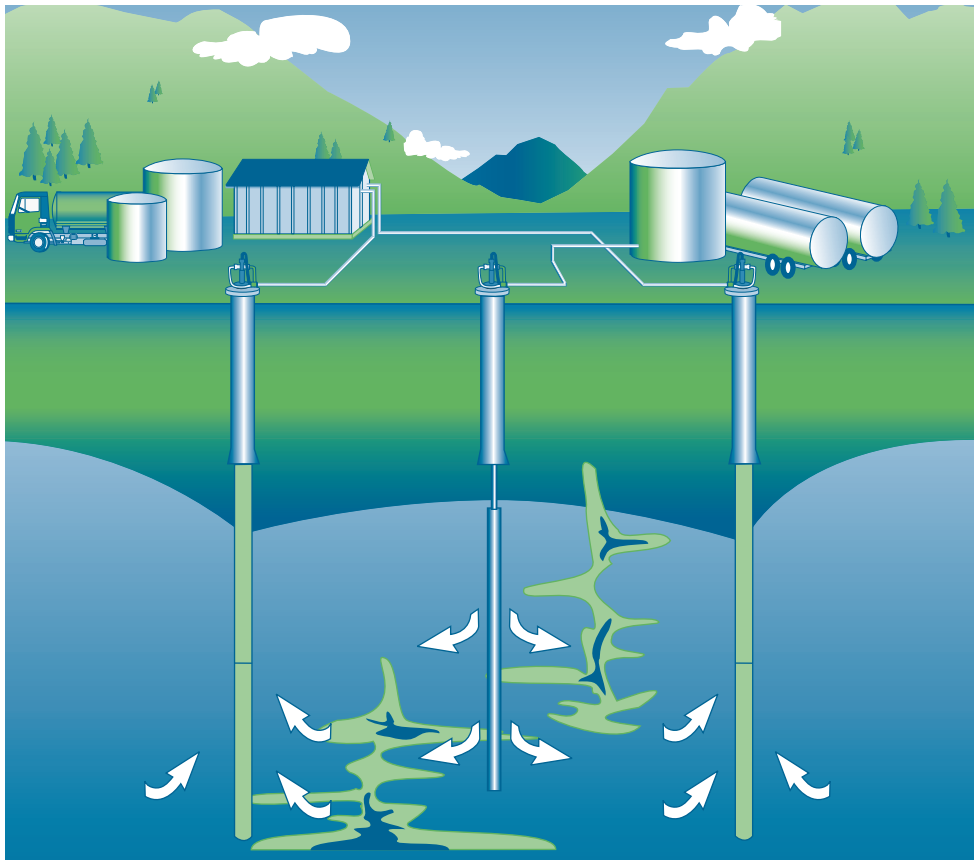




Technical/Regulatory Guidelines

Technical and Regulatory Guidance for Surfactant/Cosolvent Flushing of DNAPL Source Zones



April 2003

Prepared by
Interstate Technology & Regulatory Council
Dense Nonaqueous Phase Liquids Team

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EXECUTIVE SUMMARY

This document is intended to serve as a technical and regulatory guide for stakeholders, regulators, technology decision makers, and others involved in selecting and implementing surfactant/cosolvent flushing of dense nonaqueous-phase liquids (DNAPLs) as a remedial action.

Surfactant/cosolvent flushing is a DNAPL-removal technology involving the injection and subsequent extraction of chemicals to solubilize and/or mobilize DNAPLs. The chemicals are injected into a system of wells positioned to sweep the DNAPL source zone within the aquifer. The chemical flood and the solubilized or mobilized DNAPL is removed through extraction wells, and the produced liquids are then either disposed (usually off-site treatment) or treated on site to remove contaminants, and then reinjected to the subsurface to remove additional DNAPL mass.

Surfactant/cosolvent flushing is a mature technology in the petroleum-engineering field of Enhanced Oil Recovery (EOR), supported by decades of research and field tests. Environmental applications are relatively new but have increased in recent years. Field performance has been quantitatively assessed using several methods for a large number of sites. The technology has been shown to be effective for several DNAPL types, including spent degreasing solvents (TCE and TCA), dry cleaning solvents (PCE), heavy fuel oils, and coal tar/creosote. Laboratory work has also demonstrated applicability to PCB-containing mineral oils.

The primary appeal of surfactant/cosolvent flushing is its potential to quickly remove a large fraction of the total DNAPL mass as compared to other technologies. As an in-situ technology, it eliminates the need to excavate, handle, and transport contaminated media. It is applicable as a stand-alone technology or as a component in a “treatment train” consisting of several remedial technologies, depending on site-specific cleanup objectives.

Designing and implementing a DNAPL source-removal operation is an intrinsically complex endeavor. Surfactant/cosolvent flushing activities must be designed in such a way that uncontrolled vertical and horizontal migration of contamination is avoided. A comprehensive understanding of the subsurface environment, multiphase fluid flow, and the physical processes being employed is required to prevent remediation failure and avoid contaminating previously uncontaminated portions of the aquifer.

Technical challenges to the successful use of surfactant/cosolvent flushing include locating and delineating the DNAPL source zone and obtaining an accurate estimate of the initial DNAPL mass and its spatial distribution. Additional requirements include characterizing the hydraulic properties of the aquifer, delivering and distributing the injected chemicals to the targeted zone, and designing the optimum chemical formulation for a given DNAPL composition and soil type. The implementability of surfactant/cosolvent flushing will depend on site-specific geologic conditions and on the type of DNAPL present at the site.

Historically, the primary factors that have limited field demonstrations from proceeding to full-scale applications have been concerns regarding costs of disposal of the effluent, regulatory permitting concerns in allowing underground injection of tracers or flushing agents, and the

overall impact of unremoved DNAPL. Also, there is a general lack of information regarding the technology and a lack of personnel with expertise in applying the technology. It is truly an interdisciplinary and complex technology, requiring expertise in multiphase fluid flow, site and contaminant-specific design, optimization, and control. Selection of a surfactant/cosolvent solution is a process requiring laboratory batch and column studies and field trials. A considerable amount of laboratory work is required before implementation can commence.

To facilitate regulatory and stakeholder acceptance, it is important to include regulators and stakeholders in the decision process that leads to the selection of surfactant/cosolvent flushing as a remedy and to involve them in the process of designing and implementing the flood. There are differences in regulatory requirements based on whether the site is regulated under RCRA or CERCLA, and whether it is a federal facility, a Superfund, state, or private-party lead. While permit requirements are not a direct barrier to surfactant/cosolvent flushing, it is important that the technology user be aware of state-specific permits and/or requirements associated with the Underground Injection Control (UIC) program.

Acceptance of this technology by the regulatory community as a viable remedial alternative continues to grow as pilot and field-scale applications are completed.

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TECHNICAL AND REGULATORY GUIDANCE FOR SURFACTANT/COSOLVENT FLUSHING OF DNAPL SOURCE ZONES

1.0 INTRODUCTION

This document is intended to serve as a technical and regulatory guide for stakeholders, regulators, and technology decision makers and users involved in selecting and implementing surfactant/cosolvent flushing of dense nonaqueous-phase liquids (DNAPLs) as a remedial action. Surfactant/cosolvent flushing of DNAPLs is an emerging environmental remediation technology with limited cost and performance information. While the technology will undoubtedly be enhanced by future study, recent successes are encouraging and warrant the use of the technique in appropriate settings.

The terms surfactant/cosolvent “flushing” or “flooding” are synonymous and are interchanged throughout the document.

1.1 Scope of Document

This guidance document is one of several generated by the Interstate Technology & Regulatory Council (ITRC) related to the identification, characterization, and remediation of DNAPLs. The document describes the technology and discusses the major factors that need to be addressed to select and evaluate design and implementation work plans for surfactant and cosolvent flushing of DNAPLs. There are other documents in existence that contain a greater degree of technical detail that can be used as design manuals (NAVFAC, 2002a). For the convenience of the reader, a list of acronyms used in this document has been compiled in Appendix A. In addition, a glossary of key technical terms is included in Appendix B for reference purposes.

These technologies are continuing to evolve and mature, even as this document is being written. This document focuses on the regulatory, technical, and economic aspects of implementing these technologies for the purposes of DNAPL remediation.

1.2 Policy Implications

This document does not present a policy position regarding whether or not a DNAPL source zone should be remediated at a particular site or facility. Aside from state-specific regulatory requirements or guidance, each site has its own unique characteristics impacting whether or not DNAPL remediation should be undertaken. The conditions affecting the feasibility and potential success of DNAPL remediation are typically site-specific and multifaceted, including hydrogeologic conditions, political involvement at the facility, state or local regulations, public interaction and perception, and economic factors. The issue of feasibility and arguments for and against remediating DNAPL source areas is the focus of a recent document entitled *DNAPL Source Reduction: Facing the Challenge* (ITRC, 2002).

DNAPL sites pose special cleanup challenges because this class of contaminants can sink to great depths in the subsurface, continue to release dissolved contaminants to the surrounding groundwater for very long time periods, and can be difficult to locate. Due to the complex nature of DNAPL contamination, a phased approach to characterization and response actions is especially important for sites where DNAPLs are confirmed or suspected (USEPA, 1992, 1996a).

If DNAPLs are confirmed or suspected, a site investigation should be designed to delineate the extent of aqueous contaminant plumes and the extent of DNAPL source zones (also known as “sources”). The reason for delineating these areas of the site is that remedial goals should generally be different for the DNAPL source zones compared to the aqueous contaminant plume. While appropriate remedial goals for the aqueous contaminant plume are the prevention of further migration (plume containment) or restoration of the maximum areal extent of the aquifer to cleanup levels appropriate for its beneficial use (aquifer restoration), the DNAPL source-zone treatment goals should be focused on DNAPL mass removal and changing the source-zone architecture (the distribution of DNAPL relative to preferential groundwater flow paths through the source zone). Long-term goals involving DNAPL removal may require a phased treatment train approach to meet these stringent goals. Two remedial goals to consider for the DNAPL source zone are control of further migration of contaminants from the source zone to the surrounding groundwater to the extent practicable, and contaminant concentration reduction in the soil and/or groundwater to an established level protective of human health and the environment. At many sites, removing DNAPL mass while managing the dissolved-phase groundwater plume down gradient of the source can potentially shorten the duration for the ultimate cleanup of the site and reduce operation and maintenance costs (USEPA, 1996a).

2.0 TECHNOLOGY DESCRIPTION AND STATUS

2.1 Technology Description

A surfactant/cosolvent flushing system consists of a network of injection and extraction wells designed to hydraulically sweep the targeted volume of aquifer that is contaminated with DNAPL (see Figure 2-1). A surfactant/cosolvent fluid, having properties appropriate for the DNAPL and geosystem under consideration, is injected into the vadose zone and/or saturated zone and transported through the DNAPL zone. The injected solution interacts with the contaminants by lowering the interfacial tension between DNAPLs in the aqueous phase (mobilization), enhancing DNAPL solubility (solubilization), or altering other physical properties, as it is flushed through the zone of contamination. In situations where the DNAPL is the wetting phase in the aquifer (i.e., in direct contact with the media), the surfactant/cosolvent will reduce the interfacial tension between the DNAPL and the rock/soil matrix and make the system water-wet (the fluid that preferentially wets the mineral grain surface in a multiphase system is the wetting fluid). The *elutriate* (a mixture of the injected fluid and contaminant) and the groundwater are then captured through extraction wells. Once brought to the surface, the groundwater and elutriate are treated and either reinjected into the geosystem or discharged. Recovered DNAPL and other waste residuals are treated and/or disposed.

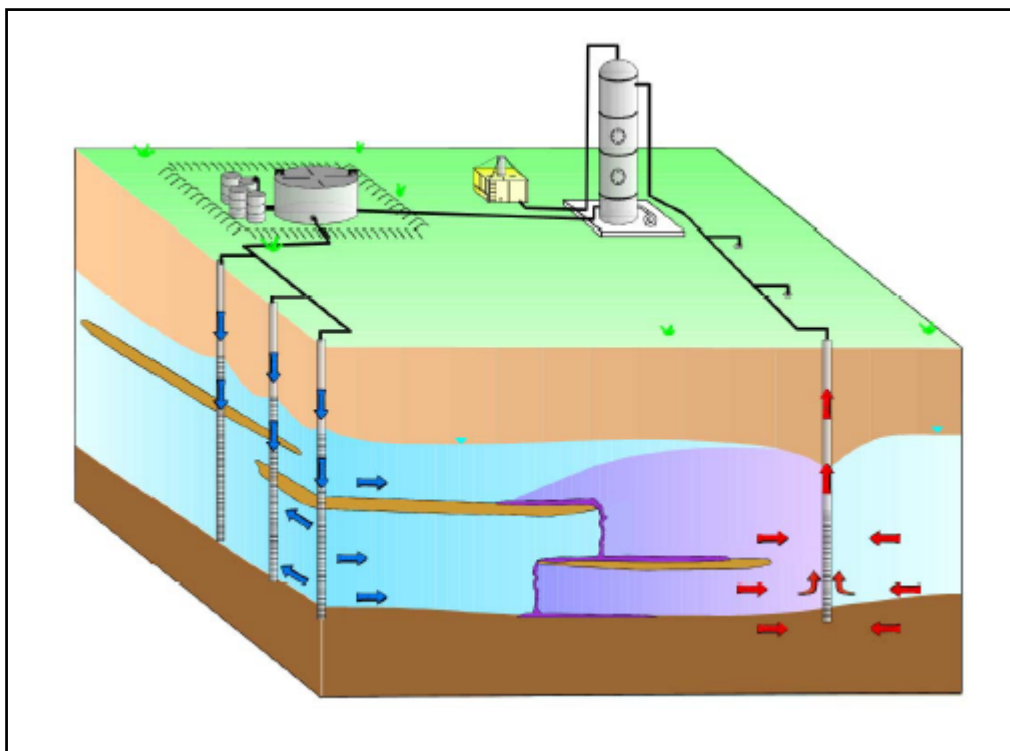


Figure 2-1. Conceptual Design of a Surfactant/Cosolvent Flushing System
(NAVFAC, 2002a)

The injected solution consists of one or more reagents, which are soluble or miscible in the aqueous phase. The use of specific reagents will vary depending upon contaminant characteristics and site conditions. The physical and/or chemical properties of the contaminant (e.g., hydrophobicity, density, viscosity, and interfacial tension with water or solid matrix) are the primary factors that dictate the choice of reagent(s). Site conditions (e.g., heterogeneity of the soil, hydraulic properties of the system, groundwater geochemistry, or soil mineralogy) also affect the choice of reagents as well as their properties in the injected solution and the means by which the solution is flushed through the target DNAPL zone. The two classes of reagents addressed in this document are the two most common: cosolvent and surfactant.

Surfactants (surface active agents) are chemical compounds whose molecular structure enables them to alter the properties of organic-water interfaces. The surfactant molecule is typically composed of a strongly hydrophilic (water-loving) head and a hydrophobic (water-hating) tail. In a DNAPL-contaminated aquifer, this property of surfactants can mobilize residual DNAPL, dramatically increasing the solubility and mass removal rate of organic molecules from the DNAPL into the mobile flushing solution. Thus, there are two primary ways in which surfactants can be utilized for DNAPL removal: solubilizing surfactant flooding and mobilizing surfactant

flooding. Regardless of the methodology applied at the site, the potential for vertical and uncontrolled horizontal migration of contaminants must be considered and measures taken to prevent such. This is especially true for mobilization, which should not be implemented for DNAPL remediation unless it can be demonstrated that the potential for vertical migration can be mitigated.

