Surfactants/Cosolvents

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December 1996

FOREWORD

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GWRTAC wishes to acknowledge the support and encouragement received for the completion of this report from the EPA TIO.

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ACKNOWLEDGMENTS

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ABBREVIATIONS

AATDF	Advanced Applied Technology Demonstration Facility
AFB	Air Force Base
BTEX	benzene, toluene, ethylbenzene, xylenes
BGS	below ground surface
CTET	carbon tetrachloride
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
1,2-DCA	1,2-dichloroethane
DNAPL	dense nonaqueous phase liquid
DOD	Department of Defense
DOE	Department of Energy
EPA	Environmental Protection Agency
HLB	hydrophilic-lipophilic balance
IWPTT	inter-well partitioning tracer test
LNAPL	light nonaqueous phase liquid
NAPL	nonaqueous phase liquid
MSR	molar solubilization ratio
PCE	perchloroethylene (tetrachloroethene)
PCB	polychlorinated biphenyl
PV	pore volumes
PT	partitioning tracer
SERDP	Strategic Environmental Research and Development Program
SPME	single phase microemulsion
TCE	trichloroethylene
UIC	underground injection control
USDA	United States Department of Agriculture
UGSD	underground sources of drinking water
USGS	United States Geological Survey
VCW	vertical circulation well

1.0 SUMMARY

1.1 TECHNOLOGY DESCRIPTION

The science and engineering of enhancing the remediation/restoration of subsurface environments with surfactant/cosolvent flushing has been tested/demonstrated generally at small scale in the field under highly controlled conditions at several locations in the U.S. and Canada. The technology is under development by various industries with scientific and engineering input and/or independent investigations occurring at several academic institutions. Funding and assistance have often been provided from the U.S. Environmental Protection Agency, the U.S. Department of Energy, and the U.S. Department of Defense.

Development of the technology is largely a consequence of the failure of pump-and-treat remediation schemes that utilize only ground-water extraction, with or without re-injection of the local ground-water, as a means of removing non-aqueous phase liquids (NAPLs) or sorbed contaminants from the subsurface. In most completed or in-progress field demonstrations, the target has been a NAPL. In these studies, the facilitated removal of the NAPL from shallow unconfined aquifers of limited surface area, at sites where flow conditions can be highly controlled and modeled, has been the intent. A very limited number of field demonstrations have used cosolvents as mobilizing or solubilizing agents. Some studies have used surfactant mixtures (i.e., nonionic with anionic) or surfactant/cosurfactant/cosolvent mixtures.

Surfactant added to injection wells at levels generally around 1 to 3% with or without additional chemicals (cosolvents, alcohols, inorganic salts, etc.) can *mobilize* and/or *solubilize* nonaqueous phase liquids. Solubilization of sorbed contaminants may also occur. These phenomena result from the surfactants ability to:

1) lower NAPL - water interfacial tension and decrease capillary forces within the porous media

2) create a stable Winsor type III middle phase microemulsion system

3) solubilize individual contaminant molecules in surfactant micelles or single phase microemulsion system

A continuum through these processes may occur during actual technology applications. Surfactant solutions with additional additives can affect other water chemistry or aquifer properties, most notably ground-water viscosity, salinity, and solid phase carbon content.

When removal of NAPL or sorbed compounds is the intent, anionic and/or nonionic surfactants are utilized, as loss of surfactant to the aquifer solids is minimized. Cationic, and to a lesser extent zwitterionic, surfactants strongly sorb to aquifer solids making them impractical for such uses. Several researchers, interested in retarding the migration of contaminant plumes, are examining the potential of cationic surfactants to increase the carbon content of the solid phase, thereby reducing subsurface transport. Others are interested in facilitating the bioremediation of contaminants through the addition of surfactants. The mechanism(s) or degree of enhancement for the latter case is not known.

In most demonstrations, surfactants or cosolvents are pumped through the aquifer displacing at least one, and more often several, pore volume (PV) of ground-water, followed by several PVs of water to remove residual surfactant. Various well designs have been used including single vertical circulation wells, injection and extraction wells, and trenches (for surface flooding) and extraction wells. From site to site, the amount of contaminant mass recovered per mass of surfactant or cosolvent added may vary widely. This variation is dependent on the site and whether NAPL mobilization or solubilization occurs at the site. As a result, the ability to capture and recover the surfactant or cosolvent may or may not be a critical factor in process economic feasibility. Unit operations utilized or suggested as components in surfactant recovery/contaminant removal operations include:

- ultrafiltration, solvent extraction, floatation, air stripping, vacuum steam stripping, foam fractionation, photochemical treatment, biotreatment, incineration, and carbon adsorption.

For example, if contaminants are removed by solubilization within micelles, air stripping of volatile contaminants from the extracted ground-water solution may allow reinjection (recycle) of the surfactant solution for several pore volumes of treatment. However, the air stripping efficiency will be reduced by surfactant solubilization, a factor which must be included in the design/operation of these systems.

1.2 TECHNOLOGY STATUS

The first documented field tests of surfactant/cosolvent flushing were performed less than 6 years ago. Since that time, over 15 field demonstrations have been completed or are in progress. Many of these are summarized in Section 3. In addition, because of the complexity of and number of variations on the technology, many investigators are involved in (a) laboratory scale investigations to address issues of surfactant/cosolvent optimization, toxicity, and fate, and (b) modeling efforts to address some of these same issues.

These technologies have not been used commercially within the U.S. to fully remediate a contaminated site; however, commercial demonstration projects have been completed. In Québec Canada, Ecosite, Inc. has used surfactants to facilitate removal of 160,000 kg of NAPL from beneath an active commercial machine shop. Most of the other field projects have been conducted solely for the purpose of feasibility and research study and technology demonstration.

2.0 TECHNOLOGY DESCRIPTION

2.1 PHYSICAL/CHEMICAL DESCRIPTION

Pump-and-treat remediation of dissolved, sorbed, and/or nonaqueous phase contaminants (NAPLs) from the subsurface has proved often times to be very inefficient and costly. Low recoveries result from: (1) slow dissolution of NAPLs into the ground-water, (2) slow diffusion of contaminants from low conductivity zones to high conductivity zones, (3) slow desorption of sorbed contaminants, and (4) hydrodynamic isolation in dead-end zones. The first three factors are associated with the fact that organic compounds in the subsurface have a much greater affinity for organic phases (including natural organic matter and NAPL phases) due to thermodynamic potentials (i.e., chemical solubilities within phases) which effectively decrease dissolution, diffusion, and desorption rates.

Upon reaching the water table of an unconfined aquifer, light nonaqueous phase liquids (LNAPLs), less dense than water, typical spread on the water-table surface. Some less dense liquids are more volatile and water soluble than dense non-aqueous phase liquids (DNAPLs), often resulting in greater vapor phase contamination of the exposed vadose zone and faster rates and magnitudes of dissolution into the ground-water. DNAPLs, on the other hand, tend to sink into the ground-water creating a plug or volume with reduced hydraulic conductivity with respect to the surrounding water. Many liquid contaminants have densities close to that of ground-water. When NAPL phases occur, three general zones of contamination may be described. These are the source or residual zone, the concentrated plume (where the center of mass in the ground-water plume occurs), and the dilute ground-water plume. Innovative technologies, and not necessarily the same one, are required for decontamination in each of these zones.

Direct pump-and-treat of a NAPL phase results in fingering of the non-aqueous phase liquid as the more mobile water moves through or around it to the well head. Pump-and-treat with reinjection of the local ground-water behind the plug in an attempt to mobilize the NAPL also is often impractical as high hydraulic conductivity water again passes through or around the NAPL plug which acts as a continuous source of slowly released contaminant, through chemical dissolution into the ground-water. The high interfacial tension at the NAPL-water interface, and the resulting capillary forces, assure oil droplet release to the mobile water phase does not occur. At some sites, the estimated (DNAPL) residual volumes in the subsurface and the initial pump-and-treat recoveries (with local ground-water) suggest remediation times of decades to centuries would be required for greater than 90% contaminant removal.

The goal of surfactant flushing is to decrease the required flushing volume by *mobilizing* and/or *solubilizing* nonaqueous liquid phases and/or *solubilizing* sorbed contaminants. These phenomena occur because the surfactant may:

1) lower NAPL - water interfacial tension, thereby decrease capillary forces within the porous media

2) create a Winsor type III middle phase microemulsion

3)   solubilize individual contaminant molecules in surfactant micelles or single phase microemulsion systems (with added cosurfactants, usually alcohols)

Surfactant molecules possess both polar and nonpolar regions. The polar region is often a sulfate, sulfonate, carboxylate, or polyethoxylate group, and often contains a succinate or sorbitan group. The nonpolar group is generally a linear hydrocarbon chain; however, it is sometimes branched and may contain a phenolic or other aromatic group. Surfactants are referred to as amphiphilic (both loving) molecules because the polar group has a large affinity for (high solubility in) polar solvents, such as water, whereas the nonpolar group has a large affinity for nonpolar or hydrophobic solvents, which include most organic liquids. Upon addition to water, the large energy requirement of solubilizing the nonpolar portion of the surfactant molecules in the water is minimized by: (1) transference of this portion of the molecule to a nonpolar solvent through the liquid-liquid interface, or (2) self assemblage of these groups, forming surfactant aggregates known as micelles.

