table IV, the enhancement is two orders of magnitude for PCE via solubilization and three and one-half orders of magnitude via mobilization (relative to water alone). For 1,2-DCE the enhancement by solubilization is approximately one order of magnitude, while being two orders of magnitude for mobilization. The increase in efficiency via mobilization versus solubilization is dramatic. The data in Table IV also demonstrate that surfactant-enhanced subsurface remediation will be of the greatest benefit for more hydrophobic compounds.

In Figure 5 solubilization and mobilization results from one-dimensional column studies are presented (Shiau et al., 1995b). Mobilization (AOT/SMDNS) achieved higher contaminant concentrations and eluted the PCE more quickly than solubilization (T-MAZ-60) (> 97% extracted in ca. 3 pore volumes). The tail on the solubilization curve indicates the reduced extraction rate and thus slow approach to complete PCE elution for solubilization (likely due to interfacial area constraints); while ca. 85% of the PCE is eluted within 10 pore volumes, less than 90% has been eluted by 30 pore volumes. Again, the potential advantages of mobilization over solubilization are apparent. From Figure 5, the aqueous PCE concentration prior to surfactant introduction is observed to be 80 mg/L. Based on this initial concentration,
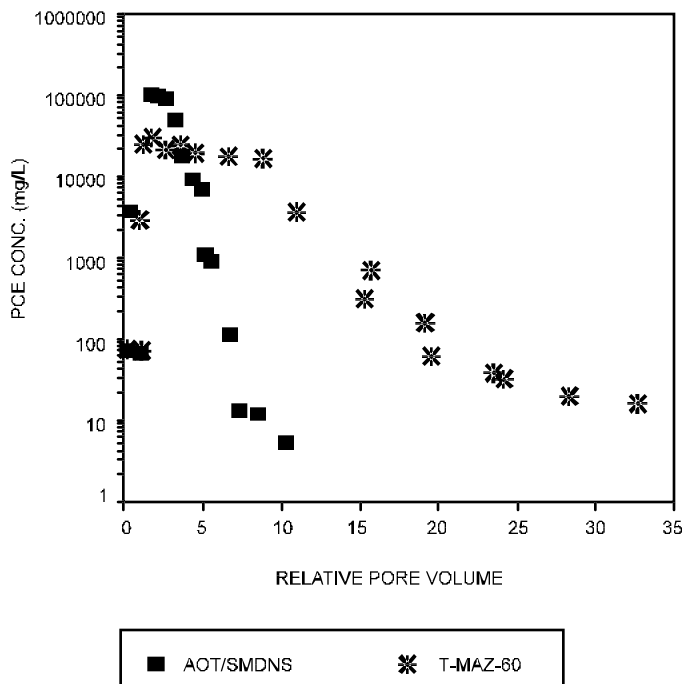

Figure 5: Column Results for PCE Elution via Solubilization (T-MAZ 60) and Mobilization (AOT/SMDNS) Systems with CRA Medium.

water dissolution would require in excess of 400 pore volumes to dissolve the residual PCE. Considering reduced mass transfer as the interfacial area decreases, the actual number of pore volumes for water dissolution is expected to be much greater than 400 pore volumes. The relative advantages of surfactant-enhanced remediation over water dissolution are apparent. It should be noted that the concentrations in Figure 5 are still several orders of magnitude above the drinking water standard. While surfactant techniques significantly expedite mass removal, protracted amounts of time may be required to achieve drinking water standards (although much less than with water alone).

It is observed that the food grade surfactants are technically viable for use in subsurface remediation activities. This may be advantageous for obtaining regulatory approval for utilizing surfactants in subsurface remediation. However, edible surfactants may be more susceptible to losses (e.g., precipitation, sorption; Shiau et al., 1995a), which can cause system failure (e.g., pore clogging due to precipitation) and will result in increased costs of the surfactant (thereby hindering the economic viability of the process). For this reason, research in our laboratories has evaluated methods for minimizing precipitation and sorption of food grade surfactants (e.g., use of hydrotropes or cosolvents to decrease the sorption and precipitation of these surfactants -- Krebbs-Yuill, 1995). Also, in other research surfactants with indirect food additive status have been evaluated that are less susceptible to precipitation and sorption (e.g., alkyl diphenyloxide disulfonates -- Rouse et al., 1993; ethoxylated alkylsulfates -- Rouse et al., 1996). Space limitations prevent a detailed discussion of techniques for limiting surfactant losses; the interested reader is directed to the above references and Shiau et al. (1995b) for more detailed discussions. Thus, surfactant selection is not only critical to the technical

Table IV: Comparison of Solubilization and Mobilization

Chlorinated Organic	GW[a] Solubility (mg/L)	Solubilization (6.5 wt%T-MAZ 60) (mg/L)	Mobilization[b] (5.0 wt% AOT and SMDNS)(mg/L)
PCE	80.6	16,900	619,000
TCE	990	14,700	594,000
1,2-DCE	5,340	37,800	557,000

[a]GW = Ground Water
[b]Surfactant concentration is based on initial aqueous volume; contaminant concentration is in middle phase system.
After Shiau et al., 1994

implementation of surfactant-enhanced subsurface remediation, but is also imperative to minimizing subsurface losses and improving the economics of implementing the technology. This will be further discussed in a later section focusing on economic considerations.