The primary purpose of a *solubilizing surfactant flood* is to increase the apparent aqueous solubility of the contaminant. Upon contact with the DNAPL, the surfactants bring about a two to three order of magnitude or greater increase in the total aqueous solubility of the DNAPL components. The second type of flood is a *mobilizing surfactant flood*. In a mobilizing surfactant flood, the primary objective is to lower the DNAPL-water interfacial tension to the point that physical mobilization of the DNAPL takes place. The “oil bank” is then displaced by continuing flushing and is withdrawn by the extraction wells. The degree of solubilization versus mobilization occurring in a surfactant flood can be controlled through appropriate surfactant selection and the use of other chemicals such as a cosolvent, electrolyte, and polymer in a formulation that is determined based on bench-scale testing of surfactant phase behavior. In both solubilizing and mobilizing surfactant floods, surfactant flooding is followed by water flooding to remove injected chemicals and solubilized or mobilized DNAPL contaminants.

Cosolvents (most commonly alcohols such as ethanol, methanol, or isopropanol) are similar to surfactants in that they alter the properties of solution interfaces and are often combined with surfactants to improve flood performance. While enhanced solubilization of DNAPLs using surfactants (one or more) is the result of *micellar solubilization*, addition of cosolvents produces “true” solutions (in a thermodynamic sense). Surfactants and small amounts of cosolvents are used to produce *stable microemulsions* and *macroemulsions*; in the latter cases, a small amount of alcohol is used as a *cosurfactant*, not a cosolvent, to stabilize the microemulsion. Cosolvent flushing can also be used for either enhanced solubilization, or microemulsification, or mobilization, although most field tests have involved only the first type of application. At least one field test examined a combination of mobilization and solubilization for LNAPL source-zone remediation (Falta et al., 1999). Because of their miscibility, alcohols can be effective in lowering the interfacial tension between water and the contaminant and/or effectively increasing its aqueous solubility. This is due to the tendency of some alcohols to partition significantly into the DNAPL phase; therefore, the density (and viscosity) of the DNAPL can be manipulated in situ through appropriate alcohol selection (Lunn and Kueper, 1999).

Surfactant/cosolvent flushing approaches fall into two categories: surfactant-enhanced aquifer, or subsurface remediation (SEAR or SESR), and cosolvent flushing. The significant differences between these processes are the mechanisms of extraction provided by the solutions that are employed. SEAR uses specialized surfactant and salt solutions to solubilize or mobilize the contaminant and can employ a combination of specialized surfactants and cosolvents, primarily alcohols. Cosolvent flushing utilizes a mixture of solvents to solubilize or mobilize the contaminant. Each process requires a unique effluent treatment system customized to the composition of the waste streams. In addition, other factors such as hydraulic control, fluid viscosity, and fluid density must be considered and incorporated into any design.

2.2 Technology Status

Surfactant/cosolvent flushing is a mature technology in the petroleum-engineering field of Enhanced Oil Recovery (EOR), supported by decades of research and field tests. Environmental applications have become more numerous in recent years (see Table 1 in Londergan et al., 2001). Field performance has been quantitatively assessed using several methods for a large number of those sites. The technology has been shown to be effective for several DNAPL types, including spent degreasing solvents (TCE and TCA), dry cleaning solvents (PCE), heavy fuel oils and coal tar/creosote. Laboratory work has also demonstrated applicability for PCB-containing mineral oils.

Both surfactant and cosolvent flushing have been applied at full scale in the field with pre- and post-flood partitioning interwell tracer tests (PITTs), closely spaced soil sampling, and volumetric DNAPL-recovery measurements to provide performance assessment. The state of Florida undertook a cosolvent flood pilot test at the Sages Dry Cleaner Site in Jacksonville, Florida. Over the course of three days, they injected over 8,900 gallons of a 95% ethanol/5% water solution and recovered approximately 10 gallons of PCE (Jawitz et al., 2000). The hydraulic conductivity of the sands containing the DNAPL zone at Jacksonville was measured to be between 3 and 7×10^{-3} cm/sec.

The U.S. Navy conducted a surfactant flood demonstration in similar Atlantic Coastal Plain sediments in North Carolina at Marine Corp Base Camp Lejeune, where the average hydraulic conductivity was an order of magnitude or more lower than at the Jacksonville dry cleaner site (Holzmer et al., 2000). They reported a high recovery of PCE DNAPL by surfactant flooding in aquifer materials, with a hydraulic conductivity of 0.5×10^{-3} cm/sec but very little in the lower, less permeable silts, which had a hydraulic conductivity of 1×10^{-4} cm/sec. A total of 76 gallons of PCE was recovered from a swept pore volume of approximately 6,000 gallons.

Working in similar sedimentary materials in San Francisco Bay in 1999, the U.S. Navy also removed 320 kg of TCA and TCE from fill at the Alameda Naval Air Station (NAS) over a 24-day period during a surfactant flood demonstration. The hydraulic conductivity at the Alameda site is between 1.7×10^{-3} cm/sec to 2.6×10^{-4} cm/sec.

At the Spartan Chemical Company Superfund site in Wyoming, Michigan, a surfactant flood pilot test was conducted during 3 days. The hydraulic conductivity at the Spartan site was between 1.1×10^{-2} cm/sec to 2.1×10^{-2} cm/sec. A total of 93.6 lbs of TCE, methyl ethyl ketone (MEK), methylene chloride, acetone and toluene was recovered.

A large-scale surfactant flood and two large-scale surfactant/foam floods were completed at Hill Air Force Base (AFB) Operable Unit 2 (OU2) with a combined swept pore volume of approximately 120,000 gallons that recovered over 1750 gallons of TCE-rich DNAPL from a large source zone. In contrast to the Atlantic Coastal Plain sediments at Camp Lejeune and the sediments at Alameda NAS, these aquifer materials are very heterogeneous and permeable, with measured hydraulic conductivities of 0.001 to 0.01 cm/sec.

Additional information on the above-mentioned cases can be found in Appendix D.

2.3 Applicability

Chemical flooding is primarily used to target the removal of DNAPLs and is not well suited for the remediation of dissolved, sorbed, or volatilized plumes. However, surfactant/cosolvent flooding may be used in conjunction with other technologies such as bioremediation or chemical oxidation to bring a contaminated site to closure. Advantages of surfactant/cosolvent flushing include the following:

- It can rapidly remove a large fraction of the total DNAPL mass trapped in the subsurface.
- It is an in-situ technology with a relatively small surface footprint that can access obstructed source zones (e.g., under buildings).
- As an in-situ technology, it eliminates the need to excavate, handle, and transport large quantities of contaminated soil/sediment.
- It enhances conventional pump and treat by removing contaminant mass, thus speeding up site remediation and closure.
- It is applicable to a wide range of contaminants, including spent degreasing solvents (TCE and TCA), dry cleaning solvents (PCE), and heavy fuel oils. Laboratory work has also demonstrated applicability for coal tar/creosote and PCB-containing mineral oils.
- It is applicable as a stand-alone technology or as an element in a more complex alternative or “treatment train” depending on site-specific remediation goals.

In considering the applicability of surfactant/cosolvent flushing, two key aspects of a site must be considered: the hydrogeologic setting and the characterization of the contaminant(s). Porous media sand and/or gravel settings are preferred to fractured rock, fractured clay, or low-permeability settings. This reflects the need to cycle fluids through a target zone in a reasonable period of time. The greater applicability of surfactant/cosolvent flushing in sands, silts, and gravels is supported by the generally poor results that have been achieved in silty clays and fractured rock. The hydrogeologic setting must be carefully taken into account during the design phase such that the application of surfactants or cosolvents into the subsurface does not create unwanted migration of contaminants. Table 2-1 outlines the general relative applicability of surfactant/cosolvent flushing for different contaminant phases in different geologic environments.

Table 2-1: Relative Applicability of Surfactant/Cosolvent Flushing

Hydrogeology	Contaminant Type or Phase		
	DNAPL Dissolved	Sorbed	Aqueous
Less Heterogeneous			
High Permeability (sand and gravel, $>10^{-3}$ cm/sec)	1	2	N/A
Moderate Permeability (silts, silty sands and clayey sands, 10^{-3} to 10^{-4} cm/sec)	2	3	N/A
Low Permeability (silty clays and clay, $<10^{-5}$ cm/sec)	4	4	N/A
Heterogeneous			
Moderate Contrasts	1	2	N/A
Large Contrasts	3	4	N/A
Fractured Rock	4	N/A	N/A

Note: 1 is the most favorable and 5 the least favorable N/A = Not Applicable

2.4 Limitations

Disadvantages of surfactant/cosolvent flushing include the following:

- Surfactant/cosolvent flushing technology is truly an interdisciplinary and complex technology, requiring site-specific and contaminant-specific design, optimization, and control.
- It's applicable to DNAPLs, not to dissolved-phase plumes.
- Selection of a surfactant/cosolvent solution is not a simple task, but a process requiring laboratory batch and column studies, and in some cases, field trials.
- A considerable amount of laboratory and modeling work is required to design a surfactant flood, which requires a financial investment prior to potential application of the technology.
- Long-term post-treatment data is currently not available to evaluate rebound effects and the ability of the technology to help attain MCLs.
- Regulatory requirements may prevent chemical injection in some states.
- Control of fluids within the subsurface must be addressed.
- This technology is probably not effective in clays or fractured rock.
- A good understanding of the location of the DNAPL is required.

- Uncontrolled mobilization of DNAPL or elutriate can result in migration of contaminants into previously uncontaminated aquifer regions.
- There is a risk that DNAPL could be mobilized and not recovered with the extraction system.
- The performance of this technology can be limited by aquifer heterogeneities.
- Extracted groundwater with surfactant/cosolvent and DNAPL requires a significant degree of handling through ex-situ treatment for ultimate disposal/reinjection.

Technical challenges to the successful use of chemical flooding (and other aggressive DNAPL source-removal technologies) include locating the DNAPL and obtaining an adequate estimate of the initial DNAPL mass. In addition, finding the optimum composition of the injected fluids for a given DNAPL composition and soil type and characterizing the hydraulic properties of the aquifer are necessary to implement a successful flood. The implementability of surfactant/cosolvent flushing will depend on site-specific geologic conditions and on the type of DNAPL contaminating the site.

2.4.1 Heterogeneity

As an advective-based remediation technology, the performance of surfactant/cosolvent flushing can be adversely affected by geologic heterogeneity. Aquifer heterogeneities can cause poor surfactant/cosolvent sweep of the area targeted for remediation. Therefore, the success of surfactant/cosolvent flushing depends upon an adequate characterization of not only the aquifer, but also the NAPL saturation and its spatial distribution in the aquifer.

Heterogeneity in geologic materials is a function of the environment of deposition and the resulting distribution of grain size and sediment textures. In an environment with low-permeability layers or units interspersed with higher permeability zones, fluids preferentially flow through higher permeability zones, thereby reducing the performance of the chemical injectate in the lower permeability zones. In the case of surfactants, a more uniform sweep may be induced by mobility control using either polymer or surfactant foam addition. “Mobility” and “mobility ratio” are multiphase fluid flow concepts that are used to describe how efficiently one fluid (e.g., DNAPL) can be swept from a porous media by another fluid (e.g., surfactant/cosolvent solution). Mobility control mechanisms are means developed by the petroleum industry to overcome the effects of geological heterogeneities. Traditional mobility control techniques have involved the use of polymer, which increases the viscosity of the injected solutions and the in-situ generation of foam in high permeability zones to divert flow into low-permeability zones.

At heterogeneous sites, mobility control is considered a necessary and integral component of surfactant/cosolvent flushing design and implementation. Mobility control improves the effectiveness of surfactant/cosolvent flushing in two important ways: (1) it significantly mitigates the effects of heterogeneities with respect to remedial performance, and (2) decreases costs, primarily by reducing the amount of surfactant required. If the hydrogeologic setting at a heterogeneous site does not allow the use of mobility control (e.g., because the aquifer will not support the necessary hydraulic gradients for propagating polymer in a timely fashion across the

zone of interest), then surfactant/cosolvent flushing may not be effective as a remedial technology at that site.

2.4.2 Low-Permeability Soils

Sediments with low intrinsic permeabilities can also limit the effectiveness of a surfactant/cosolvent flood. In addition to the sweep-efficiency issues discussed above, other challenges presented by low-permeability materials are the large hydraulic gradients and long time frames required to propagate the injectate, which may or may not be feasible in shallow subsurface formations. Low-permeability soils can be treated more effectively if the aquifer is deep (~ 50 ft below ground surface [bgs] to the aquitard), allowing higher induced gradients.

2.4.3 Migration of Mobilized DNAPL

In order to prevent potential downward migration of DNAPLs during SEAR, a competent aquitard or capillary barrier (an aquitard of appropriate thickness and $k = < 10^{-6}$ cm/sec) is usually needed to prevent downward migration of mobilized DNAPL. The type of surfactant/cosolvent flooding that can be implemented at a given site is determined by the presence or absence of a capillary barrier and the structure of the capillary barrier (e.g., fractures or macroporosity, pore-size distribution, thickness, discontinuities, etc.). Therefore, adequate information about capillary barriers is necessary to properly design a surfactant/cosolvent flood. This information includes an evaluation of the continuity and competence of the unit, including estimates of pore throat size distributions and characterization of the type of clay mineralogy. Section 3.3.6 discusses how a capillary layer might be characterized.

At a site with a competent capillary barrier, a mobilization-type surfactant/cosolvent flood may be preferable, as the mobilized DNAPL will not penetrate such low-conductivity units. A mobilization flood generally uses a surfactant/cosolvent that effects ultralow interfacial tensions (IFTs) between the DNAPL and water. Such a surfactant/cosolvent will first mobilize and then rapidly begin to solubilize the DNAPL it contacts. For homogeneous aquifers, the combination of ultrahigh contaminant solubilization and mobilization of NAPL induced by the ultralow IFTs often requires a small amount of surfactant/cosolvent solution on the order of two or three pore volumes (PVs). The end result will be the use of less surfactant/cosolvent, less time in the field to implement the flood, and, therefore, lower remediation costs. More PVs of surfactant/cosolvent flooding may be required at sites with strong heterogeneity and at sites with complex contaminants (e.g., mixtures of contaminants with widely varying physicochemical properties) and/or with high DNAPL saturations.

The absence of a capillary barrier necessitates either additional surfactant/cosolvent design considerations or the placement of a horizontal barrier to prevent vertical migration. One option is to design a surfactant/cosolvent that will solubilize DNAPL and maintain a solution that does not significantly increase in density, thus minimizing the potential for downward DNAPL mobilization. Some practitioners have applied the use of neutral buoyancy SEAR (SEAR-NB), although very limited data exists on this application (Shook et al., 1998; Kostarelos et al., 1998). The SEAR-NB application utilizes high concentrations of alcohol and viscosity controls that

offset the DNAPL density and recover the contaminant predominantly by solubilization. Using this method requires more surfactant/cosolvent, and high-alcohol cosolvent concentrations will increase SEAR application and effluent treatment costs.