The first consequence (the overall partitioning of the surfactant molecules at the water-NAPL interface) also reduces the thermodynamic energy required in forming this interface. Without surfactant present, the large amount of energy required to form a water-NAPL interface is compensated for physically by reducing in interfacial surface area. This results in a rigid or taut boundary between the two phases which can be quantified by the measurement of (a high) interfacial tension. Reducing the energy requirement to make the interface by adding surfactant, allows the interfacial area to increase or become less taut , as quantified by the measurement of (a low) interfacial tension. An increase in interfacial area may result in spontaneous formation of droplets, of very thin alternating sheets of water and NAPL separated by surfactant layers (lamella), or of other structures which *mobilize* the NAPL material. NAPL-in-water droplets which form spontaneously (i.e., no mixing energy required) have been referred to as single phase microemulsions . Single phase refers to the fact that only one aqueous phase (i.e., the microemulsion phase) is present during their development, as opposed to middle phase microemulsions, also referred to as Winsor type III microemulsions, which are formed in the presence of an additional aqueous phase. Single-phase microemulsions are basically organic liquid droplets (0.01 to 0.1 µm in diameter) suspended in water with a very high surfactant concentration at the water-organic liquid interface. These solutions are quite transparent. Middle phase or Winsor type III microemulsions are lamellar-type structures and often are cloudy.

The second consequence (self assemblage of the nonpolar groups, forming surfactant aggregates known as micelles) does not require a second phase or the addition of another organic compound; however, other organic molecules may be solubilized within the micelles. In these aggregates or micelles, the hydrophobic groups fill the core, and the polar groups are in contact with the aqueous phase water molecules. Typical micelles contain 50 to 100 surfactant molecules (i.e., monomers). A much narrower range of aggregation numbers occur for any given surfactant solution and the average number is dependent on the specific properties of the surfactant and on solution properties (i.e., temperature, ionic strength for some surfactant types, etc.). Micelle formation is surfactant concentration dependent. At surfactant concentrations below a specific value, termed the critical micelle concentration (cmc), virtually no micelles exist. Surfactant doses in excess of this value produce micelles at a concentration equal to the difference between the total surfactant concentration and the cmc. The term critical micelle concentration is really a misnomer, as this value is the specific *monomer* concentration that is in equilibrium with the micelles. Micelle formation is very much like a precipitation reaction as the number or concentration of micelles has very little effect on

the cmc. (The amount of solid in equilibrium with a saturated aqueous phase is not dependent on the aqueous saturation value.) In this case, the micellar pseudo (i.e., false) phase is formed rather than a precipitate. The term pseudo-phase is applied to micelles because they can not be separated from the aqueous phase in which they reside without destroying them. They are very dynamic entities, forming and dissaggregating spontaneously and nearly instantaneously in water upon a change in surfactant concentration. Due to counter-ion association on charged micelles, cmc values of anionic surfactants decrease with increasing ionic strength (e.g., increasing salinity). The cmc values of nonionic surfactants are less affected by ionic composition. The cmc values of common nonionic surfactants tend to be less than those of common anionic surfactants, with nonionic/anionic surfactant mixtures having intermediate cmc values. Micelles may *solubilize* aqueous phase organic compounds, resulting in further dissolution of a NAPL phase. The differentiation between micelles (containing a few non-surfactant organic molecules), swollen micelles (containing many non-surfactant organic molecules), and single-phase microemulsions (containing even more non-surfactant organic molecules) is sometimes blurred. Indeed, a continuum through these phases may occur during actual technology applications.

In addition to phase and interfacial properties, surfactant solutions with or without additional additives may affect other water chemistry or aquifer properties; most notably ground-water viscosity, salinity, and solid phase carbon content. Often polymers have been added to affect the hydraulic conductivity of the porous media, decreasing preferential flow. In the case of *mobilizing* systems, anionic/nonionic surfactants are added to injection wells at levels generally around 1 to 3% with or without additional chemicals (cosolvents, alcohols, inorganic salts, etc.). Based on the DNAPL and site characteristics, the specific surfactant that is utilized may be selected or precisely formulated as a mixture to create an optimum middle phase microemulsion, single phase microemulsion, or micellar system in the subsurface. The selection/formulation process is best described by inspection of a Winsor type diagram, as depicted in Figure 1 (Winsor, 1948). In this figure, each line representing a surfactant molecule has to parts: The straighter portion represents the nonpolar group, and the squiggly portion represents the polar group. This figure shows the possible phase behavior within a 1:1 (v:v) mixture of water and immiscible organic liquid (or NAPL). The specific phases that exist are dependent on several water chemistry and surfactant properties. For example, if a single surfactant is utilized, the hydrophobic-lipophilic balance (HLB) of that surfactant largely determines the phase behavior. If a water soluble (hydrophilic) surfactant is added, most of the surfactant will reside within the water phase, possibly creating a micellar pseudo-phase within the aqueous layer. Some, but not much, of the organic phase may be solubilized in the aqueous micelles, reducing the organic phase volume. If cosurfactants are added (usually linear alcohols) a NAPL-in-water microemulsion possibly may result. These are single-phase microemulsions (SPME) having droplets ranging in diameter from 0.01 to 0.1 µm, depending on the surfactants, cosurfactants, and NAPL phase with which they are constructed. Both micellar and SPME systems are optically transparent.

At the other extreme, if an organic soluble (hydrophobic) surfactant is added, most of the surfactant will reside within the organic phase, creating a Winsor type II organic rich reverse micelle phase. In this case, some, but not much, of the water may be solubilized within the reverse micelles. Classic type II systems should be quite impractical for aquifer restoration.
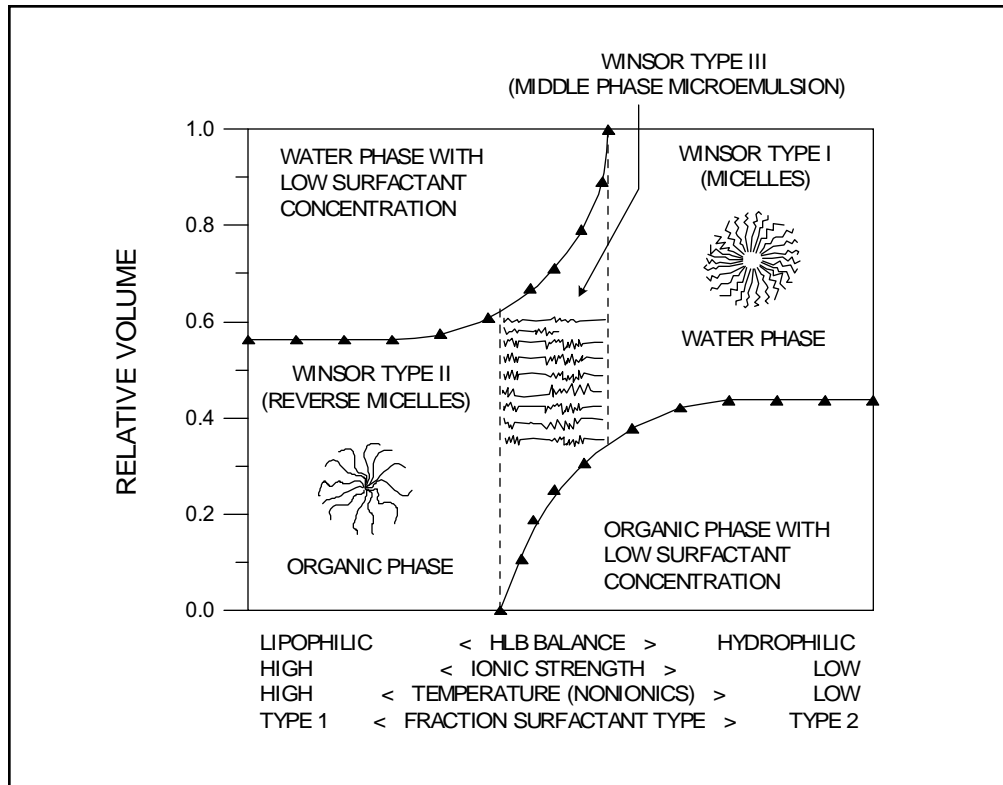
Figure 1. Typical Winsor diagram of equal volumes of organic phase and water phase with surfactant(s) and possibly co-surfactants (Adapted from Sabatini, *et al.*, 1996).

Middle Phase Microemulsions

If the hydrophilic- lipophilic functional groups of the surfactant are more balanced, a Winsor type III middle phase microemulsion will result. The term middle phase refers to the actual location of the phase in static layered solutions where clear top and bottom layers exist, separated by the middle phase. In the case of a DNAPL, the bottom layer is the excess DNAPL and the top layer is the excess water, as relationally depicted on Figure 1. Also shown on Figure 1 are some other controlling parameters, besides the HLB of a specific surfactant. The most notable is surfactant mixture ratio. Because of the wide variety of possible chemical compositions within DNAPL spills, the probability of finding an existing inexpensive high volume surfactant that produces stable middle phase microemulsions for any given DNAPL is quite low. However, the HLB value of an overall surfactant mixture can be varied quite easily by adjusting the ratio of surfactants within a mixture. It has been shown that middle phase microemulsions are possible for the chlorocarbon tetrachloroethylene, using mixtures of the branched nonionic ethoxylated surfactant Aerosol OT (AOT) and sodium mono- and di- methyl naphthalene sulfonate (SMDNS) (*Shiau, et al., 1994*). Both MPME and SPME systems form spontaneously on water, surfactant (and possible cosurfactant), and NAPL contact, as opposed to larger diameter emulsion systems which require mixing energy input.