IMPROVING THE HYDRAULIC EFFICIENCY OF SURFACTANT INJECTION/EXTRACTION

The technical and economic feasibility of surfactant-based remediation processes will depend on the ability to achieve *hydraulic control* in the subsurface while also attempting to maximize *hydraulic efficiency*. Hydraulic efficiency can be increased by: (1) minimizing the volume of injected surfactant solution; (2) minimizing the volume of fluid to be pumped to the surface (reducing treatment costs); (3) targeting injected chemicals to the contaminated zones of the aquifer (thereby preventing the movement of injected fluids towards clean portions of the aquifer); and (4) maximizing capture of resulting water-surfactant-contaminant mixtures.

One method of improving the hydraulic efficiency of surfactant-enhanced subsurface remediation is the strategic placement of *impermeable* and/or *hydraulic* barriers. Impermeable physical barriers (e.g., grout curtains, slurry walls, sheet piling) can be used to deflect flows into or away from contaminated zones by creating zones of low permeability. Hydraulic barriers (e.g., injection wells, infiltration galleries) can be used to deflect flows into or away from contaminated zones by creating zones of increased hydraulic potential (head). A recent numerical modeling study assessed the relative effectiveness of hydraulic and impermeable barriers for improving the efficiency of DNAPL remediation processes, both with and without surfactants (Gupta, 1993). The overall conclusion drawn from these results was that mass transfer of the contaminant from the residual phase to the

fluid moving through the contaminated zone should be maximized, regardless of the fluid used (e.g., air, water, chemical solution). Simple upgradient injection of surfactants followed by downgradient extraction is tremendously inefficient due to loss of surfactant to uncontaminated zones. Injection of surfactant solutions inside partially encircling impermeable barriers with downgradient deflector wells was found to be the most efficient of the systems evaluated for the surfactant-based processes. The impermeable barrier *cuts off* upgradient water (eliminates dilution of surfactant solution) and prevents migration of surfactant solutions into uncontaminated areas. Hydraulic barriers (deflector wells) provide increased gradient in addition to directional control while also having the advantage of being a temporary measure. The volumes (mass) of surfactant solution required to exceed the CMC in the contaminated zone decreased significantly (up to 65%) with barriers over simple injection/extraction (Gupta, 1993).

The use of operational measures has also been suggested for improving pump-and-treat efficiency; such measures include cyclic (pulsed) pumping, push-pull pumping, and variable injection/extraction ratios (Keely, 1989). Pulsed pumping was first proposed by petroleum engineers to improve recovery from hydrocarbon reservoirs (Aguilera, 1980). Disadvantages associated with pulsed pumping identified in laboratory and field studies include increased remediation times (due to decreased concentration gradients during resting phase), operation and maintenance issues, and lack of necessary hydraulic control (Stallard and Anderson, 1992; Armstrong et al., 1994; and Voudrias and Yeh, 1994).

Simultaneous injection to and extraction from a common vertical borehole creates a circulating flow pattern (Figure 6) within a sphere or ellipsoid around the borehole (referred to as vertical circulation wells -- VCWs), a concept previously evaluated in petroleum production. A myriad of potential benefits of VCWs can be delineated, including: (1) reduced costs over systems involving multiple wells; (2) effective hydraulic control achieved
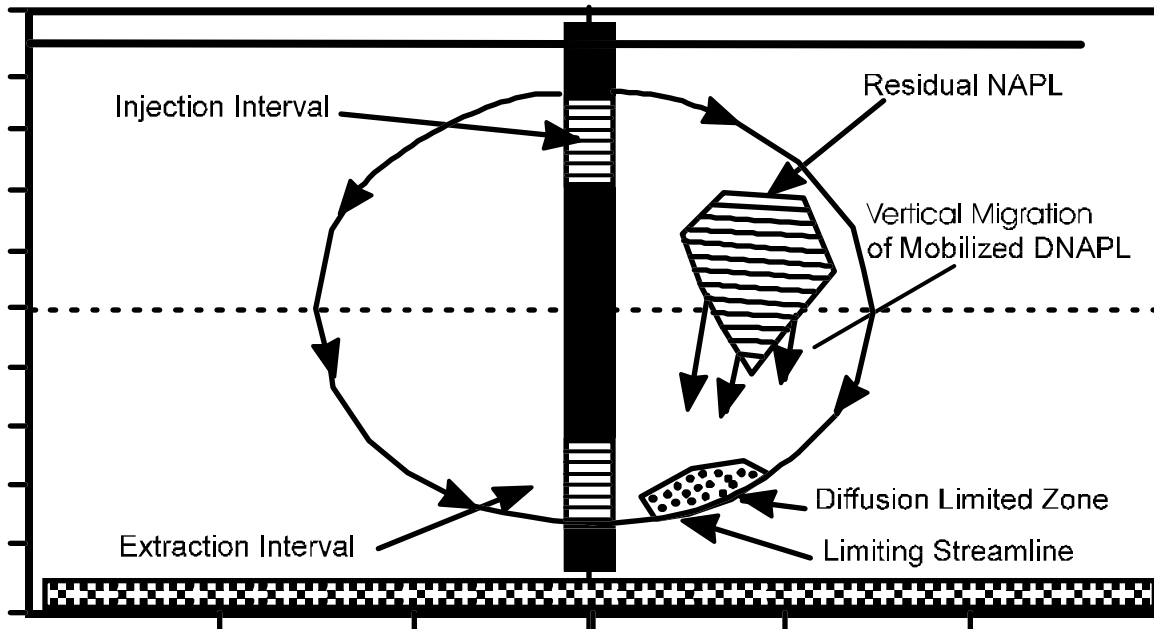