2.4.4 DNAPL Properties

The physicochemical properties of the DNAPL can also present limitations. For highly viscous DNAPLs such as coal tars, creosotes, and weathered fuel oils, recovery by mobilization may not be feasible, as the high gradients required to mobilize these DNAPLs may not be sustainable for a given aquifer depth. In addition, the formation of viscous and hydrodynamic instabilities between the groundwater and surfactant/cosolvent solution created by the low viscosity of the water and surfactant solutions compared to the DNAPL lead to fingering and bypassing of NAPL-contaminated zones. This situation may be alleviated by the use of a viscosifier such as xanthum gum polymer for mobility control. The higher viscosity of the polymer mitigates viscous fingering and also the effect of aquifer heterogeneities to provide better sweep of contaminated zones. If the DNAPL viscosity is extremely high, preheating the aquifer and the surfactant solution may be necessary.

Because a selected alcohol is not as effective as a carefully selected surfactant at dissolving DNAPL, an alcohol flood requires many more PVs of flushing solution than a well-designed surfactant flood to achieve the desired performance objective. Furthermore, for DNAPLs exhibiting higher molecular weight, viscosity, and compositional complexity, the low molecular weight alcohols are less effective at DNAPL dissolution, while the higher weight or more complex alcohols are immiscible and much less soluble in water. Therefore, the range of DNAPL types that can be flushed with cosolvent alcohols alone is relatively limited, mostly restricted to the lighter chlorinated ethanes and ethenes.

2.5 Cost

The cost of surfactant/cosolvent flushing is highly variable and is dependent on many site-specific factors such as the size of the source zone, the hydraulic conductivity of the source, the type and amount of contamination, the type of flushing application, and regulatory factors. The cost of the surfactant/cosolvent can be relatively low or extremely high depending on the size of the site, geological characteristics, and the number of PVs required to obtain the remedial objective. Recycling and reuse of the flushing solution as well as dividing the site up into parcels and treating one parcel at a time have shown the potential to greatly reduce the cost for larger sites by reducing volume and, therefore, the cost of the flushing solution. Reuse also reduces the volume of waste generated and, therefore, disposal costs. Proper selection of a flushing agent is essential for the efficiency of the flush, and bench-scale treatability testing is often required.

Estimated costs for surfactant/cosolvent flushing of DNAPL typically range between \$65 and \$200 per cubic yard of DNAPL-contaminated aquifer. As the technology advances and is applied at more sites, this range may decrease. However, hydraulic conductivity and solubility-enhancement additives are factors to likely increase the cost. The cost of surfactant/cosolvent flushing is comparable to other in-situ technologies such as in-situ stabilization/solidification,

steam injection and extraction, and enhanced bioremediation (Roote, 1997). Additional information regarding costs for surfactant/cosolvent flushing can be found in Appendix D of this document.

3.0 PREDESIGN CHARACTERIZATION

This section provides a brief summary of the DNAPL source characterization information necessary to design a surfactant or cosolvent flood. More detailed information on this subject can be found in the ITRC document on DNAPL source characterization and in the SEAR Design Manual (NAVFAC, 2002a).

Locating and adequately delineating the DNAPL source zone is a key step in gaining a sufficient understanding of subsurface conditions to design a successful chemical flood. Source-zone characterization often is more complex than traditional site characterization efforts because DNAPL migration and behavior generally create extremely heterogeneous DNAPL distributions in the subsurface. Planning and executing an adequate source-zone characterization program requires a multidisciplinary approach founded on the applied sciences of multiphase fluid flow (petroleum engineering), hydrogeology, geochemistry, and environmental engineering. All DNAPL remediation technologies (including flushing technologies) require source-specific data usually not collected during “conventional” site characterization efforts focused on the dissolved-phase plume. Remediation system failures are often attributed to poor site characterization and incomplete laboratory feasibility studies, rather than to shortcomings of the applied remedial technology.

3.1 Purpose and Objectives

The primary purpose of DNAPL source-zone characterization is to provide a framework for remedy selection and a design basis for subsequent remediation of the site. Source-zone characterization must be sufficiently complete to ensure efficient and cost-effective design, installation, and operation of the remedy.

The purpose of a predesign characterization program is to compile a design basis for the surfactant or cosolvent flood. At a minimum, the program should consist of the following elements:

- measuring the physical and chemical properties of the DNAPL that pertain to surfactant/cosolvent selection and flood design parameters;
- determining how the DNAPL is distributed in the subsurface; and
- understanding how the aquifer (geosystem) contaminated with DNAPL will affect the application, control, and extraction of chemical fluids injected into the subsurface.

The chemical composition of the site DNAPL and any variations in the composition across the contaminated zone of interest dictate the components and composition of the chemical formulation selected for a surfactant or cosolvent flood. The DNAPL composition can be determined from chemical analyses of soil samples if free-phase DNAPL is not present at the

site. Physical properties are determined from DNAPL samples or analogues based on sampling results and/or information about the process that created the DNAPL problem.

Determining the extent and spatial distribution of DNAPL ensures that the chemical flood targets the proper subsurface volume. There are many techniques that investigators have used to map DNAPL distribution. Perhaps the most precise and appropriate parameter to measure when characterizing a DNAPL source zone is saturation. Saturation is defined as the fraction of the soil pore volume that is filled with DNAPL. Depending on the degree of saturation, DNAPL will exist as either free-phase DNAPL or as residual DNAPL. Free-phase or mobile DNAPL exists when the saturation is high enough to form pore-to-pore connections over a large area, producing a continuous fluid capable of flowing under an imposed gradient or its own gravitational potential. Residual or entrapped DNAPL exists when the soil pores have been drained of mobile DNAPL, leaving behind some amount of liquid trapped by capillary forces or the surface tension that holds a liquid to a solid surface. DNAPL at residual saturation is discontinuous and immobile, unable to flow under normally imposed hydraulic gradients.

Aquifer characterization is also an important part of developing a design basis for flushing technologies. Adequate data are needed to design a system that delivers the correct amount of surfactant to the right location while maintaining hydraulic control over the injected fluids. Several aquifer characteristics (e.g., hydraulic conductivity, hydraulic gradient and aquitard surface topography) need to be defined to ensure that DNAPL removal and hydraulic control will be effectively accomplished. Detailed information concerning the heterogeneity of the contaminated zone and of low-permeability and relatively impermeable units is necessary to mitigate the effects of these and help delineate the source zone.

3.2 Geosystem Model Development

Understanding how DNAPL migrates and is trapped in the subsurface is essential to developing the conceptual model needed to guide this type of investigation. DNAPL in an aquifer is subjected to (1) viscous forces exerted by flowing groundwater, (2) gravity forces due to the difference between the density of the DNAPL and the surrounding groundwater, and (3) capillary forces caused by fluid properties and the sizes of the porous geologic media's void spaces. Void space sizes are determined by the grain-size distribution or texture of the geologic media, so heterogeneity in soil properties strongly influences DNAPL migration and distribution. Usually, both the viscous forces and the gravity forces are much lower than the capillary forces, and the DNAPL remains trapped indefinitely. However, if the combination of the viscous and gravity forces exceeds the capillary forces, trapped DNAPL will be mobilized in the direction of the effective force. Fluid properties that influence capillary forces include the surface tension of the DNAPL and interfacial tensions between the DNAPL and water. These basic concepts of multiphase flow can be used in the assessment of DNAPL migration at a given site.

A “geosystem” is the sum of all physical/chemical subsurface components that comprise a DNAPL source zone. Developing a geosystem model that includes all of the relevant information collected from the site investigation program helps to organize data collection and use and ultimately becomes the quantitative design basis for the selected remedy. The geosystem model

begins as a conceptual description of the hydrogeologic characteristics of a site and the estimated nature, volume, and spatial distribution of the DNAPL (a conceptual site model). It is formulated early in the site investigation program using available site data to build a foundation for the ensuing work and identify data gaps. The model then guides further source characterization efforts as DNAPL zone data is collected, analyzed, and incorporated into the model.

The geosystem model becomes increasingly quantitative as new data are collected and the model is iteratively updated throughout the duration of the project. The end product is a quantitative model that reflects those properties of the aquifer and its fluids that may influence surfactant or cosolvent flow through a contaminated subsurface zone. The term “model” in this context refers to a coherent description of the parameters needed to fully describe a design basis for a remedial action and does not refer to a mathematical model simulated numerically (much like a conceptual site model does not refer to a mathematical model). In the final design stage, the geosystem should be compiled into a numerical model so that predictive simulations can be used to assist the in-situ flushing design process. Table 3-1 summarizes the elements of a geosystem model that are collected during DNAPL site investigations and laboratory testing for chemical flood design (Modified from NAVFAC, 2002a). Ultimately, these data are used as input to a numerical simulator, along with surfactant phase behavior data, to simulate surfactant injection and extraction operations for SEAR design. SEAR design is discussed further in Section 4.0.

Table 3-1: Site Data Incorporated into a DNAPL Site Geosystem Model	
SITE HISTORY	
Site plans Chemical inventory records Contaminant release records Previous site investigation reports	Find the entry location(s) if possible. Use chemical inventory and contaminant release records to identify the potential location, nature, and history of previous releases or sources at the site. Use current and historic site plans to identify suspect areas such as pits, ponds, lagoons, storage tanks, and/or other chemical disposal or storage areas. Estimate the type and quantity of chemicals used at the site. Review existing site data to determine which parameters have been properly defined and which still need to be evaluated.
PHYSICAL SETTING	
Weather, topography, land use, site infrastructure Utilities, pipelines, and other surface and subsurface structures	Determine the site’s climate for hydrogeological and logistical purposes. Topography and land use may constrain site investigation techniques and the configuration/design of the flushing process system. Site infrastructure may impact the cost and duration of the site investigation and the chemical flood. Information about surface and subsurface structures should be obtained in order to avoid interference during the site investigation program or in selection of the injection/extraction wells.

Table 3-1: Site Data Incorporated into a DNAPL Site Geosystem Model

GROUNDWATER CHARACTERISTICS	
Nature and extent of dissolved-phase plume	Although surfactant and cosolvent flushing is a source-zone technology, information about the dissolved-phase plume can be helpful in delineating source zones. Contaminant concentration gradients in groundwater, in conjunction with aqueous solubility information, and biodegradation data can be used to indicate the presence of hot zones.
Aqueous Geochemistry	Obtain pH, conductivity values, total dissolved solids, and levels of cations/anions in groundwater and the water source to be used for surfactant formulation.
Temperature	The average temperature of the groundwater in situ should be measured. Surfactant/cosolvent performance must be optimized for this temperature.
SITE GEOLOGY/HYDROGEOLOGY	
Stratigraphy and Hydrostratigraphy	Characterize site stratigraphy and hydrostratigraphy. The term “hydrostratigraphy” denotes the classification of geological media into groups defined by hydraulic properties such as aquifers and aquitards. Identify the character of the principal hydrostratigraphic units, including their extent, geometry, and structure. Note any permeability variations, heterogeneity, structural traps, or capillary barriers. Understand the environment of deposition and the corresponding geologic structure/heterogeneities.
Capillary barriers/flow boundaries	Based on the above information, detail the extent, nature, and thickness of capillary barriers or low-permeability units, which will tend to inhibit downward migration of the DNAPL. Also, determine if there are breaks in the capillary barrier due to geologic unit changes, fractures, etc.
Aquifer saturated thickness	A measure of the thickness of the saturated zone.
Permeability and hydraulic conductivity distribution	Intrinsic permeability is the capacity of a porous media to transmit fluid independent of the type of fluid. Hydraulic conductivity by definition is specific only to groundwater. Since flushing technologies deal with fluids with different physicochemical characteristics, permeability distributions should be characterized.
Hydraulic gradient	A measure of the driving force for groundwater flow. Gradients influencing the targeted treatment zone must be understood to ensure that hydraulic control is achieved in the flood design.
Piezometric surface	A map of the hydraulic head in the aquifer.
Water-table fluctuations	Seasonal changes in the water table elevation should be observed, and the impact on DNAPL migration and on flushing system operation evaluated.
Grain-size distribution	Grain-size distribution provides information about site stratigraphy, permeability, and porosity. Generally, the less permeable stratigraphic units will be more poorly sorted and have smaller average grain sizes than more permeable units (see ASTM Method No. D422).
Porosity, Fraction of organic carbon (f_{oc})	These parameters are used to calculate the DNAPL saturation from the soil-contaminant concentration. Porosity is a measure of the amount of pore space or void space in a soil matrix (see ASTM Method No. D5084). F_{oc} is the fraction of soil that consists of sedimentary organic matter (not anthropogenic) (see ASA Method No. 29-3.5.2).
Geochemistry	Obtain information on soil mineralogy, soil structure, clay content, and pH.
DNAPL CHARACTERISTICS	
Density	Mass per unit volume of a substance. Measured with a pycnometer (see ASTM Method Nos. D1217 or D1480).
Viscosity	A physical property of a fluid that characterizes its resistance to flow (see ASTM Method No. D445).

Table 3-1: Site Data Incorporated into a DNAPL Site Geosystem Model

Chemical composition	The constituents of concern detected on site should be reviewed. Categorize all detected constituents as DNAPL-related or not DNAPL-related. Many solvents used in degreasing processes contain significant amounts of stabilizers and other impurities such as oil, grease, and surface-active agents that markedly change their properties.
Interfacial tension	The tension, described as force per unit length or energy per unit area, that occurs between two immiscible liquids or a liquid and a solid. Can be measured with a ring tensiometer using ASTM Method No. D971 or a spinning drop tensiometer method (see Cayais et al, 1975).
Aqueous solubility for each component	The maximum concentration of a chemical that will dissolve into water at a specified temperature and pressure. Standard literature values can be used; adjust for a multicomponent mixture using Rault's law.
Organic carbon partition coefficient, K_{oc} for each component	A measure of the affinity of a given contaminant for the organic matter in soil. Standard literature values can be used; site-specific values should be obtained from noncontaminated media similar in nature to that found in the source, so that the sedimentary organic carbon is measured rather than that from anthropogenic sources.
MULTIPHASE MEDIA SYSTEM CHARACTERISTICS	
Wettability	A measure of the preferential spreading of one fluid over a solid surface in a two-fluid system. A soil-NAPL-water system is said to be water-wet, oil-wet, or mixed-wet depending on which liquid (water or oil) has a greater affinity or preference for coating the soil surfaces (see ASTM Method No. D3152).
DNAPL saturation	Measure the contaminant concentration present in each major hydrostratigraphic unit and use the partitioning algorithm NAPLANAL and the organic partition coefficient, solubility data, soil porosity, and fraction of organic carbon data to estimate the local DNAPL saturation.
Fate and migration	Apply knowledge of DNAPL behavior to assess relative importance of dissolution, volatilization, immobilization, adsorption, and degradation mechanisms in determining DNAPL fate and migration at a given site.
Capillary pressure and capillary desaturation curves	Capillary pressure involves the combined effects of interfacial tension and wettability. It is the force per unit area, which acts to hold DNAPL in a pore throat by compressing the nonwetting-phase fluid (DNAPL) relative to the wetting-phase fluid (water). Capillary desaturation curves can be developed from laboratory experiments to describe the process of imbibition and drainage. The experimental methods are described in Bear (1972) and Corey (1986).

3.3 DNAPL Source Zone Delineation

At a site where DNAPL has not been located, site historical information, dissolved concentration plume data, and DNAPL property data will assist in defining the initial investigation areas. Defining an appropriate target treatment area is paramount to effective and efficient flushing technology implementation. Given that the purpose of chemical flooding is to remove DNAPL mass from the aquifer, proper site characterization and delineation of the DNAPL-contaminated area will ensure that the flood design targets the correct subsurface volume, thus ensuring

efficient removal of the maximum amount of DNAPL and minimizing the costly treatment of zones without DNAPL.