Solubilization

The solubilization by micelles or microemulsions is a phase distribution process if a liquid phase, solid phase, or sorbed contaminant exists after addition of the surfactant. The flushing rate of a NAPL from the subsurface, therefore, is dependent upon the solubility limit of the organic phase constituents within the micelle or microemulsion droplets. Because a large fraction of a microemulsion can be the organic phase (i.e., NAPL) itself, predicting the solubility behavior, *a priori*, essentially is impossible, and trial and error is used to formulate the correct surfactant mixture. SPME systems often contain an anionic sulfonated surfactant, a nonionic ethoxylated surfactant, a linear alcohol, and sometimes additional hydrocarbon compounds. Micellar systems are generally simple formulations of single individual anionic or nonionic surfactant mixtures, or an anionic *and* nonionic mixture. A good estimate of the solubilization potential in simple micellar solutions can generally be made prior to any experimental work. Figure 2, for example, shows the values of micelle-water partition coefficients in relationship to the octanol-water partition coefficients for a series of aromatic compounds. In this case, the micelle-water partition coefficient, K_m, is described by the following relationship:

$$K_m = [PAH]_{mic} / [PAH]_{aq}$$

where $[PAH]_{mic}$ has units of mass contaminant per mole of surfactant and $[PAH]_{aq}$ has units of mass contaminant per liter of water. This relationship can be somewhat deceiving. It would appear that those compounds which are the least water soluble have the greatest solubility within the micelles: This is not true as these values represent partition constants only, and not absolute solubilities. Through this series of compounds, as the K_{ow} value increases, water solubility decreases (recall this is a log scale) For example, the solubility of perylene in water is only 0.0002 mg / L, whereas benzene's solubility is 1,800 mg / L, a difference of more than 6 log units. To produce a 4 log unit increase in the micelle-water partition coefficient, the solubility within the micelles must actually decrease approximately 2 log units. Indeed, at saturation under standard pressure and temperature, approximately 35 benzene molecules can be solubilized by one dodecylsulfate micelle composed of 60 to 70 surfactant molecules, whereas, on average much less than one perylene molecule exists within each micelle. Micellization of contaminants, therefore, generally will require significant surfactant doses. The molar solubilization ratio (MSR) is the ratio of contaminant molecules solubilized to surfactant molecules within micelles at saturation. Hence, for benzene the ratio is approximately 0.5 for micelles composed of dodecylsulfate. The MSR for most halogenated ethenes and ethanes (PCE, TCE, 1,2-DCA, etc.) is of this same order (0.2 to 0.5), so for about every ten surfactant molecules added, approximately 2 to 5 molecules of chlorinated ethane or ethene may be recovered.

Solubilization within SPME systems is somewhat similar. In this case, however, because of the much larger volume of the microemulsion phase, more NAPL is solubilized. These systems are more complex in that the stability of the phase is partly determined by the partitioning to the subsurface materials of the many individual constituents of the microemulsion. The stability of SPME systems over long distances in the subsurface is not known.
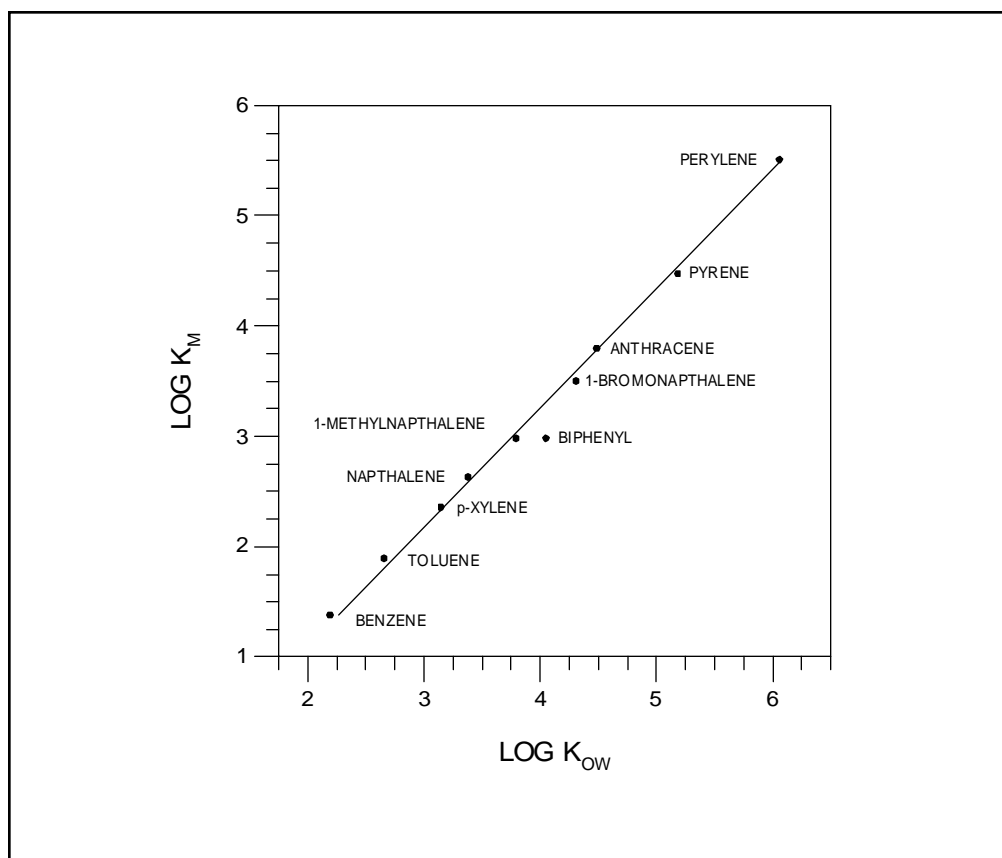
Figure 2. The relationship between the micelle-water portion coefficient (K_m) and the octanol-water partition coefficient (K_{ow}) for the anionic surfactant - dodecylsulfate (from Jafvert, *Environ. Sci. Technol.*, 25, 1039-1045, 1991).

Cosolvents

Unlike the solubility enhancements caused by partitioning into micelles or microemulsions, solubility enhancements caused by cosolvent addition generally occur because of changes in the bulk properties of the isotropic solution. An example of this type of enhancement is shown in Figure 3 for toluene in mixtures of water with methanol or ethanol. As with mixed surfactants, advantages are gained by using mixed cosolvents. Short chained linear alcohols are excellent in solubilizing small chlorohydrocarbons, whereas, larger hydrocarbon cosolvents work best for larger and more hydrophobic contaminants. Addition of short linear alcohols also enhances the solubility of the larger cosolvents.

In actual practice, the benefits of flushing with cosolvents may result from the above mentioned increase in solubilization within the aqueous phase or through the more efficient process of mobilization. Mechanisms responsible for mobilizing NAPL contaminants include: (1) creation of a single phase condition, (2) decrease in the water-NAPL interfacial tension, and (3) swelling of the NAPL by solubilization of the cosolvents within this phase. Mobilizing by creating a single phase is essentially the same as solubilizing the entire NAPL. Decreasing the interfacial tension occurs due to the changes in the surface tension of both phases (the alcohol dissolves in both phases making their chemical and physical interfacial properties more similar. Similarly, swelling of the NAPL is
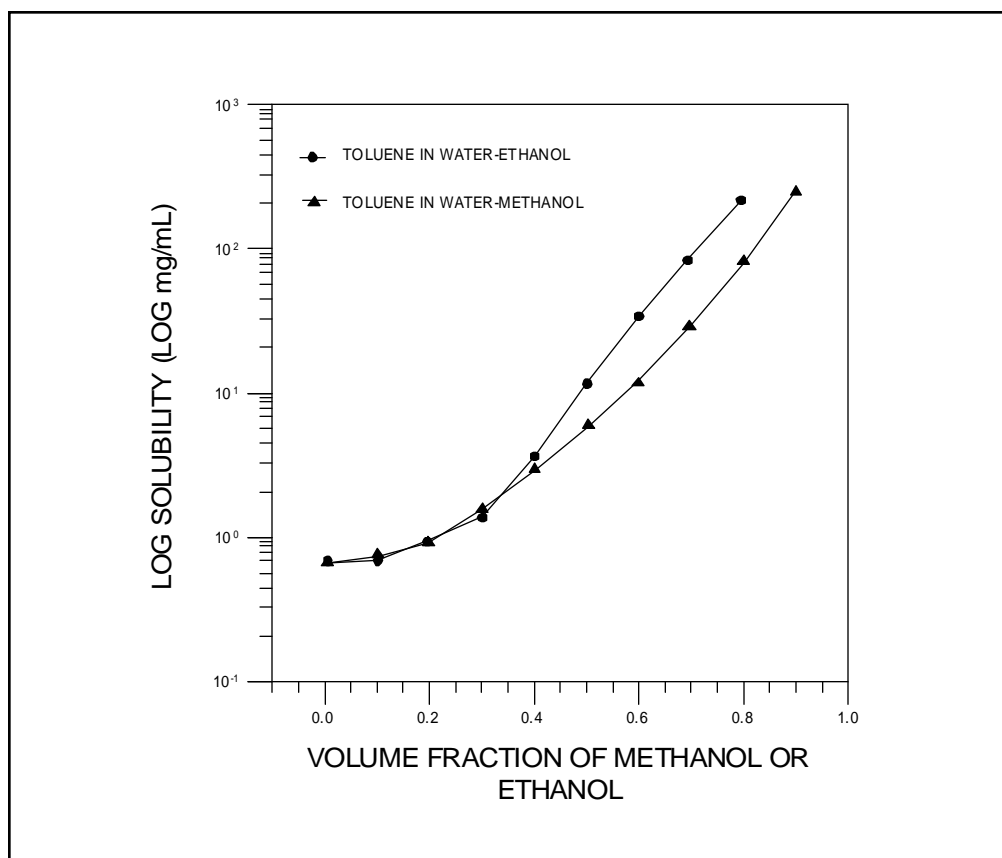
Figure 3. Solubility of toluene in water-ethanol and water-methanol mixtures (From Yalkowski, S. H., "Solubility of organic solutes in mixed aqueous solvent," Final Report to the R. S. Kerr Research Lab., U.S. EPA, contract CR811852-01-0, 1985).

accompanied by beneficial changes in phase viscosity, density, and other properties. As with surfactant systems, mobilizing, rather than solubilizing, results in: (1) use of less total material (surfactant or cosolvent), (2) use of smaller volumes of material (i.e., fewer pore volumes), and (3) shorter treatment times. However, precise formulations are required, resulting in much more intensive laboratory bench and pilot-scale work.