Figure 6: Vertical Circulation Well (VCW) Flow Pattern.

over limited volumes of the formation; (3) ability to capture DNAPLs that might sink when mobilized; (4) applicable to both light NAPLs (LNAPLs or *floaters*) and DNAPLs (*sinkers*); (5) minimizes surfactant losses; (6) minimizes volumes of fluids produced at the surface requiring treatment; and (7) induced mounding can remediate portions of the contaminated vadose zone around the well. Obviously, these and alternate systems must be evaluated on a case-by-case basis to determine optimal configurations.

Two-dimensional steady state flow induced by the VCW system in an aquifer with a regional gradient can be described using the complex potential, Ω,

$$\Omega = \Phi + i\,\psi \qquad \textbf{(1)}$$

where, Ω is the complex potential, Φ is the hydraulic potential, and Ψ is the stream function. Lines of constant Φ are called equipotentials and they describe the head distribution within the aquifer. Lines of constant Ψ are called streamlines and they describe the flow paths of ground water within the aquifer.

The two screened intervals behave as a line source and a line sink, respectively. By superposition, the complex potential for the line source and line sink can be combined, along with the complex potential for a regional gradient (lateral flow), to produce the overall complex potential for the aquifer. Using the equations for line sources/sinks and regional gradient developed by Strack (1989), the complex potential becomes:

$$\Omega = \frac{\sigma D}{4\pi}\Big[\Big(Z - \frac{a}{D}\Big)\ln\Big(Z - \frac{a}{D}\Big) + \Big(Z + \frac{a}{D}\Big)\ln\Big(Z + \frac{a}{D}\Big)$$
$$- |Z - 1|\,\ln|Z - 1| - |Z + 1|\,\ln|Z + 1|\,]$$
$$- Q_o Z\left(\frac{D - \left(z_4 - z_1\right)}{2}\right) \qquad \textbf{(2)}$$

where,

D = total length of vertical circulation well (both screens and spacer)
a = separation distance between screens (spacer)
z = x + iy
Z = X + iY
Q_o = lateral Darcy velocity
σ = strength of injection/extraction interval
z_1 = bottom of lower screen
z_4 = top of upper screen

and

$$Z = \frac{\left[z - \frac{1}{2}|z_4 + z_1|\right]}{\frac{1}{2}|z_4 - z_1|} \qquad \textbf{(3)}$$

The variable transformation from z to Z is simply a change from the global (x,y) coordinate system to a local (X,Y) system based on the geometry of the vertical circulation well.

Figure 7 shows equipotentials and streamlines for a VCW in an aquifer having a local regional gradient, where the bottom screened interval of the VCW is extracting at a rate higher than the upper screened interval is injecting ($Q_{out} > Q_{in}$). By having $Q_{out} > Q_{in}$, it is possible to approach complete capture of the injected solution; however, the extracted solution is significantly diluted by fresh ground water (this effect increases as the Q_{out}/Q_{in} ratio increases). This will result in diluted extraction concentrations for both the injected surfactant solution and the solubilized (or mobilized) contaminant. It is important to recognize that the performance of the surfactant solution relative to extraction of the contaminant is masked in the VCW system effluent by dilution due to the fresh ground water that is extracted. It is also important to note that the dilution occurs in the borehole and not in the formation; thus, surfactant concentrations in the aquifer will not drop below the CMC due to this phenomenon.

The relative performance of the VCW system versus the traditional injection/extraction (two-well) system was assessed using a two-dimensional (sand tank) model packed with glass beads. The tank, constructed of aluminum, is 36 inches wide by 18 inches high, with a 2 inch depth. The tank has adjustable constant-head end reservoirs, a glass front plate for visual observation, and piezometers for sampling and head measurement distributed horizontally and vertically throughout the tank. A known mass of DNAPL was gravity fed from the surface in each test prior to removal via surfactant solutions. Aqueous DNAPL concentrations were quantified throughout each test. Enhanced solubilization and mobilization (microemulsification) were evaluated for each hydraulic configuration (in both cases the injection and extraction pumping rates were 100 ml/min with no regional gradient).
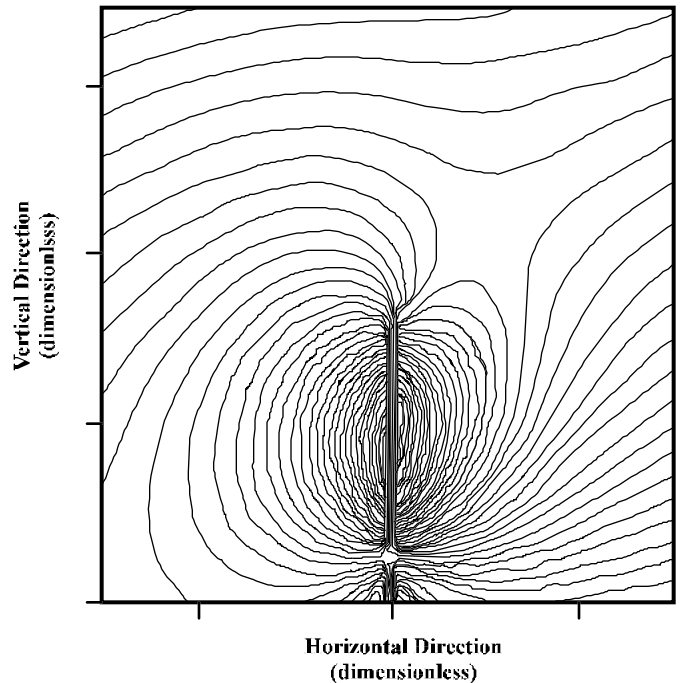