Historical information is invaluable in determining which areas of the site are likely to contain DNAPL sources. Existing geologic information, predominantly in the form of boring and drilling logs, can also provide insight on where the hunt for DNAPL should be focused. Because these type of data are typically sparse, and because source zones almost always have relatively small areal footprints compared to the dissolved-phase contaminant plume, the usefulness of previously collected geologic data is mainly limited to defining the extent of vertical heterogeneity and determining the environment of deposition. In general, existing site data collected for investigations focused on site-wide groundwater and soil contamination are too sparse to have a statistically significant chance of having detected the source, or to provide the level of detail needed at the scale of the source zone. The concept of investigation scales and other important aspects of drilling and soil sampling in the context of DNAPL site characterization are discussed below.

Source identification and characterization efforts should start with rapid noninvasive screening tools that can be used to cost effectively investigate large areas. As the program progresses and the geosystem model becomes more quantitative, more invasive techniques focused on the DNAPL source should be utilized. High-end characterization tools can be used at the end of the predesign characterization phase to provide the best possible estimate of DNAPL volume and extent and to provide a baseline with which to measure remediation performance. This is also known as the Triad Approach, which includes systematic planning, dynamic work plans, and on-site analytical tools. The methods for subsurface investigation are presented below in order of implementation during a predesign characterization program.

3.3.1 Geophysical Methods

Geophysical data provide information about site stratigraphy and geologic structure, which can be used to help identify the likely migration pathways for DNAPL for a more focused source investigation. There are many geophysical methods, including seismic surveys, ground-penetrating radar (GPR), natural gamma logging, and other electrical and magnetic techniques that can provide valuable information regarding the hydrostratigraphy and structure of potential DNAPL zones. Because geophysical methods are noninvasive and can provide relatively low-cost data sets quickly compared to other methods (e.g., drilling or excavation), they should be used early in the characterization program, especially when DNAPL investigations are being conducted over large areas. A major limitation of geophysical methods is that typically the data resolution is not fine enough to provide detailed quantitative data (e.g., hydraulic conductivity or DNAPL detection) necessary for surfactant/cosolvent design. Instead, geophysical surveys produce a broad and qualitative picture of the subsurface environment. They should be used to obtain general hydrostratigraphic information, locate large-scale substructures such as underlying aquitards, and investigate aquifer heterogeneity. GPR has proven extremely useful in providing high-resolution stratigraphic data in NAPL source zones in geologically conducive environments (predominately sand and gravel with a deeper water table). In addition, down-hole natural gamma logging has proven very effective for locating the contacts between clays and sands.

Other geophysical logging tools include electric resistance tomography, thermal-neutron tools, cross-hole radar, and emerging acoustic impedance methods.

3.3.2 Direct Push Technology and Cone Penetrometer Testing

Direct push technology (DPT) is a cost-effective alternative to conventional drilling for rapid site characterization of unconsolidated formations. DPT equipment uses hydraulic equipment to push specialized tools that provide groundwater samples, soil samples, and other geophysical measurements. A significant logistical advantage of using DPT is that the generation of investigation-derived hazardous waste is minimized. DPT-based methods provide “local” or “point” measurements, much the same as soil borings or multilevel samplers but on a much smaller scale. Groundwater wells provide depth-integrated values but still are considered to be “local” values.

Cone penetrometer testing (CPT) is a type of DPT that provides a quantitative, high-resolution tool for interpreting soil classifications. The cone penetrometer consists of an instrumented probe, which is advanced vertically into the subsurface at a constant rate. The probe consists of a standardized conical tip and a friction sleeve that provide independent measurements of vertical (tip) resistance and frictional (sleeve) resistance as a function of depth. CPT allows determination of soil permeability, stratigraphy, and strength, as well as some estimate of the rate and direction of groundwater flow through the use of a pore pressure transducer. Best suited for unconsolidated fine-grained sediments, a CPT can investigate to significant depths (typically 100 feet or more) and provide data for analysis in real time. The use of DPT is strongly recommended to facilitate the collection of closely spaced quantitative and objective hydrostratigraphic data. Various chemical sensors and other tools specifically for DNAPL site investigations have been developed recently. Although some of these can provide direct detection of DNAPL in the subsurface, a major limitation for all DPT-based tools is that the scale of investigation is miniscule compared to the volume that needs to be investigated to find discrete heterogeneously distributed DNAPL-contaminated zones.

3.3.3 Soil Borings

The objectives of a drilling program in a DNAPL zone may include one or more of the following: (1) Determine subsurface properties not obtainable by other methods; (2) Collect samples to identify contaminants, quantify contaminant mass, determine geologic properties, and/or conduct bench-scale testing; (3) Install a well or other subsurface instrumentation (e.g., lysimeter); and (4) Ground truth/calibration for geophysical methods and DPT-based tools. These objectives must be balanced against the risk of compromising capillary barriers and facilitating further downward migration of the DNAPL. Drilling in source zones should, therefore, proceed cautiously inward from outside of the source area and should be conducted with the proper precautions for protecting the integrity of capillary barriers. When drilling within the DNAPL source zone, extreme care should be taken to ensure that conduits for vertical migration are not created. Important information can be obtained from this area (i.e., depth of contamination, residual saturation, etc.), but if the investigation is not conducted properly, the DNAPL and/or the dissolved plume could be spread. Completed wells or abandoned soil borings

must be properly sealed to mitigate the potential for vertical migration. Surface casing may be used to seal off an upper contaminated zone from uncontaminated lower zones in a multilayered source zone.

Although there are a wide variety of drilling methods, many are not appropriate for DNAPL zones, especially if the objective is to sample DNAPL saturations. Wash rigs and mud rotary methods may displace significant amounts of DNAPL in front of the bit due to the delivery and recirculation of drilling fluids through the stem. Similarly, the use of air to evacuate cuttings from around the drill bit can volatilize DNAPL components in a manner equivalent to soil vapor extraction. Rotosonic drilling is an excellent method for continuous sampling and provides a large volume of core in a manner that minimizes the risk of compromising the integrity of capillary barriers. Rotosonic drilling, also known as vibratory drilling, uses an oscillating drill head or core barrel to quickly advance through the subsurface. Drill cuttings are limited and are forced into the walls of the borehole. Water or air is required to remove cuttings when drilling through rock. However, in certain environments, this type of drilling generates significant amounts of heat at the cutting bit and thereby compromises the quality of VOC sampling. For most DNAPL sites in unconsolidated sediments, drilling with a hollow stem auger (HSA) is the preferred method. Segments of the borehole can be cased off to protect uncontaminated zones by driving larger diameter surface casing to the necessary depth, and the auger itself acts as a protective casing for the sampler installed just slightly ahead of the auger bit. Also, a variety of efficient sampling systems (e.g., wireline) and sampling tools are available for use with HSA.

3.3.4 Ribbon NAPL Sampler

The Ribbon NAPL Sampler is a sampling device that can provide detailed qualitative delineation of the vertical distribution of DNAPL encountered in a borehole created by a DPT tool or conventional drilling techniques. This tool uses a dye-impregnated ribbon, which is installed in a borehole by deploying a liner in the hole. The system is inflated against the walls of the borehole, and the ribbon absorbs any DNAPL in the formation that comes into contact with the ribbon membrane. The dye in the ribbon reacts with the DNAPL, causing a significant color change. The membrane is then retrieved with a tether connected to the bottom of the liner that turns the liner inside out. At the surface, the liner is reverted, and the ribbon is examined. The presence of DNAPL is indicated by discoloration marks on the ribbon. Although DNAPL saturations cannot be quantified with the ribbon, some indication of the amount of DNAPL encountered is obtained by the relative brightness of the discoloration. The ribbon sampler was designed for site screening and is best used during early stages of site characterization to focus and optimize subsequent characterization and remediation activities.

3.3.5 Soil Sampling

This section provides an overview of collecting and analyzing soil samples from the DNAPL zone. Soil samples can be used to provide an estimate of how DNAPL is distributed vertically in the source zone by providing contaminant concentration data that can be converted to saturation estimates. Soil samples also provide an indication of the vertical heterogeneity in the zone of interest and can be used to investigate variations in DNAPL composition. Depending on the

plume size and depth, a soil-sampling program alone may be too costly to provide an accurate estimate of the volume and extent of DNAPL impact. Other methods, such as partitioning interwell tracer tests (PITTs), can be used in conjunction with soil sampling to provide DNAPL saturation and volume estimates over a meaningful scale in the field (see Section 3.5.4).

Selection of the proper sampling devices to use in recovering soil samples from a DNAPL zone depends mainly on the type of soil to be sampled. The objective is to choose a sampler that will not only maximize the recovery of sediment, but also retain as much of the fluid in the pore spaces as possible. The manner in which the recovered core is handled and sampled can help to minimize volatile losses. The rapid loss of volatile DNAPL components (up to three orders of magnitude) during standard sample handling and preparation has been well documented and has given rise to the practice of performing solvent extractions in the field (Hewitt et al., 1995). Quickly placing a portion of the soil from the sampler directly into a solvent (usually methanol) at the logging table preserves the volatile compounds in the resulting sample by lowering their partial vapor pressures. Field preservation of soil samples with solvent is necessary to obtain meaningful analytical results from a DNAPL zone.

Laboratory analyses will yield a measurement of the total concentration of each constituent detected in the soil sample. To provide meaningful source-zone data, these results need to be converted to an estimated DNAPL saturation in the subsurface. The total contaminant mass reported by the laboratory in the soil sample ideally represents mass distributed (or partitioned) between the soil, groundwater, free phase, and/or air phase. Because flushing applications are almost exclusively implemented in the saturated zone, the air phase is assumed to be negligible in partitioning calculations conducted for source zones below the water table. The partitioning of contaminant mass between soil, groundwater, and DNAPL depends on parameters such as the fraction of organic content (f_{oc}), the porosity of the sediment, and well-established partition coefficients and solubility constraints. Using these relationships and published values of equilibrium solubility data, analytical expressions can be solved to determine if enough contaminant mass is present to indicate a DNAPL. Moreover, using an iterative solver and an algorithm that conserves mass allows a saturation to be calculated if DNAPL is present in the soil sample. NAPLANAL is a freeware program developed by INTERA to convert the laboratory soil sample results to estimated DNAPL saturations (Mariner et al., 1997).

Soil samples are also collected to measure the bulk density, the grain-size distribution, and the f_{oc} of the geologic media. Grain-size analyses are used to define heterogeneity and point permeabilities in the subsurface and should be collected at a frequency sufficient to define the major hydrostratigraphic units in the DNAPL zone. The results of these tests are also used during the design process to estimate hydraulic properties based on empirical correlations (Vukovic and Soro, 1992). Samples for determination of fraction of organic carbon are collected from areas with little to no contamination and analyzed for total sedimentary organic carbon (TOC). The TOC results are then converted to f_{oc} by dividing the measured TOC by the mass fraction of dry soil.

3.3.6 Characterizing Capillary Barriers

One of the primary concerns in remediating a DNAPL zone is the potential for vertical migration of DNAPL. Vertical DNAPL migration usually is arrested by a capillary barrier (e.g., a clay aquitard) that is characterized by a pore throat distribution that prevents NAPL entry. Data on the integrity of the capillary barrier is necessary to design a chemical flood properly. The ability of a capillary barrier to prevent entry and downward flow of DNAPL is influenced by the pore-size distribution of the medium, the driving forces affecting DNAPL transport, and the wetting nature of the mineral surfaces in contact with the DNAPL. For example, very fine silt will require 100 times as much hydraulic head as medium sand before DNAPL infiltrates into it. The site investigation program should include an evaluation of whether or not there are breaks in the capillary barrier due to geologic unit changes, fractures, burrow holes, or inadequately sealed wells or borings, etc. Because DNAPL migration has been shown to occur through hairline fractures as small as 10-microns in diameter (Cohen and Mercer, 1993), it should be assumed that an aquitard can permit downward migration of DNAPL in localized areas through fractures unless it can be proven otherwise through the field investigation.

Characterizing a capillary barrier can be accomplished through the use of GPR, gamma logging, and CPT data to define topography of the unit and to delineate the aquifer/aquitard contact, analysis of clay minerals with X-ray diffraction (XRD) studies, and measurements of entry pressure with a capillary pressure test. Capillary pressure tests should be conducted with undisturbed aquitard samples to obtain an estimate of the entry pressure. Larger diameter samplers (2 inches or more) that collect cores at least 6 inches in length are recommended. There are a number of established laboratory methods, such as centrifuge, pressure cell, and mercury intrusion that are available to determine capillary entry pressure.

The presence and competency of a capillary barrier can substantially alter the design approach for a flushing application. If a thick clay aquitard acts as a competent capillary barrier at the bottom of the DNAPL zone, then a mobilization-type surfactant flood with ultralow interfacial tensions can be considered, since this is the most effective and rapid of the SEAR types. However, if there is no capillary barrier, or if the aquitard does not have high enough entry pressures, a solubilization or neutral buoyancy approach will be necessary. Therefore, accurately characterizing the extent, structure, and capillary entry pressures of an underlying aquitard is essential in designing a flood suited to the site's conditions.

3.4 Characterization of DNAPL Properties

Understanding the chemical composition of the site DNAPL and any variations in the composition across the contaminated zone of interest is important for designing an efficient flood. The DNAPL composition can be determined from chemical analyses of soil samples or more accurately from DNAPL samples if free-phase DNAPL is present at the site. Approximately 80 mL of DNAPL is usually necessary to provide the physicochemical property data needed for chemical flood design. These parameters include:

- DNAPL density,
- Viscosity,
- NAPL-water IFT, and
- DNAPL-aquifer system wettability.

It is important to remember, however, that spent chlorinated solvents are usually not the only components of the DNAPL, especially those that resulted from degreasing operations. The presence of oil and grease compounds in the DNAPL can result in markedly different physical properties than those published for the chlorinated hydrocarbon compounds in neat (i.e., pure) form. This is especially true of DNAPL IFTs, which are typically much lower than the “book” values expected for hydrocarbon compounds. In the case of spent degreasing solvents, these low IFTs are typically due to small amounts of surface-active agents used during maintenance operations.

Free-phase DNAPL samples or a reasonable analog formulated from stock chemicals based on the chemical composition indicated by the results of soil and water samples collected at the site are also needed to conduct soil column experiments in support of the flood design. Although not routinely conducted, one type of column experiment is a capillary desaturation test. The primary objective of the capillary desaturation experiment is to provide design information about the mobilization of DNAPL for the selection of an appropriate surfactant. In these experiments, the capillary forces trapping the DNAPL are first overcome by lowering the IFT with surfactant, and then allowing the viscous forces (e.g., advection) to cause the DNAPL to drain from the soil matrix. Capillary desaturation experiments determine the critical trapping number by increasing the viscous forces relative to the capillary forces. The critical trapping number is an important parameter in modeling multiphase flow in the subsurface. Available references that describe the experimental setup for measuring the capillary pressure saturation relationship include Bear (1972) and Corey (1986).

Routine column experiments conducted as part of bench-scale treatability testing involve using sediment from the source zone and site DNAPL or an analog and testing surfactant formulations for undesirable behavior (gel formation, precipitation, sorption, mass transfer limitations) at aquifer temperatures. Protocols and procedures for conducting chemical-flooding column tests can be found in Dwarakanath et al., 1999.