Rather than using conventional surfactants or cosolvents, several researchers have proposed the use of other solubilizing agents that associate or bind contaminants. Mark Brusseau at the University of Arizona has proposed using cyclodextrins as flushing agents and will be conducting a field study with cyclodextrins at Hill Air Force Base in 1996. These compounds are generally linear chains of glucose molecules with the ends joined to form a cyclic structure. Because the diameter of the ring can be controlled by the number of (glucose) sugar molecules in the chain, specific cyclodextrins possible could be used for specific contaminants. Because contaminants partition to the center of the ring, the resulting complexes are termed inclusion complexes. Suzanne Lesage and coworkers at Environment Canada have proposed using humic acids to enhance the removal of gasoline and diesel fuel constituents from the subsurface. They have performed pilot-scale demonstrations. Although humic acids are quite recalcitrant to biodegradation, an advantage of their use is that they are natural materials.

2.2   TYPICAL CONFIGURATION AND OPERATION

There is no typical configuration or mode of operation for these innovative remediation technologies. Five major considerations are listed below in designing any operation. As will become apparent from reading these, they are quite interdependent, which further complicates the configuration selection and design process.

1)   The selection of surfactant or cosolvent mixture is dependent on the removal mechanism that is anticipated: mobilizing versus solubilizing; with surfactant micelles, mixed micelles, micelles with cosurfactants, middle phase microemulsions, single phase microemulsions, or any of a semi-infinite variety of cosolvent mixtures. (note: mechanisms other than flushing such as surfactant enhanced bioremediation will be mentioned later.)

2)   The removal mechanism which is optimal depends on the interactions among the contaminants, the surfactant(s)/cosolvent(s), the subsurface porous media, and other subsurface constituents (i.e., Na^+, Ca^{2+} , Mg^{2+}, Fe^{2+}, H^+). Hence, both batch (test tube) phase-behavior experiments and column flooding studies are required.   Column flooding of aquifer material with surfactants or cosolvents is analogous to what is known as coreflooding of oil shale material with surfactants or caustics in petroleum engineering.

3)   Hydrodynamic characterization of the site is critical, and is necessary prior to modeling. The surfactant/cosolvent can be effective only if it reaches the contaminant zone and can be extracted from this zone. Hence, the configuration of injection/ extraction wells is highly dependent on site characteristics. Initial demonstrations have used single vertical circulation wells, trenches (for flooding) and extraction wells, and injection and extraction wells in all types of configurations, including horizontal wells. Prior to large field scale efforts, hydrodynamic modeling of the treatment flood is almost essential as potential problems may be discovered and averted. Low recovery efficiencies are often due to not capturing the material within the flush, rather than ineffective surfactant formulations. Preflushing with polymers or foams possibly may decrease preferential flow in heterogeneous formations.

4)   The mass or concentration of material to be removed from the subsurface must be estimated prior to and after treatment. In the past, sample cores were often taken and analyzed; however, due to aquifer heterogeneity, elaborate methods of data reduction were required to estimate the total mass or volume. More recently, interwell partitioning tracer tests (IWPTT) have been used to estimate the mass or volume of material. Because these tests are generally performed using the same well arrays that are utilized in the surfactant/cosolvent flush, they provide an accurate measure of what is present and/or removed from the zone accessible by these wells. Even in these test, dead-end zones may be not accessible resulting in calculated recovery errors.

5) Treatment is not complete upon extraction. Large volumes of water, contaminants, and surfactants and cosolvents are generated that must be treated. Several research groups are or have investigated ultrafiltration as a means of concentrating the contaminants and surfactants prior to further treatment. Other research groups are investigating or have inverstigated solvent extraction, floatation, air stripping, vacuum steam stripping, foam fractionation, and photochemical treatment as surfactant-contaminant waste-stream separation processes, whereas biotreatment, incineration, and carbon adsorption, have been suggested for contaminant wastewater treatment.

Several specific technical conditions/factors which must be considered early in design, even before laboratory experiments are conducted, are listed below. This list, certainly, is not all inclusive but is provided to give an idea of the types of conditions or issues that may be important in progressing from the laboratory to the field scale:

- aquifer heterogeneity and anisotropy
- ground-water temperature
- viscosity in the subsurface before and after surfactant contact with the NAPL
- biodegradability of surfactants/additives
- toxicity of surfactants/additives, regulatory issues regarding the use of specific surfactants
- precipitation losses of anionic surfactants with calcium or other metal species
- sorption losses of anionic and nonionic surfactants
- stability limits of mobilizing systems (separation of components over long distances)
- density differences
- fingering
- post extraction treatment of recovered material (may even effect surfactant/cosolvent selection)
- containment
- modeling requirements
- data analysis on complex mixtures (i.e., how many samples and what constituents to monitor?)
- cost-benefit analysis of the extent of area treated per mass of contaminant recovered (i.e., treat only the most contaminated areas?)

Existing and past field studies and demonstrations are reviewed in Section 3, providing a more comprehensive overview of the diversity in surfactant/cosolvent remediation strategies.

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3.0 PERFORMANCE

3.1 CASE STUDIES AND DEMONSTRATIONS

Table 1 summarizes completed and ongoing studies in which surfactants or cosolvents have been or will be injected in an attempt to facilitate contaminant removal. Following Table 1, each of these studies is summarized in more detail, with a list of published references provided for each study where available. The cases are summarized in the order of their appearance in Table 1.

Table 1. Completed or In-Progress Surfactant or Cosolvent Studies or Demonstrations

Study name	Major contaminants	Process[a]	Status
Bordon	DNAPL PCE	surfactant flushing	completed
Corpus Christi	DNAPL carbon tetrachloride	surfactant flushing	completed
Estrie Region	NAPL hydrocarbon	surfactant flushing	completed
General Motors	oils and PCBs	surfactant flushing	completed
Thouin Sand Quarry	DNAPL, chlorinated solvents	surfactant mobilization	completed
Traverse City	PCE and aviation fuel	micelle solubilization	completed
DOE Portsmith	DNAPL TCE and PCBs	surfactant flushing	in progress
Picatinny Arsenal	sorbed TCE	micelle solubilization	in progress
Industrial NJ Site	BTEX and chlorinated organics	surfactant flushing	on hold
Hill AFB	NAPL JP4 and chlorinated organics		
OU1, Test 1		cosolvent solubilization	complete
Cell 3, OU1		cosolvent mobilization	in progress
Cell 5, OU1		middle phase microemulsion	in progress
Cell 6, OU1		micelle solubilization	in progress
Cell 8, OU1		single phase microemulsion	in progress
OU2		surfactant flushing	in progress
OU2		surfactant foam flushing	scheduled

[a]If a specific process was not identified or engineered for (i.e., solubilization, SPME), the more general term surfactant flushing is used in the table.

1.   Bordon Site, Bordon Canadian Air Force Base, Alliston, Ontario Canada

Participants: SUNY Buffalo and University of Waterloo's Centre for Groundwater Research (site operator)

Demonstration date: June 1990 to August 1991

Compounds treated: 271 L of PCE added in a controlled release

Surfactant/cosolvent: unknown

Treatment Summary: The study area was a clean surficial sand aquifer with < 1% clay, and < 0.1% organic carbon in a 3 x 3 x 3 m^3 cell. The cell was constructed by driving sheet piling walls into the underlying clay aquitard. A second sheet-piling wall was installed 1 m outside the inner wall for containment. Five injection wells and five extraction wells were installed parallel to each other on opposite sides of the 9 m^2 cell. Multi-level monitoring wells were also installed. 271 L of PCE were introduced to the cell in a controlled release. The upper PCE zone (0 to 1 m BGS) was perched on a layer within the sand less than 2 cm in thickness. The lower pool was located on the clay aquitard at the base of the cell. A 2% surfactant solution was pumped through the cell. The PCE in the extracted solution was air stripped and the surfactant solution was recycled through the cell for 14 PVs.

Results: The DNAPL concentration was rapidly reduced in the cell in areas of high hydraulic conductivity. The residual PCE in the top 1 m was reduced from an initial value of 10% to a value of 1% after 14.4 PVs. At a depth of 2.5 to 3 m, where the ground was either saturated or at 20% saturation with PCE initially, the PCE saturation was reduced to 3% after 14.4 PVs. Approximately 80% of the total material was recovered, with the remaining material lost to volatilization or remaining in dead zones within the formation. The surfactant solution was initially injected into the wells with a constant-head system on each well; this later was changed to peristaltic pumps due to plugging of the injection wells.

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References:

Fountain, John; Waddell-Sheets, Carol ; Lagowski, Alison; Taylor, Craig; Frazier, Dave; Byrne, Michael. Chapter 13: Enhanced removal of dense nonaqueous-phase liquids using surfactants, in *Surfactant-Enhanced Subsurface Remediation: Emerging Technologies*, ACS Symposium Series 594, Dave A. Sabatini, Robert C. Knox, and Jeffrey H. Harwell, eds., 1995.

Fountain, J. C. and Hodge, D., Project summary: Extraction of organic pollutants using enhanced surfactant flushing: Initial field test (part 1). NY State Center for Hazardous Waste Management, February, 1992.