Figure 7: Cross Section Showing Streamlines for a VCW System in an Aquifer with a Regional Gradient. Injection in Upper Zone, Extraction in Lower Zone, Regional Gradient from Right to Left.

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Preliminary studies of the VCW system and two-well systems have also been conducted in three-dimensional sand tanks (Roberts et al., 1993; Chen, 1995).

Plotted in Figure 8 are the mass recovery curves for the two-well and VCW systems using the surfactant-enhanced solubilization mechanism for residual saturation of PCE. A 4.56 weight percent (wt%) solution of T-MAZ 20 was used during the solubilization studies. The interfacial tension of this solution is 5 dynes/cm. The curves show that the VCW system achieves higher effluent contaminant concentrations (increased mass recovery at early extraction volumes) due primarily to reduced dilution by uncontaminated ground water (i.e., improved hydraulic efficiency). The surfactant recovery is likewise expected to be greater in the VCW as surfactant lost to the uncontaminated portions of the aquifer is minimized. Decreasing efficiency in the VCW system is observed at ca. 5 liters. If the initial efficiency of the VCW had been maintained it appears that the remediation would have been complete within 10 liters; however, in reality it required greater than 30 liters to approach 100% recovery of the PCE. Thus, the tailing of the VCW mass removal curve negates the advantage of the initially higher concentrations

Plotted in Figure 9 are the mass recovery curves for the two-well and VCW systems via surfactant-enhanced mobilization (again for residual saturation of PCE). The surfactant system used was 1.3 wt% AOT and 3.6 wt% SMDNS, which produced an interfacial tension of 5×10^{-3} dynes/cm. It can be seen in Figure 9 that the two-well system approaches a plateau at ca. 70% recovery of the PCE; visual observations indicated that some of the mobilized residual was lost from the flowlines due to vertical migration. It is very encouraging to note that this did not occur in the VCW system and that removal efficiencies approached 100% for PCE in the VCW system. However, a significant decline in the extraction efficiency of the VCW system occurred at ca. 5 liters. It is interesting to note that, if not for this decline in efficiency, the

VCW system could have remediated the PCE before significant PCE extraction in the two-well system was observed.

The change in efficiency for mobilization using the VCW system (ca. 5 liters in Figure 9) was due to the accumulation of a diffusion-limited mass of contaminant at the fresh water-surfactant solution interface (i.e., the outermost streamline) of the VCW (see Figure 6). Because the fluid outside the streamline (i.e., the ground water) contains no surfactant, the surfactant system at this interface is diluted and no longer exists as a middle-phase system. At this interface, slow diffusion-limited dissolution of this contaminant mass reduces the efficiency of the extraction process, as reflected in the long tailing of the mobilization mass recovery above 5 liters. It is suggested that this phenomenon can be addressed through relatively simple operational variations in the VCW system; i.e., reversing injection-extraction direction, operating with three screened intervals with alternating injection and extraction points, etc.

In summary, the VCW system has potential advantages over the two-well system relative to hydraulic capture of the mobilized residual. The efficiency of the VCW system will be maximized when operational variations prevent the limiting effects of dilution at the outermost streamline. The VCW system also has the distinct advantage of higher surfactant recovery compared to the two-well system and potentially lower volumes of water to be treated at the surface.

ECONOMIC CONSIDERATIONS FOR TECHNOLOGY IMPLEMENTATION

In conventional pump-and-treat remediation of a site containing residual saturation of a DNAPL, it is not uncommon for contaminant concentrations in the ground water to be well below their solubility
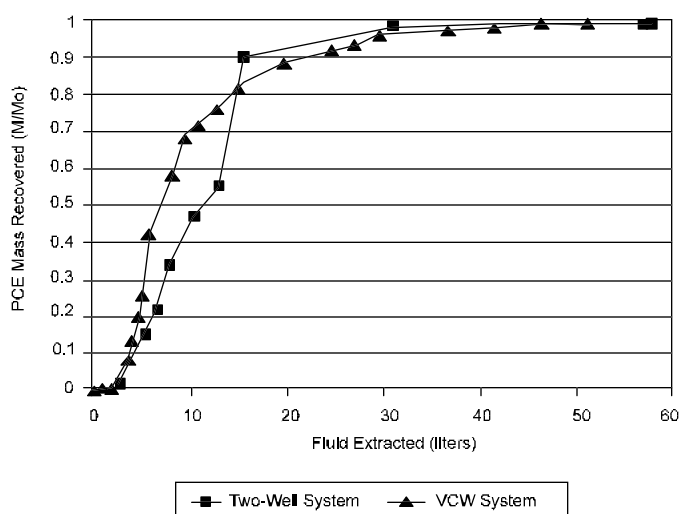