3.5 Aquifer Characterization Methods

Characterization of the source-zone hydrogeology is needed to predict and/or optimize flood performance. Adequately characterizing the hydrogeology of the DNAPL zone is one of the most critical components of the SEAR design process. The hydraulic properties of the contaminated aquifer directly affect the design of the flushing well field, as well as the flow rates, amounts of chemical reagents needed, and the duration of flushing operations. Optimization of the chemical flood performance is conducted in tandem with numerical modeling of the aquifer conditions. The objectives of the aquifer characterization program include obtaining estimates of hydraulic conductivity and the pore volume of the DNAPL zone, and testing sustainable injection and extraction rates for the aquifer and the wells. The SEAR hydraulic testing program generally

consists of installation and construction of injection/extraction wells, slug/bail tests, pumping tests, and conservative interwell tracer tests (CITTs). Finally, the design and implementation of a PITT can assist in predicting the quantity and distribution of DNAPL mass in the subsurface for a robust flood design.

3.5.1 Well Installation and Construction

The stratigraphy of the DNAPL-contaminated zone should be understood prior to well installation to properly position the screen and provide representative data on the hydraulic properties of the DNAPL-contaminated zone(s), as well as to prevent DNAPL migration into uncontaminated areas. Well-construction details are provided in Section 4.0 of this document, and detailed information on well construction can be found in *Groundwater and Wells*, edited by Driscoll (1986). As a general rule, aquifer test and process wells should have a large diameter and be constructed carefully in accordance with technical specifications for high-performance process wells (not monitoring wells). Well-installation practices should include accurate calculation and documentation of all materials used in constructing the well, the filter pack, and the seal and in grouting/cementing the remaining annulus. The final step in constructing a high-efficiency well is to develop it properly using surge blocks or similar devices that can effectively move fine-grained sediments from the filter pack and even the aquifer itself into the well bore, where the sediments are evacuated with a pump or bailer. Development should be conducted in stages across successively lower segments of the screen, while periodically removing the sediment-laden water in the well bore.

3.5.2 Slug Tests

Slug testing is a relatively inexpensive and quick way of obtaining hydraulic conductivity from a short single-well test. The slug tests provide hydraulic conductivities and transmissivity for the immediate region surrounding each well. By testing each well in a well array, an indication of the spatial variation of hydraulic conductivity in a well field can be obtained. Slug tests are also useful in testing the hydraulic performance of a remediation well. Slug tests can be conducted on extraction, injection, and monitoring wells. Pneumatic slug tests are usually preferred to ensure that as large of an aquifer volume as possible for slug tests is tested, and to minimize both the production of contaminated groundwater and the need to decontaminate equipment. Test results need to be carefully analyzed to separate out skin and filter pack effects from the aquifer response. A drawback to slug tests is their relatively small scale of investigation.

3.5.3 Pumping Tests and Conservative Interwell Tracer Tests (CITTs)

While slug and bail tests only provide information about the subsurface environment in the vicinity of one well, pump tests and more complex multiple-well tracer tests provide estimates of the hydraulic properties of the flow system at the scale of the entire pore volume of the treatment area. In these types of tests, water is pumped from one or more wells, and the resulting hydraulic response is measured in other nearby wells. These responses can then be analyzed to provide hydraulic parameters for use in designing a chemical flood, including hydraulic conductivity and permeabilities for the hydrostratigraphic units incorporated into the geosystem model. The

collection of depth-discrete hydraulic information using multilevel samplers (MLS) is recommended in aquifers with layered heterogeneity for improved remedial design parameters. Additionally, pump tests can be used to determine parameters relating to individual wells in the well field, including specific capacity and well efficiency. Detailed discussions for the analysis of pump test data for various aquifer types and conditions can be found in most hydrogeology textbooks, such as Domenico and Schwartz (1998).

Due to the importance of hydraulic control in flushing operations, a multiple well–forced gradient hydraulic test has been developed that provides well field–scale transport properties in addition to the hydraulic parameters derived from pump tests. This test, known as a conservative interwell tracer test (CITT), involves not only injection and extraction operations in the well field similar to the planned flood, but also the transport of a nonpartitioning or conservative tracer across the target zone. CITTs are usually essential to the SEAR design process because they provide the swept pore volume (how much of the DNAPL zone is contacted by the injected fluid), the residence time (how long it takes the advective front of the injected fluid to traverse the contaminated zone), and tracer recoveries (a measure of how much of the injected fluid was captured at the extraction wells). Ultimately, CITTs provide an understanding of how forced-gradient flow systems behave in the aquifer volume affected by the well field array, and how well those fluids are controlled during injection/extraction operations. These issues have been critical to obtaining regulatory approval for SEAR applications. Conducting a CITT also allows injection/extraction processes and methods to be tested and refined in the field before conducting the more complex and expensive PITT and chemical flushing operations. The main objectives of a CITT include obtaining the following:

- hydraulic parameters of the aquifer,
- data on the heterogeneity of the aquifer,
- sufficient information to calibrate the geosystem model of the aquifer,
- an estimate of the swept pore volume for each well array,
- an estimate of the tracer residence time in the subsurface, and
- estimates of the sustainable injection and extraction rates.

Arrival times and other results from CITTs can be analyzed using several techniques, including curve matching and the method of moments. Method of moments analysis can be used to analyze CITTs for hydraulic parameters such as swept pore volume, residence time, Darcy velocity, and hydraulic conductivity. Additionally, the second temporal moment of the tracer concentration curve can be used to compute an estimate of the Péclet number and the longitudinal dispersivity, both measures of heterogeneity in the geosystem (Jin, 1995a, b).

3.5.4 Partitioning Interwell Tracer Tests (PITTs)

In certain cases, a partitioning interwell tracer test (PITT) can be used as an additional remedial design tool to the CITT to better evaluate the volume and spatial distribution of DNAPL within the subsurface. It can provide data useful for predicting the quantity of chemicals required to achieve target cleanup levels and, subsequently, the anticipated duration and cost of flushing implementation. Several studies have concluded that a soil-coring program alone is unlikely to provide reliable estimates of the volume of DNAPL at the field scale (Mayer and Miller 1992;

Bedient et al., 1999). PITTs have also been used as remediation performance assessment tools to measure system effectiveness by determining how much DNAPL remains in the subsurface (Meinardus et al., 2002).

The field implementation of a PITT consists of the injection of a suite of conservative and nonconservative tracers into one or more wells and the subsequent production of the tracers from one or more nearby extraction wells. PITTs conducted in the saturated zone use groundwater as the carrier fluid, while air is used as the carrier for PITTs conducted in the vadose zone. The nonpartitioning (conservative) tracers pass unhindered through the DNAPL zone, while transport of the partitioning tracers is retarded by interaction with the DNAPL. After the tracer slug is injected, potable water is injected to drive the tracers across the zone of interest. The tracer responses at monitoring and extraction wells are used to estimate the average DNAPL saturation, the swept pore volume, and the total volume of DNAPL in the subsurface. The experimental and theoretical basis for the use of partitioning tracers is presented in detail in Jin (1995), Jin et al. (1995), and Dwarakanath (1997). The execution of a PITT requires the completion of a series of tasks, including tracer selection, design simulations, implementation, and analyses.

Because the PITT is a relatively new and innovative technology, it is useful to be aware of its limitations and some of the consequences associated with improper tracer test design and/or implementation. In a heterogeneous aquifer, PITT performance may be limited by permeability contrasts that cause tracers to preferentially flow through the more permeable zones of the aquifer. Tracer response data from an alluvial aquifer at Hill AFB OU2 illustrate that it is possible to measure the volume of DNAPL in low-permeability sand underlying a sandy zone with a permeability contrast of one order of magnitude between the sand units (Meinardus et al., 2002). However, at the Marine Corps Base Camp Lejeune site, where there was a similar permeability contrast of about an order of magnitude, a poor sweep of tracers was experienced through a low-permeability, clayey silt unit (hydraulic conductivity of 5×10^{-5} cm/sec), which resulted in an underestimate of DNAPL volume (NAVFAC, 2002a). Since the PITT did not effectively penetrate the bottom one to two feet of the aquifer, DNAPL saturations from soil-sampling results were used to estimate the DNAPL volume in the lower portion of the aquifer. The geometry of the capillary barrier/aquifer contact can also add uncertainty to the PITT estimate for similar reasons.

The PITT technology continues to develop, with recent advancements that make the test more cost-effective, including less costly tracers and better detection limits and detection systems. DPT-based “quick-PITT” systems should be available for rapid DNAPL site assessments in the future.

3.6 Characterizing Groundwater and Source Water Chemical/Fluid Properties

Table 3-1 includes a summary of the suggested parameters for groundwater characterization for flushing design purposes, along with the appropriate analytical methods. During the hydraulic-testing phase, groundwater samples are typically collected and analyzed for geochemical parameters. Background concentrations of anions and cations derived from certain inorganic minerals and clays including iron species, potassium, sodium, and chloride should be measured,

because they can significantly alter the behavior of the surfactant formulation. For example, cation exchange involving calcium in soils can cause mobilization of soil fines that will plug the aquifer formation and drive the surfactant molecules into the DNAPL, resulting in loss of surfactant and inability to recover DNAPL. Potential cation exchange concerns are specific to the site's geochemistry and to the particular surfactant being utilized. Additionally, groundwater samples collected before the remediation effort and analyzed for the constituents of concern provide a baseline that can be used for long-term comparisons with post-SEAR data as the plume undergoes natural attenuation. In addition to groundwater samples, the samples from the source of water, i.e., the potable water source to be used on site for mixing the surfactant solution, should be collected and tested. Source water samples should be analyzed for geochemical parameters and temperature. Bench-scale tests for flushing design should be conducted with site groundwater and site source water.

4.0 SYSTEM OPERATION CONSIDERATIONS

Designing and implementing a DNAPL source removal operation is with few exceptions an intrinsically complex endeavor. Chemical flushing activities (and any other aggressive source-removal technology) must be designed in such a way that uncontrolled vertical and horizontal migration of contamination is avoided. A comprehensive understanding of the subsurface environment, multiphase fluid flow, and the physical processes being employed is required to prevent remediation failure and avoid contaminating previously uncontaminated portions of the aquifer.

The purpose of this section is to familiarize the reader with the design and operation of flooding operations and to discuss the important issues that need to be resolved to effect a successful and economical remediation. Chemical flood design is an iterative process that proceeds by identifying and filling data gaps to achieve a final design that is tailored to the specific site to be remediated. The primary objective in designing a chemical flood is to remove the maximum amount of contaminant with a minimum amount of chemicals and in minimal time while maintaining hydraulic control over the injected chemicals and contaminant. Design challenges include determining the extent and volume of the DNAPL, finding the optimum surfactant solution for a given DNAPL composition and soil type, and accounting for heterogeneities present in the subsurface environment. In order to design a robust flood for the expected heterogeneities in the treatment zone, numerical modeling tools should be used in the design process. Sensitivity simulations conducted during the design work can indicate what parameters are particularly important and can simulate how the system may respond to heterogeneities that may be present in the source zone. However, simulations are only as useful as they are accurate in reflecting actual site conditions and surfactant flow properties. The accuracy of field and laboratory data is, therefore, important.

4.1 Design & Construction

The selection of the most appropriate surfactant/cosolvent approach is made only after considering the issues of applicability and limitations as outlined in Section 2.0 and thoroughly

assessing the characterization criteria described in Section 3.0. The design process should begin with a conceptual design and proceed through a final design that results in a process flow and instrumentation diagram, a site layout plan, and a work plan. Field personnel can use these documents to properly implement the system as designed. Figure 4-1 is a general schematic of a surfactant/cosolvent process system, which illustrates the different types of components typically incorporated into a flooding operation.

Although surfactant/cosolvent flushing solutions vary substantially, there are similarities in process design and construction across the spectrum. Each technology variant requires that a fluid be flushed through the subsurface and contact the zones containing DNAPL. The hydraulic design must strive for effective sweep efficiency and hydraulic control. Also, key logistical and field implementation issues must be accounted for in the plan. For example, variations in the chemical composition of the flushing solution can have a profound effect on the performance of the technology. It is, therefore, imperative that the mixing and the delivery systems provide acceptable accuracy in mixing and injection.

The major design and construction issues can be categorized into four major subsystems:

- **Laboratory Studies and Chemical Selection:** focusing on the selection of the surfactant/cosolvent, the optimum formulation for the site, and the amount of chemicals needed;
- **Subsurface Design:** involving delivery and recovery system (injection and extraction wells);
- **Unit Process Design:** including the design and installation of the chemical mixing and injection system and the attendant control and sampling systems; and
- **Waste Management Operation:** focusing on the treatment of the extracted groundwater and elutriate.

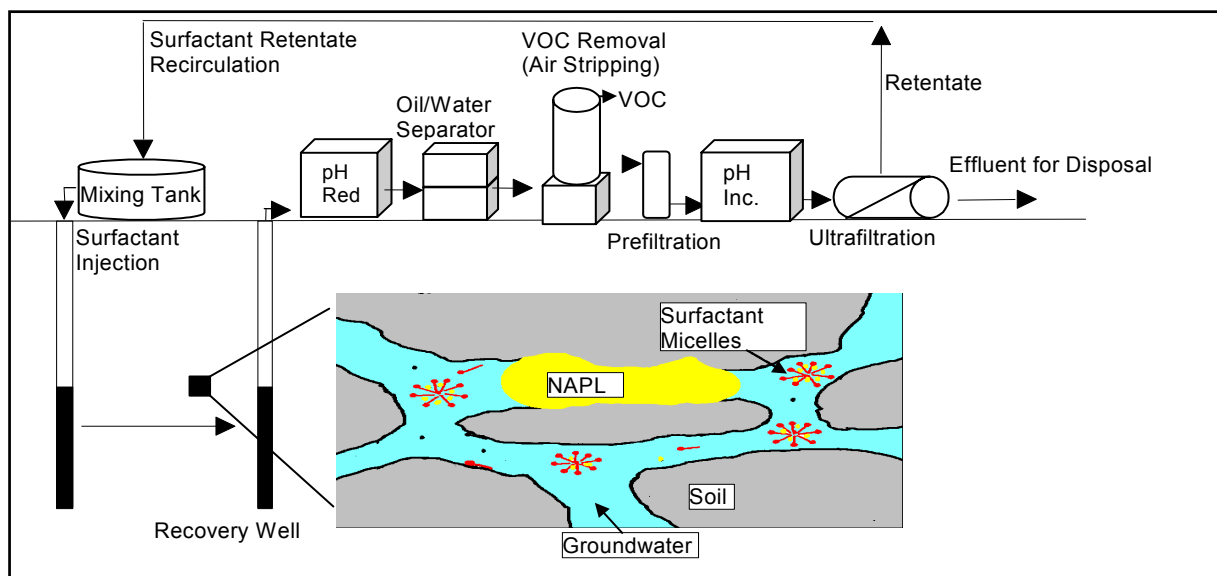


FIGURE 4-1. Schematic of Surfactant/Cosolvent Process System

The injection system and recovery infrastructure should be designed concurrently. This includes injection wells, extraction wells, hydraulic control wells, monitoring wells, and all piping connecting the wells to the injection and recovery system. Much of the injection/recovery system design is completed during the modeling stage of the design process. The modeling results are used to determine well spacing, screened intervals, injection and extraction rates, required chemical volumes, and remediation durations. A wide variety of injection and extraction scenarios or configurations can be used, depending on site conditions and remedial objectives. These include injection wells, horizontal wells, trenches, infiltration galleries, or aboveground sprayers or leach, vertical circulation wells, and others. The delivery infrastructure must be chemically and physically compatible with the contaminant, the flushing solution, and the geochemical profile of the groundwater system. The piping and process equipment connecting the systems must also be designed to handle the design flow rates.