2.   Corpus Christi Dupont Site

Participants:	SUNY Buffalo and Dupont Corporate Remediation Group
Demonstration date:	June 1991 to February 1993
Compounds treated:	Carbon tetrachloride (CTET) as a DNAPL at 1000 mg / L in both core and water samples from the test zone (the site was at a chlorocarbons manufacturing plant)
Surfactant/cosolvent:	unknown
Site Characteristics:	CTET was present at shallow depths, underlain by a thick clay aquitard (barrier to vertical migration). The target zone was a 12 ft fine grain sand lens with variable smectitic clay content (1 to 15%), 0.025 to 0.031% organic carbon, and 12,000 mg / L total dissolved solids at 12 to 24 ft below ground level, making the overall test area 25 by 35 ft. The formation had moderate hydraulic conductivity ($>= 10^{-3}$ cmsec). An array of 6 injection wells and one central extraction well were used. This project was completed in four phases. In the first phase a 1% surfactant solution was pumped to the injection wells with the extraction solution air stripped to remove the PCE. The surfactant solution was recycled. Phase II was similar with one well being replaced. In Phase III a new surfactant was used. In Phase IV a smaller area was tested.
Results:	In the first two phases, completed in 6/91-8/91 and 3/92-6/92, respectively, the surfactant was found to sorb considerably and biofouling of the above ground tanks occurred resulting in the change of surfactant. The initial concentrations in monitoring wells were 200-300 mgL with concentrations jumping to 800-900 mg / L at the point that the surfactant reached 0.5% in the monitoring wells (i.e., about 1 PV). The average concentration of CTET in the solution recovered was 790 and 219 mg / L for Phases I and II, respectively. After 12.5 pore volumes, a total of 73 gallons of CTET were removed.

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Fountain, J. C.; Waddell-Sheets, C., A pilot field test of surfactant enhanced aquifer remediation: Corpus Christi, Texas,   Extended Abstract from ACS symposium in Atlanta Georgia, September 27-29, 1993.

Fountain, J. C. "A pilot scale test of surfactant enhanced pump and treat, in Proceedings of Air and Waste Management Association's 86th Annual Meeting, Denver, Colorado, June 13-18, 1993.

3.   Estrie Region, Machine Shop

Participants: Ecosite Inc., Quebec City, Qc., Canada

Demonstration date: 1993-1994

Compounds treated: over 160,000 kg of hydrocarbon cutting-oil laden soil under a building

Surfactant/cosolvent: nonionic, biodegradable surfactants

Treatment Summary: The site was under a machine shop in Estrie Region, Qc, Canada, with the contamination extending from 2 to 4.3 m beneath the concrete slab floor. The volume of contaminated soil was estimated to be 1,800 m^3 with approximately 1 m of free floating phase. The soil was composed of fine sand with 10-12% silt. The watertable was at approximately 3 m BGS. The hydraulic conductivity was 10^{-4} cm/sec. 400 injection-extraction wells were installed in 3 distinct zones:

A peripheral network to hydraulically isolate the contamination, a second zone used only to extract the oils and washing solutions, and a third zone which was used both to inject and extract material. The extract was processed on-site in a wastewater treatment system. Laboratory feasibility trials were performed to: select the surfactant, evaluate biodegradability and toxicity of wash solutions, and plan hydraulic controls. A computerized system for data acquisition was installed to monitor ground-water movement.

Results: First, the watertable within the contaminated area was raised 2 m by injecting washing solution using the injection/extraction wells. Over a combined 50 day period (20 and 30 days in 1993 and 1994, respectively) 37.6 m^3 of free phase oil was recovered. In the second step, 8 cycles of washing over 60 days resulted in a cumulative mass of oil recovered of approximately 160,000 kg. Most of this was emulsified oil. After extraction, high microbial levels of hydrocarbon degraders were found in the soil.

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References:

Ross, Arnold; Boulanger, Charles; Tremblay, Charles, In situ remediation of hydrocarbon contamination using an injection-extraction process, Remediation *Management*, March/April, pages 42-45, 1996.

4. General Motors NAO R&D Center, Surfactant Washing Demonstration

Participants: General Motors NAO R&D Center

Demonstration date: 1991

Compounds treated: up to 6,000 ppm PCB and 67,000 ppm other oils (from soil cores)

Surfactant/cosolvent: unknown

Site Characteristics: The site consisted of a five acre parcel surrounded by a containment wall of clay and cement (previously installed) to a depth of 60 ft below the surface. The contamination was confined to the upper 15 ft of the subsurface fill material. Within the five acre site, surfactant was applied to a test plot, 10 ft in diameter by 5 ft deep. The leachate was biotreated for surfactant and oil removal, followed by adsorption of

the PCBs on activated carbon. In other tests performed on the leachate, the surfactant solution was concentrated with a Romicon Model HF-Lab-5 ultrafiltration unit with either a XM50 or a PM500 membrane.

Results: About 10% of the contaminants were recovered after 5.7 PV. During a similar test the following year, an additional 14% was recovered after 2.3 pore volumes. In the ultrafiltration experiments, 67% of the surfactant mass was recovered with the PM500 membrane, with 90 and 83% of the PCBs and oils being retained, respectively. The XM50 membrane did not capture the surfactant quite as efficiently (46%), however retained approximately the same fraction of PCB and oil (94% and 89%, respectively).

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References:

Abdul, A. S.; Gibson, T. L., "Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyls from sandy materials," *Environ. Sci. and Technol,* 25:565-670, 1991.

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5.   Thouin Sand Quarry, Québec Canada:

Participants: Department of Geological Engineering, Laval University, Québec, Canada, and Ministry of Environment and Fauna, Ground Water Division, Canada

Demonstration date:	1995

Compounds treated: Oil waste and chlorinated solvents in the form of DNAPL, density = 1.02, viscosity = 18 cp.

Surfactant/cosolvent: The washing solution was designed after several laboratory column experiments and after construction of several phase diagrams.

Treatment Summary: The site is located approximately 20 km northeast of Montréal and is characterized by a thin silty sand layer (2 m) underlain by a 30 m thick deposit of silty clay. Waste oils and organic compounds dissolved in water have been flowing in ditches and nearby creeks. The test plot, 4.3 m by 4.3 m and covering less than 0.075% of the area, was equipped with one central injection well, four recovery wells spaced in a square, and 12 multilevel observation wells. Recovery wells were 3 meters from the injection well, resulting in approximately 17 m^3 of contaminated soil in the saturated zone within the treatment area. The pore volume was approximately 6 m^3. During well installation, 42 soil samples were taken. The average initial DNAPL concentration was 55,000 mg / kg dry soil. The test plot was flooded with: (1) 1.34 PV water, (2) 0.54 PV polymer, (3) 0.9 PV surfactant, (4) 1.6 PV polymer, (5) 1.4 PV water, (6) and finally with an injection of bacteria and nutrients to increase biodegradation of the remaining DNAPL.

Results: In the zone swept by the washing solution, 86% of the residual DNAPL was recovered using 0.9 pore volumes of surfactant and those rinses described above. DNAPL between extraction wells was not removed well due to insufficient flow in these areas. The use of a polymer solution before and after injection of the surfactant solution appeared to be beneficial in insuring that the surfactant solution swept the majority of the total treated volume, despite the heterogeneity of the soil. Rinse cycles were not completed because of weather.

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References:

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6.   Traverse City Field Test

Participants:
Institute for Applied Surfactant Research, U. of Oklahoma, R. S. Kerr Environmental Research Laboratory, Ada OK, The U.S. Coast Guard, and Dow Chemical Co., Inc, Midland MI.

Demonstration date:
June, 1995

Compounds treated:
PCE and aviation fuel at up to 1000 µg / kg and 1000 mg / kg, respectively. PCE in the ground-water was typically at 10 µg / L.

Surfactant/cosolvent:
540 gallons of 60 mM Dowfax 8390

Site Characteristics:
The test occurred in a highly conductive sand formation with natural ground-water velocities of 3 to 5 ft / day. The saturated zone was at a depth of less than 10 ft below the surface. The primary objectives were to: (1) evaluate a vertical circulation well (VCW) system, and (2) maximize surfactant recovery. Laboratory batch and column studies were first performed to test removal efficiencies of the contaminants and the surfactant. Modeling studies were performed on the VCW system. The vertical circulation well was a single borehole well system with two 5 ft screen lengths separated by a 3 ft spacer. The screens were isolated from each other within the well with packers. Water/surfactant was injected through the top screen and water/contaminants/surfactant extracted through the bottom screen. Preliminary tracer studies were conducted at the site prior to installation of the VCW to characterize the system hydraulics. 540 gallons of surfactant solution were added at a surfactant concentration 10 times the cmc value (3.8 wt%).

Results:
It was found that due to the high hydraulic conductivity at the site, the extraction rate necessary to capture the surfactant and solubilized contaminants had to be about 10 to 15 times the injection rate. Removal of the contaminant (i.e., PCE and methylated alkanes) was increased by approximately 5 to 7 times above normal concentrations in the ground- water. After accounting for the tremendous volume of dilution water added, estimated enhancements were 40 to 90 times background levels with water alone.

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7.   DOE Portsmouth Gaseous Diffusion Plant, Piketon OH

Participants: INTERA, Inc., SUNY at Buffalo, The University of Texas at Austin

Demonstration date: Scheduled for Fall, 1996

Compounds treated: Multicomponent DNAPL, mostly TCE (approx. 90%), PCB's (approx. 800 mg/ L of the DNAPL), and other chlorinated solvents

Surfactant/cosolvent: Various surfactants have been tested in the lab.