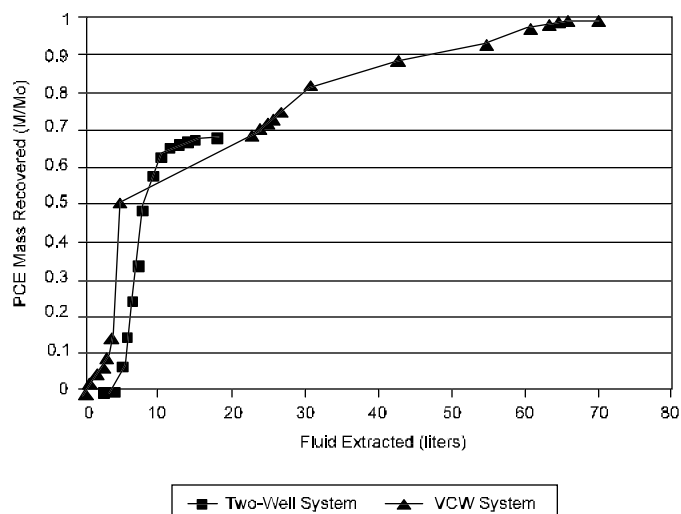Figure 8: Effluent Mass Recovery Curves for Surfactant enhanced Solubilization.

Figure 9: Effluent Mass Recovery Curves for Surfactant-enhanced Mobilization.

values. For a given mass of residual DNAPL and a given ground-water extraction rate, the time required to remediate an individual DNAPL should be proportional to its aqueous solubility. This is plotted in Figure 10, where R is the ratio of the total mass of the particular DNAPL in the soil to the recovery water flow rate (pounds per gallon per minute) and the aqueous concentrations of the chlorocarbons are assumed to be 10% of their solubility limit (e.g., due to nonequilibrium effects, dilution). Thus, increasing values of R generally indicate either more DNAPL mass for a given volume of ground water extracted, or lower ground-water extraction rates for a given DNAPL mass; both of these will result in greater remediation times. Also shown in Figure 10 is the remediation time required for surfactant-enhanced pump-and-treat remediation; surfactant introduction significantly reduces the remediation time for the more hydrophobic DNAPLs (i.e., aqueous solubilities less than about 3000 mg/L).

The curves for surfactant-amended pump-and-treat remediation in Figure 10 were generated assuming that the recovered water has a sodium lauryl sulfate surfactant concentration of 1.7 wt. % or 10 times its CMC (CMC = 0.006 M) (Rosen, 1989), and the concentration of DNAPL in the surfactant micelles corresponds to an aqueous DNAPL concentration of 10% of its aqueous solubility. Molar solubilization ratio (MSR) values utilized were 0.275 for tetrachloroethylene (PCE, aq. solubility = 200 mg/L), 0.20 for trichloroethylene (TCE, aq. solubility = 1100 mg/L)

(Sabatini and Knox, 1992), 0.15 for 1,1,2,2-tetrachloroethane (aq. solubility = 2900 mg/L), and 0.10 for 1,2-dichloroethane (1,2-DCA, aq. solubility = 8690 mg/L). The relationships shown in Figure 10 provide reasonable estimates of relative costs for sodium lauryl sulfate as evaluated in this preliminary economic analysis. It is recognized that incorporating changes in mass recovery over the course of remediation (as documented in Figure 5) will more accurately capture the absolute times (and costs) of remediation. However, the baseline case of conventional pump-and-treat will be similarly impacted, minimizing the impact on the comparative observations presented below.

Another major concern with surfactant-enhanced pump-and-treat technologies is the initial cost of surfactant required to fill the aquifer. This cost can be greater than $20 million for a very large aquifer or less than $1 million when targeted to the residual DNAPL zone. Figure 11 shows surfactant capital cost for PCE remediation with varying aquifer volumes and surfactant prices. Two different R values (ratio of PCE in the aquifer to water removal rate) are shown. The surfactant concentration is set to theoretically allow complete remediation of PCE in seven years. An aquifer volume of 50 million gallons corresponds roughly to 25 acres cross-sectional area by 20 feet thickness at 30 percent porosity; 10 million gallons corresponds to 5 acres with the same thickness and porosity. This range is not unusual for dissolved contaminant plumes; however, residual saturation zones are
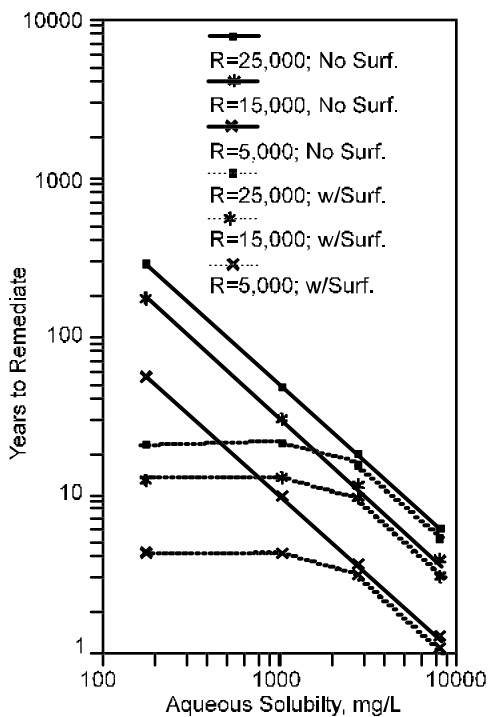