Another major component of the flushing system involves the collection and subsequent treatment of the extracted groundwater and elutriates. The design of this subsystem will in part depend on the extraction technique, which might utilize submersible pumps or vacuum-enhanced extraction. The treatment process components should be selected based on the composition of the effluent streams. It will be necessary to characterize the type and concentrations of contaminant, surfactant, and/or cosolvents; the potential need to recycle or reinject some portion of the treated streams or components; and the final disposition of the streams, e.g., discharge to publicly owned treatment works (POTW) or other waste-disposal options. Predictions of the amount and chemical composition of the recovered fluid to treat throughout the flood are obtained from numerical simulations conducted during the design process.

Flood-based remediation technologies require not only a careful and systematic design process, but also an extremely reliable, robust, and well monitored process system to implement the test successfully in the field. The first field applications involving modern surfactant/cosolvent flushing were labor-intensive, requiring continuously manned operations for several weeks at a time to control and monitor the batch-mode injection, extraction, and sampling operations manually. In the late 1990s, flushing implementations began benefiting from use of innovative and portable process systems. These systems, designed to automate the conduct of the floods as much as possible, are controlled by a supervisory data acquisition and control system (SCADA). A SCADA is capable of monitoring and supervising the injection and extraction of fluids and automatically controls sampling from various monitoring locations. It can also log and store system parameters such as injection and extraction rates, chemical parameters, and the various water pressures in the process system. Flow rates can be controlled by an automated flow-control system located in a trailer-mounted mobile unit. Samples can be taken and analyzed automatically with an in-line system such as a direct-injection gas chromatograph (GC) system. This analytical automation greatly reduces labor requirements and provides both real-time process data and data of higher quality.

4.1.1 Laboratory Studies and Chemical Selection

Laboratory studies are an essential component in the design of a successful surfactant/cosolvent system. Laboratory studies are typically carried out prior to field-scale demonstrations and are generally conducted in a university or specialty-consulting laboratory. These studies should be undertaken to select or design the specific chemical formulation that will effectively remove DNAPL from the contaminated soil. It is important to realize that each site requires a tailored design and that simply taking a formulation that was successful at one site and applying it to another site will most likely lead to failure (AATDF, 1997).

The contaminant type, matrix characteristics, and groundwater geochemistry are unique for each site, so that a site-specific laboratory program will be necessary to design an effective surfactant/cosolvent system. Laboratory studies can also provide information on the potential field performance of a surfactant/cosolvent flushing system. While laboratory studies will not ensure that DNAPL can be efficiently removed by surfactant/cosolvent flushing at the site, if a chemical system does not remove DNAPL from soil samples in the laboratory, the chemical system will likely not effectively remove DNAPL contamination from soil at the site.

The hundreds of different surfactants commercially available can be grouped into one of four categories: anionic, nonionic, cationic, and zwitterionic. Generally, only anionic and nonionic surfactants are acceptable for most flushing applications. Even within these two categories, there are hundreds of surfactant structures derived from synthetic and natural sources. Factors to consider in screening and selecting surfactants and cosolvents include

- prior application experience;
- potential effectiveness for the desired application;
- cost;
- public and regulatory perception;
- biodegradability and degradation products;
- toxicity to humans, animals, and plants; and
- ability to treat/handle resulting extracted fluids (AATDF, 1997).

As discussed in Section 2.1, there are two main mechanisms for DNAPL recovery: mobilization and enhanced solubilization. Surfactants/cosolvents can be selected to emphasize one mechanism over the other. Laboratory screening for the two mechanisms are different. Mobilization requires reducing the capillary forces that trap the DNAPL in the saturated soil by reducing the interfacial tension. By definition, all surfactants/cosolvents reduce interfacial tensions (IFTs). However, the degree of IFT reduction may be controlled by tailoring the surfactant/cosolvent formulation. For example, ultralow IFTs may be induced to produce a mobilization-dominated system if a sufficient volume of DNAPL is present in the target zone. If the DNAPL saturations are low, the ultralow IFT system will act as a super-solubilization system and solubilize any mobilized DNAPL. This behavior was observed in the 1996 AFCEE surfactant flood described in Londergan et al. (2001). Solubilization consists of incorporating the contaminant in the micelles, requiring that surfactant concentrations be greater than the critical micelle concentration (CMC), and maintaining the surfactant concentrations as the surfactant flows through the soil. In some cases, such as in fractured media, it is necessary to use a high-IFT surfactant system to

emphasize solubilization. The solubilization properties of an anionic surfactant can be adjusted and optimized by varying the electrolyte concentration; thus, the formulation typically includes an electrolyte (e.g., sodium chloride and calcium chloride [CaCl₂]). A cosolvent, such as isopropyl alcohol, often is added to prevent surfactant gel formation (also called liquid crystals), so that the resulting microemulsion (or surfactant-contaminant-water phase) has an acceptable viscosity. The addition of cosolvent also influences the surfactant-phase behavior, so the effects of cosolvent addition on the surfactant solution must be examined under a range of system salinities. Because cosolvents complicate wastewater treatment, ongoing technology development has focused on surfactants that have no or minimal cosolvent requirements (NAVFAC, 2002a).

Laboratory testing of interfacial tension also can be used to evaluate the effects of surfactant class and structure, surfactant concentration, salinity and ionic strength, pH, makeup and dilution water effects, and effects of exchanged calcium. Phase-behavior tests involve mixing the surfactant solution with the DNAPL and allowing it to equilibrate at the appropriate ambient aquifer temperature. The number of resulting phases and the volume changes are characteristics of the phase behavior (i.e., the interaction of the phases) (AATDF, 1997).

Component solution stability should be monitored throughout the laboratory studies (i.e., the phase behavior should be monitored over time). If chemical combinations or phases separate during laboratory testing, that combination can be eliminated from further study. Precipitation of surfactant or other components from solution when mixed with DNAPL, groundwater, or matrix material is a cause for concern, and alternate formulations should be considered (AATDF, 1997).

4.1.2 Subsurface Design

Most of the major subsurface design issues should be identified during the predesign stage of the process. The injection/recovery design (i.e., well spacing, number of wells) should be completed in conjunction with the numerical simulation phase of the project. The selection of well spacing and geometry (i.e., an injection and extraction well pattern) is an important first step in the design process. The adverse effects of hydrogeologic factors, such as the natural hydraulic gradient and aquifer heterogeneity, can typically be offset by the selection of a robust well pattern.

Key issues to be considered in designing a well field for surfactant/cosolvent flushing include the following:

- **DNAPL extent/distribution:** As described in Section 3.0, careful site characterization is required to identify the location of the contaminant in terms of the extent of the contaminated zone and the distribution of the DNAPL within the source zone. Estimating the extent of DNAPL target zones at a site and the volume of DNAPL in those zones (both pooled and residual) is often the most difficult aspect of site characterization. Surfactant/cosolvent flushing is applicable for contamination in the vadose and saturated zones, but the distribution must be known in order to develop a practical flushing scheme. The permeability of the various contaminated layers is more of a key factor for consideration than the depth of the contaminant.

- **Permeability:** Surfactant/cosolvent flushing solutions must be able to pass through the contaminated zones to contact the contaminant in a reasonable period of time. This depends on the permeability of the strata, which can be measured as hydraulic conductivity, with favorable values in the range of 1.0×10^{-4} cm/sec or higher, and limiting factors in the range of $>1.0 \times 10^{-5}$ cm/sec (Sabatini et al., 2000). The more thorough the evaluation of the distribution of hydraulic conductivities within the remediation zone, the more effective the design of the flushing system. This parameter is also used to define the degree of hydraulic control that must be incorporated into the injection/extraction system design.
- **Heterogeneity:** The degree of permeability variation within the target DNAPL zone will also dictate sweep efficiency and to what degree vertical DNAPL mobilization will take place. The presence of low-permeability units, for example, may provide adequate capillary barriers to arrest downward DNAPL migration.
- **Sweep efficiency:** This issue is related to heterogeneity and permeability. There are a multitude of injection/recovery scenarios that could be used at a site. When dealing with purely saturated flow, the key issue is to achieve uniform flow path distribution within the flushed zone. By achieving a uniform flow field, dead spots are minimized, and removal efficiency is maximized. The design should also take into account preferential flow paths and be designed to eliminate short-circuiting within the subsurface. The most proven and accepted field-flushing methodologies include a five-spot configuration, line drive, and in some special cases, vertical well circulation. Sweep efficiency can be improved by incorporating mobility-control techniques, such as injecting foam and/or polymer.
- **Practical issues:** Infrastructure such as buildings and buried utilities can significantly impact the system's layout and footprint. Sufficient space needs to be provided to construct the required systems. For example, pile drivers for sheet pile walls, backhoes for trench construction, and tankage for fluids, all have significant space requirements.

Achieving sufficient hydraulic control to minimize the risk of injectate or DNAPL escaping out of the well field is of great importance in the design of chemical-flushing operations. Although incorporating physical groundwater barriers such as slurry walls or sheet piling to affect containment has been used on some small-scale field demonstrations, installing physical barriers for larger-scale flushing applications is unrealistic. In the absence of such physical barriers, incorporating hydraulic control wells into the well field, along with the optimization of extraction and injection flow rates, is an effective and cost-efficient method of achieving hydraulic containment. The number of hydraulic control wells necessary to accomplish hydraulic containment will vary with the hydrogeological characteristics of the site. For example at Hill AFB OU2, due to the narrow basin shape of the underlying aquitard and the low hydraulic gradients at the site, a single hydraulic control well upstream of the injection wells was adequate to maintain hydraulic control. At other sites, two or three hydraulic control wells could be required for a similar well configuration. An appropriate strategy for achieving hydraulic control

should be selected and verified during the conduct of the design simulations. In many cases, a combination of slight over-extraction (higher pumping rates) and the use of hydraulic control wells is sufficient to provide hydraulic control. A dual injection system, in which injection wells are installed with multiple screened intervals, can help provide vertical hydraulic control.

In order to develop an optimal design that meets the above listed objective, the SEAR design process utilizes simulations to predict the dynamics of the surfactant flooding process. Numerical models provide a tool for investigating and predicting how variations in subsurface properties will affect a chemical flood design. The design process typically involves iterative runs of a numerical model that represents the geosystem. The resulting numerical model is used to design the well field, to design tracer tests that amplify and refine the geosystem data, and finally to select the key design parameters for the surfactant/cosolvent flushing. Modeling results can be used to make the design more robust with respect to potential performance variations caused by uncertainties in site characterization. The following paragraphs discuss the use of simulations for SEAR system design and optimization.

Elements of a chemical flood design that are typically optimized using numerical models include

- injection and extraction flow rates necessary for adequate hydraulic control;
- mass of surfactant required to solubilize and/or mobilize the DNAPL;
- effect of heterogeneities on recovery of the DNAPL and chemical injectate; and
- duration of the preflush water flood, chemical flood, and postflush water flood.

A multiphase fluid flow and transport model such as the University of Texas chemical flooding simulator (UTCHEM) is required to solve the multiphase flow problems posed by in-situ flushing. UTCHEM is a multiphase, multicomponent, three-dimensional modeling program capable of simulating DNAPL migration and groundwater flow and transport in aquifers. However, a basic single-phase groundwater flow model, such as MODFLOW, can be used in a limited capacity to represent the geosystem to assist in preliminary well field design, including the selection of the well pattern, well spacing, and flow rates. It may also be used to design a conservative tracer test; however, a nonconservative, or partitioning, tracer test and the flushing process itself require a three-dimensional (3-D) multiphase transport model.

The numerical simulation design process typically includes model construction, model calibration, and, finally, predictive simulations to assist in the selection of operational parameters for the flood. The first step involves implementing the available and pertinent geosystem parameters (as described in Section 3.2) into the numerical simulator and utilizing that model to help design a well field for the flood. Following development of a well field design including well locations and screen intervals, simulations may be conducted to design interwell tracer tests. Tracer test data and available aquifer test data is then used to calibrate the final numerical model for permeability and DNAPL volume and distribution. The final step in the design simulation process requires incorporating surfactant-phase behavior data collected during chemical selection studies. At this point, a multiphase fluid flow and transport model must be used. Multiphase flow simulations are conducted to study the dynamics of flooding the DNAPL-contaminated zone with the selected chemical formulation. The variables that have a major influence on the flood design but are uncertain are investigated using sensitivity simulations to affect a design robust

enough to overcome these uncertainties. These variables include uncharacterized heterogeneities in permeability and DNAPL distribution. Results of these sensitivity studies are then used to select the surfactant injection scheme, determine chemical requirements, and establish injection and extraction rates for different phases of the flooding operations. The modeling predictions typically utilized to finalize a design study are

- amount of DNAPL (and contaminant) recovered from within the model aquifer (by each extraction well);
- amounts of surfactant and cosolvent (if used) recovered by each extraction well;
- pressure/water level at the injection and extraction wells;
- histories of contaminant, surfactant, DNAPL saturation, microemulsion, and pressure at selected times during the predictive simulation; and
- total effluent concentrations of contaminant, surfactant, cosolvent (if any), and electrolyte as a function of time for each extraction well.

4.1.3 Unit Process Design

The injection/recovery system usually consists of a mixing system, in addition to the individual surfactant injection wells and hydraulic control wells that make up the well field. Proper design of the mixing and injection subsystem is another crucial step in a successful chemical flood. In many cases, especially using the ultralow IFT mechanism, the specifications of the flushing chemical require precision mixing and injection and, in some cases, special handling precautions. If these specifications are not satisfied, the performance of the chemical flood may be diminished or hazardous. For example, when using cosolvents, the potential flammable hazard demands the selection of appropriate explosion-proof equipment. These processes must also be coordinated and integrated with the extraction and treatment processes if extracted fluids are to be reinjected at the site.

A generic flow schematic for an injection system is shown in Figure 4-2. The flow diagram for a surfactant flood can vary dramatically depending on site conditions and the surfactant selected for the project.