Treatment Summary: This demonstration is funded by the U.S. DOE, Morgantown Energy Technology Center, Morgantown WV. A partitioning tracer test is to be conducted in July, 1996 to measure the volume of DNAPL between 2 existing wells at the site. In the Fall of 1996, a DNAPL solubilization test will be conducted at the X701B area at the DOE Portsmonth Plant. The contamination occurs in the Gallia sand and

gravel aquifer. The hydraulic conductivity is approximately 10^{-2} cm/sec. The two wells, spaced 15 ft apart and 20 ft deep have produced free phase NAPL.

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8.   Picatinny Arsenal, New Jersey

Participants: U.S. Geological Survey and University of Virginia (Funding Source: EPA's Office of Exploratory Research, project active though Sept. 1996)

Demonstration date: Summer, 1995

Compounds treated: TCE at low concentrations sorbed to subsurface soil (no apparent free phase NAPL)

Surfactant/cosolvent: Triton X-100

Treatment Summary: This site is located on a golf course. TCE contamination is within a sand and gravel aquifer at concentrations of approximately 1 to 5 mg/kg with aqueous phase concentrations of 1 to 5 mg / L. The water table is approximately 10 ft below the surface, with a lower confining unit 10 to 15 ft thick at 50 ft below the surface. The test site is up gradient from an existing pump-and-treat system, installed as an interim remedy, as the site is a listed Superfund site. Three injection wells, 10 ft apart, were installed perpendicular to the natural gradient and tangential to the pump-and-treat extraction well, approximately 100 yards down-gradient. One monitoring well is located 30 ft up-gradient and three monitoring wells located down-gradient at 10 ft intervals from the injection wells. Clean water was pumped to all three injection wells for approximately 30 days at 3 gal / min. The water in the center injection well was replaced with 400 mg / L Triton X-100 at the same flow rate for 30 days while clean water continued in the outer wells. Clean water was pumped to all three wells for an additional 4 months. The purpose of this study was to investigate whether the surfactant would increase the rate of desorption of TCE from the solid phase. Hence, researchers are modeling the transport of the surfactant and the TCE. The Picatinny Arsenal is a USGS National Research Site.

Results:	Researchers are currently processing data and completing modeling efforts.

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References:

Di Cesare, D. and Smith, J. A., "Effects of Surfactants on the Desorption Rate of Nonionic Organic Compounds from Soil to Water," *Reviews of Environmental Contamination and Toxicology*, 134:1-29, 1994.

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9. Industrial New Jersey Site

Participants:	New Jersey Institute of Technology, GHEA Associates, Inc.
Demonstration date:	To be determined, the project is on hold.
Compounds treated:	Chlorinated organics and BTEX at levels of 1,000 to 2,000 mg/ L.
Surfactant/cosolvent:	A nonionic surfactant
Treatment Summary:	The site is active and used for machining operations. There is a clay barrier about 10 ft below the surface and the hydraulic conductivity in the clayey unconfined zone is low. Because the site is characterized by low permeability and is shallow, the design consists of straight lines of alternating feed trenches and extraction wells. The feed trenches will be saturated with the surfactant solution during operation, with water removed from the alternating (with the trenches) rows of extraction wells.

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References:

Gotlieb, I.; Bozzelli, J. W.; Gotlieb, E., Soil and Water Decontamination by Extraction with Surfactants, *Seper. Sci. and Technol.*, 28:793-804, 1993.

10. Hill Air Force Base Sites - Summary

Funded primarily through the DOD/DOE/EPA Strategic Environmental Remediation Demonstration Project (SERDP), the Advanced Applied Technology Demonstration Facility (AATDF) and the U.S. EPA Research Laboratory, Ada Oklahoma, nine test cells have been constructed at Operational Unit 1 (OU1) on Hill Air Force Base, near Salt Lake City, Utah. Other studies are completed, underway, or in design stages at Operational Unit 2 (OU2). Hill AFB is a CERCLA site listed on the National Priorities List. At OU1, an early SERDP study involved ethanol flushing, conducted by researchers from the University of Florida. Currently, eight treatability studies are under way at OU1. Technologies under investigation, each with a dedicated field cell, include: steam flushing for NAPL mobilization (Tyndall AFB and Praxis Environmental Technologies), air sparging (Michigan Tech.), flushing with cyclodextrins (U. of Arizona), flushing with co-solvents (Clemson), flushing with a surfactant/alcohol single phase microemulsion (SPME) (U. of Florida), flushing with a surfactant that solubilizes (U. of Oklahoma), flushing with a surfactant that mobilizes (U. of Oklahoma), and in-well sparging (same as in-well aeration) (U. of Arizona). In addition, at Operational Unit 2, two demonstrations using surfactants are scheduled: one organized by INTERA for 1996, and the other by researchers at Rice University for 1997.

At OU1, the design of each test is process dependent, however, each test cell that will undergo some type of flushing is basically the same. Each cell is constructed of sheet piling driven into a clay layer approximately 30 feet below the surface, each occupying a rectangular surface area of 3 m x 5 m. The sheet piling has inter-locking grout-sealed joints to hydraulically isolate the cell from its surroundings. This type of containment is sometimes referred to as a Waterloo Barrier system. The sand and gravel aquifer is approximately 15 to 20 ft below the surface to the clay aquitard. Four injection and three extraction wells are located on the opposite 3 m sides of each cell. Well screens are variable from the clay layer to above the water table. In the interior are 12 evenly spaced sampling wells, each with nested ports at 5 vertical depths. The saturated zone pore volume (PV) within each cell is variable from 1,000 to 2,500 gallons per cell. For all of the flushing experiments (those with surfactants, cosolvents, and cyclodexdrin), the flushing rate will be approximately one pore volume per day. Prior to and after treatment of each cell, a partitioning tracer test has or will be performed. The mix of tracers will be designed according to the expected volume of NAPL within the cell before and after treatment. Among the tracers, hexanol and dimethylpentanol may be included. The surfactant and cosolvent demonstrations are summarized below enumerated by the site cell number at which each test has or will be performed.

CompoundsTreated: The cells are quite variable with respect to water content, although in general about 6 to 9% residual NAPL exists within the saturated zone pore space of each cell. The NAPL is composed largely of JP4 jet fuel (approx. 90 to 95%), with lesser amounts of chlorinated organic solvents (chloroalkenes and chlorobenzenes) and even some PCBs. A nearby landfill has contributed to the contamination.

Test 1, Operational Unit 1, Hill Air Force Base, Utah

Participants: University of Florida

Demonstration date: 1994-1995

Surfactant/Cosolvent: 70% ethanol, 12% n-pentanol, and 28% water mixture

Treatment Summary: This was the first test performed at Hill AFB and consisted of treatment with a cosolvent mixture. Prior to all testing, the water table in the cell was raised to 5 meters below ground surface to saturate the NAPL smear zone. The first test was an inter-well partitioning tracer test (IWPTT) in which bromide (as a nonreactive tracer) and a mixture of methyl alcohols were pumped through the cell. In the cosolvent flushing test, approximately 40,000 L (about ten pore volumes) of the cosolvent mixture (70% ethanol, 12% n-pentanol, and 28% water) were pumped through the cell over a 15 day period. The intent was to solubilize (not mobilize) the NAPL. A final inter-well partitioning tracer test was performed. In all tests, samples were taken from the 60 internal monitoring wells (12 nested wells at 5 depths) and the three extraction wells. Soil cores were also collected.

Results: The first IWPTT indicated a NAPL content of 7% of the porosity. Results indicated that > 90% of several target contaminants and > 75% of the total NAPL mass was removed. The co-solvent pumping strategies were not optimized based on cost considerations, as post-treatment of the NAPL and co-solvent was not attempted. The primary goal was to conduct this study as a proof-of-concept test, and to extend the database for research and development purposes.

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References:

Annable, M. D.; Rao, P. S. C.; Hatfield, K.; Graham, W. D.; Wood, A. L., Use of Partitioning Tracers for Measuring Residual Napl Distribution in a Contaminated Aquifer: Preliminary Results from a Field-Scale Test, proceedings, 2nd Tracer Workshop, Univ. of Texas, Austin, TX.

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Cell 3 at Operational Unit 1, Hill Air Force Base, Utah

Participants: Clemson University

Demonstration date: Summer, 1996

Surfactant/Cosolvent: Either tert-butanol or isopropanol, mixed with n-hexanol

Treatment Summary: The 3 m x 5 m test cell contains approximately 1,500 gallons of water (i.e., the PV). A partitioning tracer test was performed on the cell with bromide, ethanol, methanol, tert-butanol, methyl-hexanol, and dim-ethyl pentanol as tracers. From this test, the estimated amount of NAPL in the cell is 60 gal. The experimental plan is to pump water, followed by 5,000 to 7,000 gal of alcohol mixture, followed by water. It is anticipated that most of the NAPL will be removed before the total volume of alcohol is pumped. The earlier cosolvent test at Hill AFB performed by The University of Florida group (Test 1, Operational Unit 1) was designed to solubilize the NAPL. The intent in this test is to mobilize the NAPL to basically remove it in a plug. Formulating a cosolvent mixture that will mobilize this specific complex NAPL has required extensive laboratory work.

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Cell 5 at Operational Unit 1, Hill Air Force Base, Utah

Participants: University of Oklahoma

Demonstration date: Summer, 1996

Surfactant/cosolvent: An Aerosol OT/Tween series surfactant mixture with added $CaCl_2$ will be used. Many (if not all) Tween series surfactants have U.S.D.A. food grade additive status.

Treatment Summary: The intent is to mobilize the NAPL with a middle phase microemulsion. Initial partitioning tracer tests have been performed. It is anticipated that 10 PV or less of mobilizing surfactant mixture will be added at a rate of one PV per day, followed by 5 PV of water. During treatment 3,000 to 4,000 samples will be collected from the extraction and multiport sampling wells for chemical and surfactant analysis.