Figure 10: The Remediation Time Required for Very Insoluble Contaminants with 1.7 wt percent Surfactant and Water (R = ratio of mass of contaminant in aquifer to water removal rate — lb/gpm).
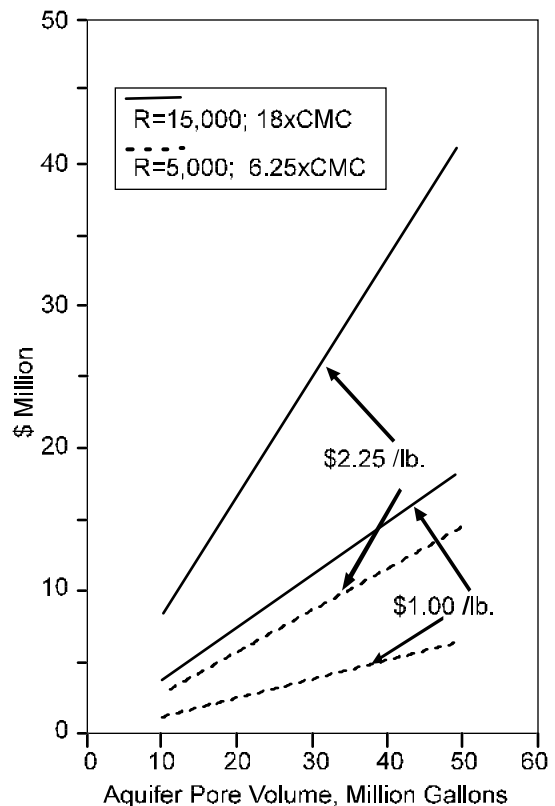

Figure 11: Initial Surfactant Cost as a Function of Aquifer Pore Volume.

typically only a fraction of this size. These results show that surfactant remediation should be targeted to the residual saturation zone (where it provides the greatest benefit) as well as the importance of minimizing surfactant losses (i.e., sorption and precipitation).

Based on the capital costs of the surfactant and given that multiple pore volumes of injection will be utilized, economics dictate surfactant recovery and reuse. In a typical hydraulic regime, recovery wells will likely produce more water than is injected to maintain hydraulic control, which can result in a significant bleed stream. Figure 12 demonstrates the cost of surfactant losses without a recovery step from the bleed stream. The cost of surfactant recovery from the bleed stream is typically only a small fraction of the cost of lost surfactant.

In order to identify the most economic surfactant recovery process, a base case was studied. In the base case, DNAPL contaminated water is extracted at the rate of 500 gpm, the bleed stream is 150 gpm, and 350 gpm of treated water is reinjected along with surfactant. It is assumed that DNAPL concentrations in the reinjected water should be at or below the 0.5 ppb level. The treatment process will be based on chemical/physical differences between the DNAPL, surfactant and ground water.

The initial separation can be based on differences in micellar/ aqueous properties, volatility, surfactant/solution properties, or organic/aqueous properties. Potential unit operations to achieve the recommended separation are listed in Table V. Two process

Table V: Unit Operations Considered

SEPARATE DNAPL FROM FEED
Air Strip
Steam Strip
Vacuum Steam Strip
Pervaporation
Organic Extraction
Biotreatment

SEPARATE SURFACTANT FROM BLEED
Waste
Foam Fractionation
Al, Ca Precipitation; Cation Exchange
Micellar Enhanced Ultrafiltration (MEUF)
MEUF combined with Foam Fractionation

DESTROY/SELL DNAPL
Incineration
Carbon Adsorption
Recycle/Sell/Store
Biotreatment

schemes are recommended based on economics and proven ability to remove DNAPL and surfactant to the desired levels. If the recovered DNAPL has no value, standard air stripping of the process feed will remove the DNAPL and leave the surfactant for reinjection. Catalytic incineration of the DNAPL can be utilized, followed by caustic scrubbing to remove HCl. The surfactant is recovered from the bleed stream using a combination of ultrafiltration and foam fractionation. Ultrafiltration is most efficient down to the CMC level and foam fractionation is very efficient below the CMC level. If the DNAPL has sufficient value to a reclaimer or can be recycled to an adjacent operation, vacuum-steam distillation becomes attractive. Surfactant is recovered from the bleed stream as in the previous case.

The initial design and cost estimates in this preliminary analysis assume that surfactants have only minor impacts on stripping efficiency. Recent research has demonstrated that micellar solubilization decreases the overall efficiency of the stripping process by reducing the aqueous contaminant activity and thus the driving force for volatilization (Lipe et al., 1996). Foaming may also result, which can create significant operating problems (Lipe et al., 1996); vacuum stripping has been shown to minimize this effect (Choori, 1994). Also, for nonvolatile compounds liquid-liquid extraction has demonstrated potential given that the reduced activity due to micellar solubilization is considered (Hasegawa et al., 1996). Incorporation of such effects was beyond the scope of this analysis.