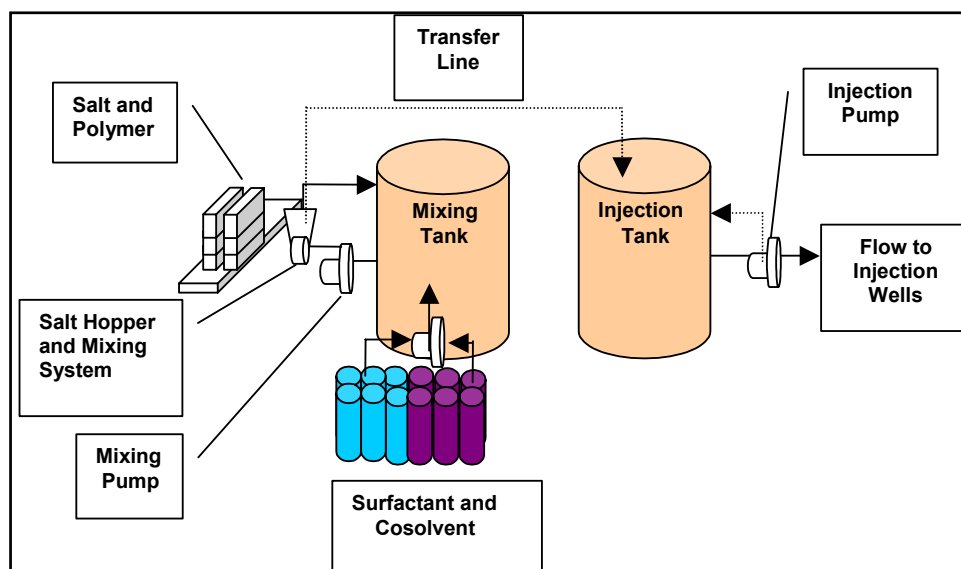


FIGURE 4-2. Schematic of Surfactant/Cosolvent Injection System

The injection/recovery system design factors include the following:

- **Flow rates:** Since the subsurface hydrogeology controls the rate at which fluids can be injected, the injection flow rate is usually determined using aquifer testing during the predesign phase and subsequent numerical simulations during the design phase. Aquifer testing is used to test hydrogeological properties at the site, including injection rates, injection pressures, and recovery rates. Aquifer information is then placed into the model that is used to design the injection/recovery scheme for the site. The resulting design parameters should include individual flows to each injection well. This information is then used to select piping, tank sizes, mixing system capacity, and pump sizes.
- **Source or makeup water:** It is also important to incorporate the makeup water source into the design. The overall flow process can change substantially depending on whether a fresh water source is used or fluids produced from the subsurface are recycled. For example, small changes in water quality (e.g., calcium) can have a profound effect on performance of a surfactant system optimized for ultralow IFTs.
- **Injection pressure:** In many cases, fluids are injected under pressure to improve sweep efficiency. The injection pump and piping must be designed to handle the potential maximum pressure expected during flushing operations. In addition, wells must be designed to handle the design injection pressures.
- **Chemical volumes and concentration of flushing solution:** The volumes, characteristics, and concentrations of the flushing solutions should also be determined during the bench-testing portion and the modeling conducted during the design stage. Information that should be obtained includes the target injection concentrations (covered

in the bullet below), chemical recycling if necessary, chemical properties, and volumes. Each unit process must be designed to account for these issues.

- **Chemical mixing considerations:** Several mixing alternatives exist, including prefabricated hydraulic and mechanical mixing systems. The systems can also utilize electronic mixing processes that analyze the concentration of the surfactant or cosolvent and automatically inject the desired amount. This is particularly important when recycling the flushing solution. Maintaining a constant concentration of the flushing solute can be easily achieved with the use of an integrated chemical sensor injection system. In general, the optimal surfactant/cosolvent electrolyte ratio should be carefully monitored to achieve the design performance specification for the flood. Mobility control using polymer requires additional specialized process equipment and expertise to properly hydrate and mix polymer and the surfactant injectate. The increased viscosity of the resulting solution needs to be taken into account when selecting pumps and process monitoring equipment. Some injectate ingredients may also require additional mixing requirements. For example, the electrolyte solution in the surfactant formulation usually requires mixing aqueous solutions of dry chemicals.
- **Flammability and other health and safety issues:** Typically, aqueous surfactant solutions will pose minimum risks regarding flammability or toxicity. Surfactant raw material may be prepared with short chain alcohols (e.g., ethanol and isopropanol) to increase the active concentration. Safety precautions are required when handling these types of surfactant materials. When alcohols are used as the primary flushing reagent or as a cosolvent in the surfactant flood, engineering control should be carefully designed to prevent the hazard of alcohol flammability.
- **Process chemical storage:** Material Safety Data Sheets (MSDSs) for chemicals used on site should be kept on site in the work plan. Chemical storage procedures depend on the volume required for each chemical. Typically, secondary containment is required for bulk storage of chemicals. A general rule of thumb is to design the secondary containment volume to hold 110% of the largest storage vessel staged in the containment area.
- **Regulatory issues:** Another key design issue that must be considered is regulations that could affect the injection of surfactants, cosolvents, or other operational aspects of the flood. It is important to review regulations, obtain the proper permits, and discuss the proposed process with regulators to ensure regulatory concerns are addressed. Regulatory issues are discussed in Section 7.0.
- **Economics of labor vs. automation:** Operations and maintenance (O&M), monitoring, and engineering labor are required to operate a system. The number of operators needed depends on the size and complexity of the system. For relatively new environmental technologies, such as surfactant/cosolvent flushing, a significant amount of time may be required for monitoring and engineering to evaluate the operation of the system and prepare reports of the operations. The cost benefit of automating the system should be evaluated. An automated system provides continued control, monitoring, and alarms that

notify the operators when certain parameters deviate from design specifications. For a site in a remote area, automation increases the flexibility of the system and reduces the cost for traveling and operation (Meinardus et al., 2000).

Ensuring that the equipment operates within design parameters during the project is very important. The less labor-intensive the operations are, the more cost-effective the project will be. As a result, it is important to minimize unforeseen labor efforts through effective equipment design. Most of the process equipment that will be used during a surfactant/cosolvent flush can be obtained off the shelf and can be operated with minimal maintenance. The process equipment may include oil/water separators and other treatment equipment, filters, surfactant solution make-up tanks, pumps, flow control, valves, pipes, and process-monitoring equipment. Much of the process equipment is modular and can be trailer-mounted.

4.1.4 Waste Management Operation

The technical and economic viability of surfactant/cosolvent flushing depends not only on the successful injection and extraction of the chemical flushing solutions, but also on the handling and treatment of the recovered fluids. Because of the need to accommodate the significant number of variables that are contaminant- and site-related, surfactant/cosolvent flushing projects are site-specific (Roote, 1997). Consequently, methods for handling or treating produced fluids will be customized, depending on the nature of the produced fluids, the existing wastewater treatment infrastructure if any, and the objectives of the project. Laboratory testing is necessary to develop an effective treatment process for site-specific applications. However, general process flow diagrams that incorporate well-known separation technologies exist (AATDF, 1997).

In cases where the source zone to be remediated is very large, surfactant/cosolvent flushing may not be economical unless surfactant/cosolvent can be recovered from the produced fluids and reused (AATDF, 1997). Although recycling the materials may not be a critical factor for most projects, in all cases the elutriate treatment system will be an important component of the total remediation process. However, ease and efficiency in isolating and concentrating the contaminant from the various waste streams that will be generated is not only dependent on the downstream elutriate treatment system processes, but should be considered as a key criteria in the selection and design of the surfactants/cosolvents flushing solutions. Customizing the flushing solutions to provide both effectiveness in contaminant removal and optimization of methods for handling and treating recovered fluids will yield the most cost-effective processes.

If an economic analysis indicates that recycling of the produced fluids may be feasible, proper engineering devices should be incorporated into the aboveground treatment to maximize the portion of the generated fluid to be reused. In general, recycling is only economic if higher surfactant/cosolvent concentrations (> 3 wt%) and multiple PVs (> 3 PV) are injected. The reuse of surfactant/cosolvent solutions is less difficult than cosolvent reuse. Processes used for recycling surfactant/cosolvent include ultrafiltration, pH-adjustment, and precipitation. The properties of the surfactant/cosolvent formulation to be used and economic considerations determine which of these recycling processes is selected.

Separation/treatment technologies include gravity separation, dissolved-air flotation, chemical demulsification, acid treatment, heat treatment, air stripping, steam stripping, membrane separation, biological treatment, evaporation, solvent extraction, pervaporation, oxidation, and addition of absorption media. Carbon adsorption is an acceptable application for polishing the treatment system effluent to discharge standards, but it is generally not a good stand-alone treatment for surfactant/cosolvent flushing systems. In most cases, combinations of several of these technologies are required to satisfy the goals of the remediation program (AATDF, 1997).

The potential to discharge some amount of surfactant/cosolvent in the treated effluent stream exists for all scenarios. Depending on the final disposition of the effluent, an understanding of the toxicity and biodegradability of the residual materials may be required. These environmental toxicity and biodegradability data (e.g., chemical oxygen demand [COD] and biochemical oxygen demand [BOD]) should be available from the surfactant/cosolvent manufacturers or can be measured using standard wastewater analytical techniques. Another significant characteristic of surfactants that must be understood is the potential to create foam in some treatment processes, which can severely inhibit the efficient treatment of the effluent stream.

In addition to wastewater, other wastes can be generated in the implementation of surfactant/cosolvent flushing processes. Representative samples of each type of waste should be collected and analyzed as appropriate to characterize the media for disposal. A summary of these procedures follows:

- **Soil:** Contaminated soil waste is typically generated during installation of process wells and monitoring wells.
- **Hydrocarbon off-gas:** Off-gas treatment may be necessary and can be achieved through engineering controls, such as granular activated-carbon canisters.
- **Solid waste:** These types of wastes typically include personnel protective equipment (PPE) and material contaminated by contact with DNAPL.
- **Free phase DNAPL:** Recovered free-phase DNAPL in the treatment process unit must be disposed of in accordance with applicable requirements.

4.2 Site Preparation

Site preparation is important to ensure that the site is suitable for application of the technology. Following are the key issues:

- availability of storage space to hold chemicals;
- space for process equipment;
- need for secondary containment;
- electrical service; and
- availability of other infrastructure and utilities, including water, compressed air, sanitary facilities, and telephone service.

Equipment should be protected from inclement weather to avoid unnecessary maintenance and repair issues. For example, it is recommended that wells be protected to prevent debris from entering the well bore and damaging or impeding pumps and other process equipment. Outside electrical connections must be installed correctly to avoid electrical hazards in wet locations. Gauges, computer components, and electronic components can also be damaged during a chemical flood if leaks develop that spray or drip on the equipment.

4.3 System Startup

Prior to the operation of the system, a safety check should be completed to ensure that all aspects of the process are working properly and safely. All electrical connections should be watertight and explosion-proof to minimize health and safety issues. All equipment should also be wet tested and calibrated. If the equipment used to mix the injectate is not working properly, it could result in an ineffective or even detrimental flood.

Before starting a surfactant/cosolvent flood, system components necessary for metering and monitoring (e.g., flow meters, pressure transducers) need to be calibrated and/or proved out. Piping and fluid conveyance subsystems should be tested for leaks, proper flow routing, and flow rate control at anticipated process flow rates with potable water for the injection system and groundwater for the extraction system.

4.4 System Operation

An ever-present challenge in conducting remediation projects is the occurrence of the unexpected. The loss of power or the failure of extraction well pumps could compromise the flood and hydraulic control over fluids in the subsurface if not rectified in a timely fashion. Therefore, not only project managers, but also field technicians should be aware of the consequences of a process upset. Field technicians should not only specialize in their area of expertise, but also have a working knowledge of the overall process so that system maintenance and repair issues can be addressed quickly and effectively. In addition, system operators must remain alert to changing field conditions to keep operations running smoothly, especially during the chemical injection period of a flood, which is relatively short in duration. A well-designed surfactant flood must be implemented and executed correctly to be successful.

A surfactant/cosolvent flood typically consists of several consecutive operational phases:

- initial water flood (and electrolyte addition),
- surfactant/cosolvent injection period, and
- postsurfactant/cosolvent injection water flooding.

The purpose of the initial water flood is to establish steady-state flow conditions in the aquifer. In addition, this water flood is usually used to establish a fairly homogeneous electrolyte concentration in the target volume to precondition the aquifer geochemically. This ensures that the surfactant/cosolvent will have the appropriate salinity for optimum performance. This phase can also serve as a “shake down” and prove out period that provides the opportunity to check that the process equipment is functioning properly. The initial water flood usually requires one

pore volume or more of flooding with the electrolyte solution of the appropriate concentration. Flow rates and water levels should be static and stable before proceeding on to the chemical injection phase.

Surfactant/cosolvent injection proceeds without flow interruption from the initial water flood for a number of pore volumes as specified in the flood design. This phase of the flood typically requires two to 10 pore volumes of throughput, depending on surfactant/cosolvent efficiency, DNAPL type, hydrogeologic conditions, and remedial objectives. Process monitoring of the effluent in real time can be used to make this phase more dynamic by providing indications of where in the well field surfactant/cosolvent flow should be focused and when surfactant injection operations can cease (see Section 5.1).

Finally, the chemical injection period is followed by a water flood or water drive in order to transport fluids across the target zone and recover the injected fluids and contaminant at the extraction wells. The number of pore volumes required during this phase is usually a minimum of 1.5 times the number of pore volumes used for the surfactant flood. If a PITT is used to measure final DNAPL saturations in the aquifer following the flood, it can be combined with the final water flood as long as surfactant concentrations in the aquifer are sufficiently reduced to prevent false partitioning of tracers into the surfactant/cosolvent instead of any remaining DNAPL. Such partitioning should be investigated during the bench-scale testing phase of an in-situ flushing project by conducting a preflood PITT and then a surfactant flood in a column filled with field soil and contaminated with DNAPL from the site. Once the column has been surfactant flooded, a postsurfactant flood PITT should be conducted to provide an independent mass balance (in addition to volumetric measurements) and to determine if the surfactant remaining in the column interferes with the partitioning tracers.

5.0 PROCESS MONITORING

The purpose of this section is to describe the monitoring requirements to ensure a successful chemical flood. Major monitoring tasks include

- process quality control,
- hydraulic control (water level),
- injection/extraction system/fluid flow rates,
- waste stream monitoring, and
- sampling and analytical methods (surfactant/cosolvent contaminant analysis and groundwater quality monitoring).

5.1 Surfactant/Cosolvent Contaminant Analysis

A key factor contributing to the successful application of this technology is the ability to ensure that the surfactant/cosolvent is doing what it was designed to do. In some cases (e.g., Type III or ultralow interfacial tension floods), small fluctuations in electrolyte concentrations or ratios can have profound effects on the performance of the technology because the chemical system can be pushed into unfavorable phase behavior. Moreover, the migration of the injected fluids should be

monitored to ensure that they are flowing through the targeted areas. In addition, cost and time savings can be realized by monitoring concentrations of contaminants of concern (COCs) in recovered fluids and evaluating when the remediation goals have been met at the site. As a result, it is very important to monitor both surfactant and contaminant concentrations during a surfactant/cosolvent flood. The frequency and locations of that monitoring is dependant on the subsurface conditions at the site and the site-specific conditions. There are several critical areas where monitoring should be conducted in any flushing scenario. These areas are listed in Table 5-1.

Table 5-1: Locations and Frequency for Key Analysis during Operations

Location	Target Analytes	Frequency
Recovered fluids	Surfactant/cosolvent, Na ⁺ /Ca ⁺² , COC	Site specific
Injection solution	Surfactant/cosolvent, Na ⁺ /Ca ⁺²	Site specific
Unit process	Surfactant/cosolvent, COC	Site specific
Monitoring wells	Surfactant/cosolvent, COC	Site specific

Although each situation is unique and the sampling frequency is listed as “site specific,” it is believed that a minimum of 20 to 30 sampling events will be required to define the breakthrough of surfactant and contaminant. The following sections describe in more detail the need to monitor at various locations. Depending on the project, automation may be incorporated into the process to save time and money.

5.1.1 Recovered Fluids

In many cases, the amount of surfactant/cosolvent and contaminant recovered during a project is measured by evaluating the dissolved concentration in the recovered fluids multiplied by the volume of fluids recovered. In order to provide an accurate calculation, the recovered flow of fluids must be carefully recorded and documented. In addition, samples must also be taken at sufficient intervals to allow for an accurate measurement of mass. The interval required to provide this level of accuracy depends on data objectives required for the site, project life expectancy, and size of the project. Also, if surfactant is being reused, analyses will also be required to determine how much additional “fresh” surfactant/cosolvent will be required to achieve the specified injection concentration.

In most cases, conservative tracer testing and numerical modeling are utilized to determine or predict expected breakthrough of injected solution and contaminant. This information is then used to design a sampling plan or approach. During a typical flushing project, the sample

frequency is set so that a minimum of 20 to 30 data points is collected from each well during the flood. This number of samples provides enough data to plot an effective breakthrough curve and measure trends throughout the test.