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Cell 6 at Operational Unit 1, Hill Air Force Base, Utah

Participants: University of Oklahoma

Demonstration date: Summer, 1996

Surfactant/cosolvent: An overall 3.6 wt% solution of Dowfax 8390 will be used. This is a solubilizing (micelle forming) diphenyloxide disulfonate surfactant mixture; the same one used at the Traverse City site.

Treatment Summary: The intent is to solubilize the NAPL within surfactant micelles. The specific Dowfax surfactant was chosen largely because of its low sorption potential in the subsurface due to the dual negative charges on each monomer. Ten pore volumes of surfactant will be used followed by 5 pore volumes of water. It is anticipated that this system will be less efficient than the mobilizing system used in Cell 5: Ten pore volumes may not be sufficient to reduce the residual NAPL concentration to below 10% of the original value. An initial partitioning tracer test has been performed, with the surfactant flushing test scheduled for summer, 1996. Similar sampling will occur as in Cell 5.

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Cell 8 at Operational Unit 1, Hill Air Force Base, Utah

Participants: University of Florida, Largely funded by the DOD/AATD at Rice U.

Demonstration date: Summer, 1996

Surfactant/cosolvent: Brij 97 ($C_{18}EO_{20}$) with n-pentanol as a cosurfactant. This formulation makes a Winsor Type I single phase microemulsion.

Treatment Summary: The primary goal is to solubilize NAPL constituents within a single-phase microemulsion (SPME) system. Initial laboratory studies were performed in batch, column, and 2-D tanks using the NAPL and sedimentary material from the site and other materials. Over 70 commercially available formulations were used in lab studies. Pre- and post- treatment partitioning tracer tests will be performed. In the SPME test, it is anticipated that 2 PV of water, 5 to 7 PV of surfactant/cosurfactant, 2 PV of surfactant (alone), and 5 PV of water with be flushed through the cell, in the order listed. The PV is estimated to be about 2,500 gallons. Samples will be taken from the 12 multiport sampling wells and the three extraction wells. The waste mixture (surfactant/cosurfactant/NAPL) will be stored on-site for off-site disposal (probably incineration).

Results: These study will provide much needed information on SPME systems, however, will not provide complete information on costs associated with possible future full-scale applications as this is not the primary intent.

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Monthly Progress Reports are available from the Advanced Applied Technology Demonstration Facility for Environmental Technology, at DOD/AATDF, Rice University, Energy & Environmental Systems Institute, M.S. 316, P.O. Box 1892 (or 6100 S. Main St.), Houston, Texas 77251 (or 77005).

Hill Air Force Base, Utah, OU2, Surfactant with Polymer

Participants: INTERA, Inc., Center for Petroleum and Geosystems Engineering at U. Texas at Austin, and RADIAN International, Austin, TX

Demonstration date: Summer, 1996

Compounds treated: DNAPL, mostly TCE with some PCE and 1,1,1-TCA

Surfactant/cosolvent: Surfactant

Treatment Summary: Funding for this project is from the U.S. Air Force Center for Environmental Excellence (AFCEE) and INTERA, Inc. The University of Texas performed the design of the surfactant flood and a partitioning tracer

test, and RADIAN International performed the treatment engineering. INTERA, Inc. was the principle contractor and performed all field injection-extraction operations and applied for all permits. The specific site was a shallow sand and gravel aquifer at OU2 on Hill AFB. Three in-line injection wells and 3 in-line extraction wells were installed with a monitoring well midway between the injectors and extractors, and a fourth injection well located 10 ft behind the line of 3 injection wells. The distance between the lines of injection and extraction wells was 20 ft.

The project has two phases. In Phase I, which took place in April and May of 1996, a pilot test was performed: (1) to demonstrate that hydraulic control of injected fluids was possible, (2) to quantify the volume of DNAPL by conducting a partitioning tracer test between the injector and extractor wells, (3) to show that surfactant could be injected and extracted at the designed rates, (4) to test a steam stripper on the effluent stream, and (5) to identify any potential problems and gain some experience with the sampling and chemical analysis methods.

The second phase was scheduled for August, 1996, and lasted 30 days. Approval from the U.S. EPA and Utah Dept. of Environmental Quality was expected in July. The goal was to attempt to remove as much of the DNAPL with a micellar flood as possible. Initially polymer was going to be used also. A partitioning tracer test was to be performed subsequent to the surfactant flood to test for residual organic phase.

Results:
The partitioning tracer test indicated that approximately 800 gallons of DNAPL is present in the test section of the aquifer. During the solubilization test, with an 8% surfactant injection over 0.6 days (0.6 pore volumes), the TCE concentration in the central monitoring well rose from approximately 600 mg / L prior to the injection to 40,000 mg / L after. The maximum DNAPL solubilization capacity was calculated to be 61,000 mg / L for this surfactant injection concentration. The concentrations in the 3 extraction wells were lower, likely due to dilution caused by streamtube convergence on this wells. Problems with surfactant foaming in the steam stripper occurred during this phase, which the investigators attempted to remedy in Phase II.

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Hill Air Force Base, Utah, OU2, Surfactant/Foam Flood

Participants:	Rice University, funded by DOD/AATDF at Rice University
Demonstration date:	planned for 1997
Surfactant/cosolvent:	a sulfosuccinate anionic surfactant, followed by air, followed by more surfactant
Treatment Summary:	This test will be conducted without a physical barrier system in place. First, surfactant will be injected, and will fill the high hydraulic conductivity (permeable) zones, sweeping out residual contaminant. Second, air will follow the surfactant creating a foam in the high permeability zone(s). Third, the next slug of surfactant is added, and should enter the formerly less permeable zone, sweeping out residual contaminant. The (surface) area to be treated is approximately 6 m by 6 m with injection wells placed parallel and across from extraction wells.

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3.2   LABORATORY STUDIES

Many investigators are involved in bench and pilot scale laboratory studies. The results of these efforts are too extensive to completely review here. The Physical/Chemical Description Section (Section 2.1) discuss results from some of these efforts. In addition, many researchers are working to improve existing computational tools (i.e., models) for predicting transport in porous media with emphasis on surfactant mobilization or solubilization of contaminants and cosolvent transport. Many citations provided in the General Reference Section (Section 8) are of these laboratory and modeling studies.

4.0 TECHNOLOGY APPLICABILITY

4.1 TECHNOLOGY DEFINITION

A quick review of the information presented in Section 3 indicates that under the all encompassing heading of *in situ* remediation with surfactants and/or cosolvents numerous variations on this theme exist. Indeed, in the current state of the technology, the number of strategies applied are *more* numerous than the number of sites where demonstrations have or currently are taking place. Thousands of surfactants are commercially available, yet researchers have had less than 10 years of experience in working with these materials in the laboratory and field on sorbed or nonaqueous phase liquid contaminants. On the other hand, there is a tremendous wealth of very closely related information available from petroleum engineering, food science, and other disciplines that can and has been utilized to accelerate technology development. Still, the motivation in these other disciplines and the systems are totally different.

In the end, *in situ* remediation with surfactants and/or cosolvents likely will evolve into a well defined *group* of standard technologies all with surfactants and cosolvents as the common denominator. However, currently there is no standard technology in the bunch (i.e., one that has been demonstrated numerous times and is widely regarded as an acceptable alternative technology), and no formula for what will work or what will not work. Due to the wide diversity of subsurface contaminants and site characteristics, optimal field-scale applications always will be very site specific. The design and operation of exemplary case studies have been accomplished by interdisciplinary teams of hydrogeologists, environmental engineers, geochemists, surfactant chemists, petroleum engineers and/or chemical engineers, with necessary input from other fields as well.

4.2 SITE AND CONTAMINANT CHARACTERISTICS

The most promising application appears to be removal of NAPL material from the source zone and concentrated plume of NAPL spills or sites. In particular, treatment of DNAPL spills may prove effective, where the residual portion of the DNAPL is trapped within a finite volume in pores due to capillary forces. Application of the technology to a massive diluted ground-water plume has not been attempted, and is most likely cost prohibitive because of the capital cost of the surfactant and/ or of the cost of treating the extremely large volumes of contaminant-dilute water for surfactant recovery. Ultrafiltration, countercurrent solvent extraction, photochemical treatment, incineration, biotreatment, carbon adsorption, floatation, foam fractionation, air stripping, and vacuum steam stripping have all been suggested for or performed at small scale for water/NAPL treatment. Sites where surfactant/cosolvent technologies have been or will be (in the near future) demonstrated have been highly characterized hydraulically. All have been in unconfined zones, generally with moderate to high hydraulic conductivity, with clay aquitards at reasonably shallow depths (5 to 15 m), most with vertical containment barriers in the form of engineered hydraulic gradients or constructed sheetpile walls. In the case of Waterloo barrier cells, the grouted joints allow for saturation and flushing of the contaminated vadose zone. Although not tested or demonstrated at the field scale, the use of surfactant/cosolvent technologies in serial combination with other *in situ* technologies may show promise, such as surfactant/cosolvent flooding to removal the majority of source contamination followed by bioremediation of the remaining residual contaminants, surfactants, and/ or cosolvents. Although remediation of low concentrations of sorbed compounds with surfactant

flooding technically is feasible, it may prove to be cost prohibitive except for some specific cases where ecological risks are high for other treatment or no treatment alternatives.

4.3   ALTERNATIVETECHNOLOGIES

Alternative technologies (to surfactant/cosolvent flushing) may be broadly defined to include any technology that treats or contains contaminants in the subsurface. As with surfactant/cosolvent flushing, the efficacy of these alternatives is very dependent on the specific contaminant(s), contaminant concentration(s) and mass(es), and site characteristics. For example, several standard or proven technologies have been proven to work under specific conditions where surfactants would never be considered for use. Yet these same technologies would fail miserably at sites where surfactant or cosolvent flushing would prove quite successful. Because of these differences, some of these alternatives likely may prove to be useful in combination with surfactant/cosolvent treatment.