The hypothetical case studied represents an extremely large volume of residual DNAPL contamination; such a case was selected to highlight the important factors in designing surfactant-enhanced subsurface remediation. It was assumed that 5 acres of contaminated soil, 20 feet in depth, had an average porosity of 0.30, and the void fraction contained 13 volume percent DNAPL. The DNAPLs present were assumed to consist of equal volumes of PCE, TCE and 1,2-DCA. This equates to 5.74 million pounds of PCE, 5.16 million pounds of TCE and 4.46 million pounds of DCA. The surfactant was assumed to cost $1.00 per pound and was added in sufficient quantities to achieve 15 times its CMC in the recovered water. In this analysis, 20 percent of
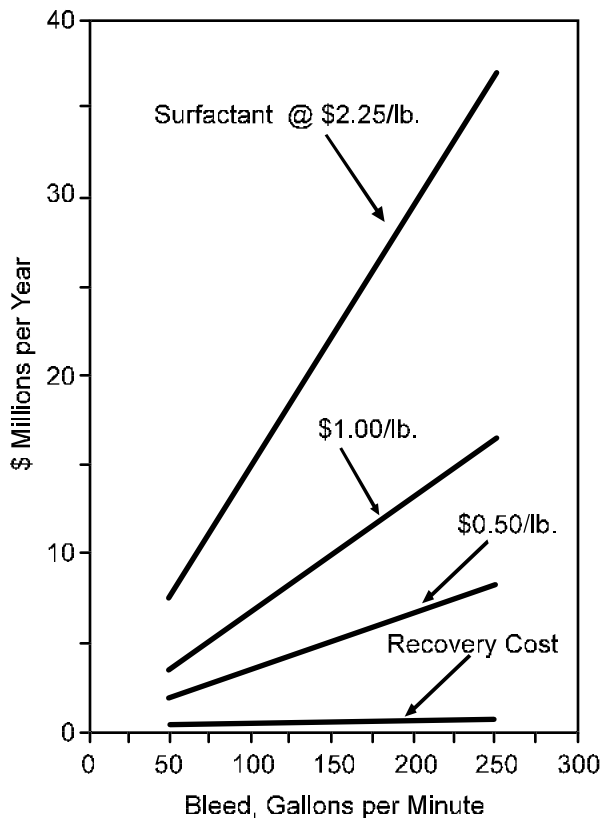

Figure 12: The Cost of Surfactant Losses without a Recovery Step from the Bleed Stream.

the surfactant was assumed to be lost due to adsorption in the first two pore volumes. This surfactant loss is consistent with surfactant adsorption values of 10 mg/g or greater (Rouse et al., 1993), and illustrates the economic importance of minimizing surfactant losses. The recovery wells were assumed to operate at 500 gpm and the bleed stream necessary was assumed to be 150 gpm. The recovery stream was assumed to contain 330 mg/L TCE, 400 mg/L PCE and 950 mg/L 1,2-DCA (based on MSR values above and assuming aqueous concentrations at 10 percent of solubility limits and no competitive effects of solubilizates), giving a theoretical remediation time of seven years.

A total of 68 injection and recovery wells were assumed along with piping to the treatment facility. The DUALL Division of MET-PRO Corporation recommends three air strippers in series to treat 500 gpm process water containing PCE, TCE and 1,2-DCA. The columns are 9 feet in diameter with 28 feet of packing. Global Environmental estimates that a catalytic incinerator operating at 1000° F with 30 ft³ of Englehard catalyst will achieve 99 percent destruction efficiency. (Allied also manufactures a catalyst that can be used with high chloride streams.) The hot gas stream must be quenched to about 180° F. A 5-foot diameter caustic scrubber is recommended for removing HCl from the cooled gas stream with a design efficiency of 99.5 percent. The cost of ultrafiltration and foam fractionation will depend on the specific surfactant used. Conservative costs were utilized based on previous work at the University of Oklahoma (Dunn et al., 1985). Based on this analysis, the approximate capital cost is $3,570,000 and the annual O&M cost is $940,000 (see Krebbs-Yuill et al., 1995 for more details).

As an alternative, costs for the vacuum-steam stripping case were estimated. AWD, a division of DOW, estimates installed costs of $3 million for a 5-foot diameter column, package boiler (1500 to 2000 lb/hr steam), and instrumentation. The overall capital cost for this approach is $5,070,000, with the annual O&M costs at $765,000 (see KrebbsYuill et al., 1995 for more details). Costs will increase rapidly if the water requires significant pretreatment for inorganics and if operating problems are experienced due to the presence of the surfactant. Again, the actual tower dimensions may increase due to micellar effects (Lipe et al., 1995).