Standard technologies that have been applied include:

- pump-and-treat (which may hydraulically contain the area)
- physical barriers or cut-off walls
- excavation with incineration, solidification, disposal, or other final treatment process
- soil vapor phase extraction
- air sparging
- in-situ bioremediation

Innovative technologies include:

- steam extraction
- addition of electron acceptors, and/or microorganisms
- chemical sorption barriers (these can be cationic surfactants)
- and treatment walls or trenches

Most notable among the treatment walls is use of zero valent iron (iron filing or shavings) which can reduce (dechlorinate) chlorinated organic compounds. The products of the reaction are ferrous and ferric iron and hydrocarbons which are less toxic and more biodegradable. Use of iron is very safe and iron is relatively inexpensive; however, this technology may be suitable for only specific contaminants, and even then, complete dechlorination may not occur. Additionally, long term maintenance may be an issue.

5.0 COST

Few, if any, comprehensive comparative cost analyses have been performed on existing or hypo-thetical surfactant/cosolvent technology applications. In a chapter by Krebs-Yuill *et al.* (1995), eco-nomic considerations have been tabulated, with estimated costs based on remediation of sites contaminated with PCE, TCE, and 1,2-DCA in DNAPL form, utilizing a solubilizing micellar surfac-tant at different surfactant prices per mass. A conclusion reached in this study was that surfactant recycling or recovery would be necessary in order for large-scale solubilizing remediation efforts to be cost effective, due to surfactant costs. No consideration was given to mobilizing systems or any cosolvent systems. No consideration was given to costs associated with: field-scale equilibrium partitioning tracer tests or other specific site assessment operations, site characterization, model-ing, chemical analysis, and initial laboratory batch and column studies. Indeed, these costs may be only a fraction of the total cost for large flushing operations, however, they have been the major cost investment in experimental and demonstration tests to date. Given the complexities in designing and fully optimizing such systems, design costs could remain quite high for the near future. Be-cause the surfactant is one of the largest operating expenses, particularly if it is not recovered, estimates of total cost are somewhat proportional to the cost of total flushing agent(s), which may be proportional to the total volume of subsurface NAPL removed. Even in cases where the surfac-tant/cosolvent is recovered, costs will be proportional to the amount of surfactant used due to costs associated with surfactant recovery unit operations. Current prices of typical commercial large-volume surfactants are in the range of $1 to $2 / lb. If effective and practical (i.e., nontoxic) mobiliz-ing flushing agent formulations are developed, the volume and associated cost of these agents may be of lesser concern as the ratio of NAPL removed per volume of flushing agent applied may be reduced substantially.

Below is a summary list of basic (non-overhead type) capital equipment and design and operational cost requirements. The costs associated with each category are highly dependent on the specific items used within each category (i.e., well type, surfactant type, specific unit operations employed). Also not included on this list, but an integral consideration in design and cost effectiveness is time of treatment. Operational costs are nearly proportional to time. Because the time frame required for pump-and-treat may be shortened considerably through the addition of chemical flushing agents, an overall minimum cost always exists which can be evaluating by comparing the trade-offs be-tween total operational costs (over time) and the cost of flushing agent employed (to reduce this time).

Design Costs

- Laboratory batch and column studies (feasibility)
- Equilibrium partitioning tracer tests or other site assessment tests
- Site characterization, specifically for surfactant/cosolvent flushing

Capital Costs

- Injection/recovery wells and pumps
- Barrier construction, if any
- Contaminant/surfactant concentration/recovery unit operations
- Contaminant destruction unit operations

Operating Costs

- Surfactant/cosolvent
- Well operation
- Operating costs of concentration/recovery/destruction unit operations
- Electricity/power requirements
- Maintenance
- Labor

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6.0 REGULATORY/POLICY REQUIREMENTS AND ISSUES

6.1 FEDERAL REGULATIONS

Document EPA-542-R-96-001 (1996) issued by the U.S. EPA Technology Innovation Office states:

"Injection wells are regulated by the Underground Injection Control (UIC) program under the Federal Safe Drinking Water Act. Under the UIC program, injection of any fluid into a well is prohibited, except as authorized by permit or rule. State UIC programs may be delegated complete or partial enforcement responsibility (or primacy) by EPA. Twenty-five State UIC programs have been delegated complete primacy, while ten hold primacy over some portion of the State UIC program. If a State does not seek primacy, or its program is not approved, EPA enforces the Federal UIC program for that State. Fifteen State UIC programs are administered by EPA Regional Offices."

"Injection wells incidental to aquifer remediation and experimental technologies are distinguished from hazardous waste injection wells and are designated as Class V under the UIC program. Class V wells covered by the Federal UIC program are authorized by rule and do not require a separate UIC permit. A Class V well regulated by a State UIC program may require a permit. While permit requirements are not a direct barrier to *in situ* ground-water remediation, States that require UIC permits are noted in the summary table." (see State regulations below)

"The purpose of the UIC program is to protect underground sources of drinking water (USDW) by prohibiting injections that may affect water quality in USDWs. Contaminated aquifers at Superfund sites may not serve as a USDW. For this reason, UIC requirements may not apply to wells at CERCLA sites."

6.2 STATE REGULATIONS

No state has a direct regulatory prohibition on injection technologies for treating contaminated aquifers. A few states have policies that discourage use of injection technologies, having rejected most or all proposals on technical or policy grounds. About two-thirds of the states have allowed injection of some type remediation agent, most frequently nutrient injections to enhance bioremediation. Eleven states have allowed surfactant injections with most occurring at CERCLA sites. Some states require closed systems or some evidence (i.e., a comprehensive monitoring program) that all injectant will be removed.

States that require UIC permits include: Colorado, Florida, Georgia, Hawaii, Maine, Mississippi, Nevada, Oklahoma, Oregon, South Carolina, Texas, Utah, Vermont, Washington, West Virginia, and Wyoming. Many other states have little or no experience and *may* require an UIC or state permit. Others *do* require a state permit.

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7.0 LESSONS LEARNED

7.1 TECHNOLOGY LIMITATIONS/CONSTRAINTS

As stated in the Technology Summary Section, it has been less than 6 years since completion of the first field demonstration of subsurface remediation with surfactants/cosolvent flushing. Hence, it should come as no shock that the most critical limitations to widespread acceptance of the technology appears to be the general lack of information regarding the technology and the lack of personnel with expertise in applying the technology in the field. It is truly an interdisciplinary and complex technology, requiring site and contaminant specific design, optimization, and control. Because the technology is new and its application is so site specific, there are no standard design criteria or design models available. For example, the act of selecting a surfactant solution is not and should not be viewed as a *simple* act, but a process requiring laboratory batch and column studies and field trials. Currently, there are no formulae or answers to the basic questions: What surfactant, cosolvent or mixture works best for a given site? What technologies should be used to recover/separate the surfactant or contaminants? How much surfactant will be lost by sorption to the subsurface particles? What can be done about subsurface heterogeneity?

It is quite likely that the application of a surfactant-based technology could be made cost effective at many existing contaminated sites, particularly if it is a flushing technology where only the most highly contaminated zone is treated. A considerable amount of laboratory and modeling work is required before such determinations can be made, however, which requires financial investment prior to possible application of the technology.

As stated previously in Section 4, *in situ* remediation with surfactants and/or cosolvents likely will evolve into a well defined *group* of standard technologies with surfactants and cosolvents as the common denominator. This group may or may not include:

- flushing with micellar surfactants (solubilization)
- flushing with surfactants to emulsify NAPLs (mobilization)
- flushing with cosolvents to mobilize NAPLs
- flushing with cosolvents to solubilize NAPLs
- injection of cationic surfactants to attenuate contaminant migration
- flushing with surfactant-modified clays
- flushing with colloidal gas aphrons
- in situ biosurfactant production
- formation of surfactant foam barriers to control hydraulic conductivity
- excavation followed by soil washing with surfactants

Not all of these technologies are flushing technologies, and the list suggests the diversity among processes through which surfactants potentially may be employed to facilitate or enhance subsurface soil remediation.

7.2   SELECTION CONSIDERATIONS

Technology selection must be based on process specific informational requirements and informational requirements that are shared with other alternative technologies. Shared informational requirements are those site characteristics which must be collected independent of the technology selected. Site characteristics include formation hydrogeology and contaminant distribution, phase behavior (of contaminants as NAPLs or sorbed compounds), and chemical composition. These characteristics can be known only by core analysis and through studies with observation wells. This site information is required for modeling existing conditions, and is important in later modeling of treatment scenarios. These scenarios may include alternate treatment technologies and various surfactant/cosolvent technologies or processes.

Because injection of surfactants in the subsurface may involve additional ecological risks beyond those already existing at each site, it is imperative that:

1)   Careful laboratory phase distribution and column flood tests be performed.

2)   Design should be governed by accurate hydrodynamic modeling and comprehensive process considerations (e.g., overall performance and compatibility of the surfactant: to mobilize or solubilize, be recovered from the subsurface, and be recovered in recycle operations).

3)   Some form of assessment, such as an IWPPT, should be performed to estimate contaminant saturation and distribution, before, during, and after the project.

4)   A pilot-scale feasibility study should be performed prior to full scale implementation.

5)   Controls or measures should be put in place to assess performance in relation to what was expected at each stage from column, pilot, to full scale demonstrations.

Besides reducing ecological risks, these steps should identify critical data needs, minimize the risk of process failure, and in the long term save time and other resources. This list of specific informational requirements is short, only because within each lies numerous specific requirements which must be met before proceeding fully to the next level of implementation.

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