For a given contamination site, there is a cost tradeoff between the number of wells (assuming the optimum pumping rate per well is known and fixed), the time required for remediation, the size of the treatment process, and the initial surfactant cost. This is shown for our base case in Figure 13 where the above-ground process is air stripping-incineration with surfactant recovery of the bleed. The negative net present value, discounted at 10 percent, is plotted against the gpm of well water recovered. Again, it is emphasized that these numbers should be viewed in a relative sense (remembering the simplifying assumptions made in the analysis). The surfactant concentration is varied to give a theoretical remediation time of seven years; therefore, the initial surfactant cost decreases with increasing gpm. The cost of wells and the above ground processing costs increase with increasing flow rate. For the base case, the optimum flow rate, corresponding to the minimum negative net present value, is about 500 gpm. Initial surfactant costs due to adsorption losses were not included since they were assumed not to vary between cases.
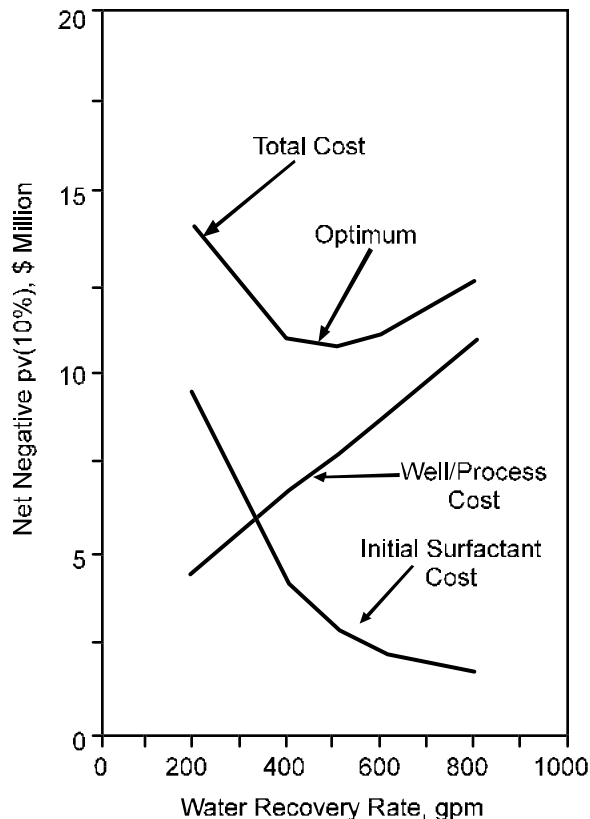

Figure 13: Cost Optimization for a Five Acre Surfactant Flood.

The cost benefits of a small, well defined area of contamination can be shown in the following example using pump-and-treat technology to remediate residual DNAPL from only 1/4 acre covering a depth of 20 feet and treating 35 gpm using air stripping and incineration. The contaminated soil contains approximately 125,000 pounds of residual PCE and estimates indicate it will take another 41 years to remediate. The operating cost is $125,000 per year and the net negative present value of this operating cost, discounted at 10 percent, is $1.225 Million. Adding $350,000 of surfactant (@ $1.00/lb) and $120,000 capital for surfactant recovery, the remediation time is decreased to about 3 years. If the additional operating cost is about $30,000 per year, the negative net present value is decreased to $545,000. Not only is the cost to the company reduced, but also a very undesirable environmental liability will be eliminated sooner.

Part of the initial surfactant cost may be recovered at the end of the remediation project. This would be accomplished by continued water flooding at a reduced rate without surfactant addition. Only the surfactant recovery portion of the above-ground process would be operated. The surfactant should retain a fair fraction of its original value, especially to another surfactant-enhanced remediation project (assuming regulatory approval of *used* surfactant). As an alternate, a site may be compartmentalized with a smaller initial volume of surfactant shifted from compartment to compartment (resulting in decreased capital costs of surfactant

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but increased remediation time). Maximizing recovery of surfactant from the subsurface will also be necessary if there is environmental concern regarding residual surfactant in the aquifer.

In summary, surfactant-enhanced pump-and-treat remediation is effective for DNAPL chemicals with relatively low aqueous solubilities, but requires surfactant reuse to be economical. From this preliminary analysis, the best surfactant recovery process is probably a combination of microfiltration and foam fractionation. Total project costs can be minimized by (1) defining the area of residual saturation, thus minimizing the volume of soil requiring surfactant flooding, and (2) balancing the number of wells and volume of water to be treated with the cost of surfactant and surfactant concentration required to achieve remediation. For relatively small areas of residual saturation (i.e., acres or less which is common even for dissolved plumes having dimensions in miles), surfactant-enhanced pump-and-treat via solubilization can be less expensive, on a present value basis, than pump-and-treat alone. The economics for mobilization will be even more favorable than solubilization, especially if surfactant slugs of less than a pore volume can be utilized followed by polymer drives, etc.; future research should evaluate such methods for environmental applications. When external costs are incorporated into the analysis (e.g., regulatory or public mandates, liability, property transactions, etc.), it is obvious that surfactant-enhanced subsurface remediation has the potential for widespread implementation.

NOTICE

QUALITY ASSURANCE STATEMENT

All research projects making conclusions or recommendations based on environmentally related measurements and funded by the Environmental Protection Agency are required to participate in the Agency Quality Assurance Program. This project was conducted under an approved Quality Assurance Program Plan. The procedures specified in the plan were used without exception. Information on the plan and documentation of the quality assurance activities and results are available from the Principal Investigator.

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