Another key issue is the location of sampling points. In the absence of good design information (e.g., a CITT or PITT), sampling and monitoring flow at individual recovery wells provides a great deal of important information, including potential preferential flow paths, differences in breakthrough times, and flushing performance in different areas of the treatment zone. However, this is not accomplished without additional expense, and it is recommended that the design basis be adequate enough to include such uncertainties and to avoid such additional costs. In some cases, it may be sufficient to monitor the combined recovered flow at a single location, although the system cannot be optimized in terms of surfactant delivery during the flood without sampling individual recovery wells.

5.1.2 Injection Solution

On any flushing project, a critical logistical issue is the mixing and injection of the flushing solution. Whether the solution to be used is a surfactant, cosolvent, additive (Na^+ , Ca^{+2}), or a mixture thereof, field personnel who are mixing and injecting the solution must meet the design specifications for the project. This is especially true for surfactant-surfactant and surfactant-cosolvent mixtures. Also, when fluids are being recycled, the mixing process can become quite complex, which reinforces the need for careful quality assurance and control monitoring of the injected solution.

As mentioned in previous sections, the sampling and monitoring plan will vary depending on site conditions, flushing solution, degree of recycling, mixing process, and data quality objectives. In some cases, the surfactant/cosolvent is mixed in batches and sampled prior to injection to ensure specifications are met. Field-screening tests such as titration, surfactant probes, and phase behavior tests can be utilized to test fluids without the expense of gas chromatograph (GC) or liquid chromatograph (LC) analysis. If any of these methodologies is incorporated, QA analysis using GC or LC should be conducted to verify the effectiveness of the selected method.

If a continuous mixing system is utilized, an inline sampling and analysis system may be more cost-effective. Inline samplers can be used to collect the samples from the desired locations. The samples can then be analyzed on site using GC or LC to obtain real-time data. This system can even be integrated with the chemical mixing system to meter in the required amount of chemicals.

5.1.3 Unit Processes

At most sites, unit processes are used to either remove contaminants from the recovered solution or concentrate surfactant/cosolvent for reuse. It is important to ensure that each of these processes is performing within design criteria. To do this, samples should be taken and analyzed appropriately. Most of these processes can easily be designed to reach steady state and operate with very little fluctuation in performance. As a result, the sampling frequency may not be as

intense as that required in the injection or recovery streams. However, it is still very important that the sampling plan incorporate a high enough frequency to ensure that the process is operating within design parameters and to provide an accurate estimate of contaminant mass recovered by the system.

5.1.4 Monitoring Wells

Sampling monitoring wells during a chemical flood is an important way of confirming hydraulic capture (vertically and horizontally) and monitoring progress within the targeted zones. Monitoring wells should be placed below, above, and around the zone to be remediated to measure for both surfactant escape and changes in contaminant concentrations. Multilevel samplers and monitoring wells can also be installed within the remedial zone to measure the concentrations of injectate and contaminant within the test cell. This information can be very useful in guiding remedial efforts to ensure the flushed solution contacts the areas of highest impact. The sampling frequency for these wells depends on the travel time of the flushing solution to the sampling point. This can be predicted using modeling and/or tracer testing. Once the expected time of migration is calculated, the sampling interval can be designed so that the impact at the monitoring location is not missed.

5.2 Groundwater Quality Monitoring

One of the criteria for determining the success of chemical flushing is a significant reduction in aqueous contaminant concentrations observed in the injection, recovery, and monitoring wells after the chemical flood. Before the surfactant/cosolvent flood, a suite of baseline groundwater samples should be collected to determine the preflood aqueous contaminant levels. Typically, these samples are collected immediately before the surfactant flood, during the prestabilization pumping period (presurfactant water flood). Care should be taken in interpreting the results of groundwater samples from the well field taken during and after the flood. For example, if the treatment zone only covers a portion of the contaminated plume, contaminant levels in the wells located at the edge of the treated area will be biased by groundwater drawn from the untreated zone. However, surrounding groundwater during the flood will not bias the wells near the center of the treated zone.

Postflood groundwater sampling should be carried out after the groundwater system is re-equilibrated. An analysis of the groundwater flux should be conducted to determine when postflood groundwater samples should be collected. To assess any rebound of contaminant concentration, postsampling events can be conducted quarterly, semiannually, or annually, depending on the magnitude of groundwater flow across the zone of interest.

Additional groundwater samples can also be collected from selected wells outside the treatment zone to verify that DNAPL and surfactant did not migrate out of the well field due to the surfactant/cosolvent flood. Sentinel wells can also be used to monitor aquifers without DNAPL contamination above or below the treatment zone to verify that undesired migration of injectate or contaminant is not occurring during the flood.

5.3 Injection/Extraction Flow Rate Monitoring

The injection and recovery flow rates should be monitored closely during the flood. Accurate flow rate measurement will be crucial for estimating the recovered NAPL and surfactant/cosolvent mass as previously described. In addition, unbalanced injection and extraction rates will result in poor sweep efficiency or hydraulic capture in the treatment zone. Even worse, significant fluctuation of the water table might exert hydraulic control over the injected surfactant/cosolvent in the DNAPL zone.

Most extraction system processes are amenable to automatic control using common process control software. Alarm systems can be installed to provide the capability of emergency shutdown if the system fails. During the flood, operators should manually record the injection and recovery rates regularly, along with other pertinent operational parameters. These parameters may include transferring flow rates, pressure readings of the process units, integrity of the filter and/or membrane, liquid levels in intermediate and waste storage tanks, effluent water quality, and quality of air emissions.

5.4 Waste Stream Monitoring

An air stripper might be used to remove dissolved VOCs. The water quality before and after use of the air stripper should be monitored closely to evaluate treatment efficiency. Proper action and adjustment (via changing the air-to-liquid ratio) should be taken to resolve the stripper performance if contaminant levels are above treatment objectives. This is especially crucial if surfactant and groundwater are recycled and reinjected. An air emissions permit may be required for such systems, and in some cases, a secondary treatment device such as a carbon filter may be required to treat VOC emissions from an air stripper.

During the flood, a significant amount of fine particulates will typically be extracted. The accumulation of these particles in the prefiltration or pumping system may impair performance if the clay content of the aquifer is significantly high. Periodic cleanup of the solid sludge will prevent any major damage of the process equipment. Exhaustion of carbon canisters for air emission control could occur quite rapidly if significant quantities of VOCs and cosolvents are dissolved in the waste stream. Loss of recovered NAPL (such as chlorinated solvents and gasoline fuel) as a result of volatilization could be significant during the aboveground treatment. Therefore, the recovered NAPL volume could be significantly underestimated based on the collected NAPL volume from the treatment system. If foaming results due to the presence of the surfactant, the addition of proper antifoaming agents into the waste stream will effectively eliminate the problem.

5.5 Sampling and Analytical Methods

Groundwater sampling should be conducted with under-flow conditions to minimize the interference of colloidal particles in the pump. For different liquids and air streams, the standard operation procedures of sampling at that specific site should be followed to maintain sample integrity and prevent cross-contamination. Typically, field blank samples should be taken at a

frequency of ten percent of the total samples collected. The presence of surfactants will reduce volatilization loss while collecting groundwater samples. Sometimes, bubbles might be present in the headspace of sample vials due to the surfactant solution, but these do not significantly affect analytical results.

VOCs analysis is conducted with common gas chromatograph methodology. If a purge-and-trap sampler is used at GC, the presence of surfactant might produce a foaming problem. This problem could be resolved by either directly injecting the sample into the GC if at high VOC levels, or adding antifoamer to the sample cuvette before purging the samples. Surfactant analysis is carried out by titration or common high-performance liquid chromatograph (HPLC) methodology with different detectors.

6.0 PERFORMANCE ASSESSMENT

Assessing the performance of a chemical flood can be done in a variety of ways. Perhaps the most direct method is measuring the amount of DNAPL mass removed. This can be complicated, however, given the uncertainty associated with estimating the initial amount of DNAPL mass present at a site. The performance of a surfactant/cosolvent flushing system can be measured by the following metrics: (1) the final average DNAPL saturation (i.e., the volume percent of the pore space that still contains DNAPL); (2) the percentage of the initial contaminant mass removed; (3) the source strength or mass flux of contaminants emanating from the source; (4) the percentage of the injected chemicals recovered (a measure of the efficiency of hydraulic control); and (5) the risk associated with any DNAPL remaining after treatment, as well as the risk reduction accomplished with the DNAPL-removal action.

Monitoring contaminant and injectate chemical concentrations at sentinel locations outside of the treatment zone can provide another performance measure related to hydraulic containment and flood efficiency. Sampling capillary barriers to verify that these units have not been impacted by vertical migration should also be considered. To be useful, both these performance measures have to be based on an accurate preflood characterization of baseline conditions.

With respect to evaluating the effectiveness of DNAPL removal, the final average DNAPL saturation is a more stringent standard than the percentage of DNAPL recovered, which overlooks the risk of unremoved DNAPL. Usually, if the DNAPL recovery is high, the recovery of injected chemicals will also be high; however, the opposite is not necessarily true, as poor sweep of contaminated zones may occur even if injected fluids are effectively captured. If the recovery of DNAPL is low, evaluating the recovery of injected chemicals may provide some insight as to why this occurred. If poor recovery of injected chemicals is obtained, it is necessary to determine the risk associated with the compounds remaining in the aquifer. In all cases, the risk of unremoved DNAPL and the reduction of risk due to the removed DNAPL should be considered in assessing the technology performance (NAVFAC, 2001, 2002a, 2002b).

Performance assessment measures differ from system monitoring to ensure that the surfactant/cosolvent system is operating as designed. Meeting performance criteria (system monitoring) is dependent on the following:

- maintaining the quality of injected chemicals;
- maintaining hydraulic capture of fluids in the well field;
- maintaining a sufficient duration of chemical flooding and postinjection water flooding operations; and
- monitoring system parameters and recording data to validate that the performance criteria have been met (NAVFAC, 2002b).

Remedial objectives, performance criteria, and exit criteria should be established early in the project, as they directly impact the design and operational strategy of any selected remediation system.

7.0 REGULATORY

There are a variety of regulatory concerns that may be associated with the implementation of surfactant/cosolvent flushing since these technologies involve the introduction of flushing reagents into contaminated groundwater, typically through injection wells. While surfactant/cosolvent flushing offers significant benefits, its use may be restricted or prohibited by regulatory or procedural barriers in certain states. To facilitate regulatory acceptance, it is important to include regulators as part of the team that originally selects surfactant/cosolvent flushing as a remedy and to involve them in the process of designing and implementing the flood. If specific permits are not required, review and approval of the work plans are typically the formal mechanism by which regulatory approval is obtained.

7.1 Permitting

For CERCLA sites, the remedial alternatives must satisfy Applicable or Relevant and Appropriate Requirements (ARARs). Non-CERCLA sites (RCRA sites, private sites, state Superfund sites, federal facilities, etc.) may also have potentially applicable regulations at the state and federal level. In particular, Underground Injection Control (UIC) regulations may be applicable for both CERCLA and non-CERCLA sites.

The UIC program, under the Federal Safe Drinking Water Act, regulates injection wells. Under the UIC program, injection of any fluid into a well is prohibited, except as authorized by permit or rule. The purpose of the UIC program is to protect underground sources of drinking water by prohibiting injections that may affect water quality. State UIC programs may be delegated complete or partial enforcement responsibility (or primacy) by USEPA (USEPA, 1996b). As of June 2001, USEPA had delegated primacy for all well classes to 33 states, Guam, the Commonwealth of the Mariana Islands, and Puerto Rico. Seven states share primacy with USEPA, which administers UIC programs for the remaining states, the Virgin Islands, American Samoa, and Native-American lands (See Figure 7-1).

and Drug Administration (FDA) direct food-additive status (some referred to as edible surfactants), which are common in food products and other consumer goods (Shiau et al., 1994; Roote, 1998). Though selection of food-grade surfactant for environmental application appears less critical as the regulatory acceptance of this technology increases, use of food-grade surfactant still provides some advantages, such as being easily biodegraded in the subsurface if left behind and having less impact on wastewater treatment plants during aboveground treatment. However, there are only a few direct food-grade anionic surfactants available for selection as compared to nonionic surfactants. Most food-grade nonionic surfactants may be difficult to use in recovering NAPL due to their high sorption losses. Their use also makes it more difficult to achieve an optimal microemulsion system.

Different surfactant types and structures represent a wide range of toxicity to animals and plants. The ingestion hazard to humans of many anionic or nonionic surfactants is low (e.g., swallowing residual dish soap is not harmful, and ingestion of larger amounts may result in diarrhea). However, some of these surfactants may be hazardous to aquatic life. For example, ethoxylated alcohols (which have been used in remediation projects and are common in detergent formulations, including dish soap and laundry detergent) are toxic to fish but are not a significant environmental concern when used as household detergents because they readily degrade in biological wastewater treatment systems.

7.1.2 Waste Disposal

Handling and treatment of fluids recovered from surfactant/cosolvent flushing is a critical component to the success of a surfactant/cosolvent project. The ability to cost effectively handle the fluids produced should be considered and evaluated concurrently with the design of the surfactant/cosolvent solution. Modifications to the solution design may be necessary to develop a system that is effective in contaminant removal and also cost-effective. The disposal of these fluids and the associated permits need to be considered in the planning stages.

As explained in Section 2.0, once the groundwater/elutriate mixture is recovered, the groundwater and elutriate are treated and either reinjected into the geosystem or discharged. Common treatment processes include gravity separation, dissolved-air flotation, chemical demulsification, acid treatment, heat treatment, air stripping, membrane separation, biological treatment, evaporation, solvent extraction, pervaporation, oxidation, and addition of absorption media. The primary objectives of produced fluids treatment will depend on the specific project scenario and remediation goals. Possible produced fluids treatment objectives (AATDF, 1997) include the following:

- separation and reuse or recycling of “used” surfactants and cosolvents;
- separation and reuse of recovered product (free-phase DNAPL), if applicable (e.g., fuel oil, solvents);
- reduction of contaminant levels in the produced fluids to the extent necessary and economical before discharging to a POTW or industrial WWTP;
- production of an effluent that can be discharged to a WWTP without adverse impacts (e.g., foaming);

- reduction of site contaminants and pollutants in the produced fluids to the extent necessary to discharge the water to surface water under a NPDES permit; and
- concentration of an organic and/or inorganic phase for separate, off-site disposal or treatment with discharge or reuse of the water.

If the volume of the fluids produced is relatively low, it may be cost-effective to haul all of the fluids off site for treatment or disposal. Incineration of the fluids may be required. If it is possible to separate free-phase DNAPL, it may be possible to recycle this material. Typically, the waste hauler and incinerator facility will be familiar with the regulatory and paperwork requirements for shipping and disposing of the fluids. The generator of the fluids should review the procedures to ensure that all applicable regulatory requirements are being followed.

In addition to the fluids that may need to be discharged to a POTW or surface water under an NPDES permit, other wastes generated may include wastewater treatment sludge and residual solids, spent carbon, and spent ion exchange resin. These wastes must be managed and properly disposed of in order to avoid cross-media transfer of contaminants. Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDRs), which require treatment of wastes to best demonstrated available technology (BDAT) levels prior to land disposal, may sometimes be determined to be ARARs for CERCLA response actions. These wastes may or may not meet the treatment levels set by BDAT in all cases. The ability of the surfactant/cosolvent flushing treatment process to meet required treatment levels is dependent upon specific waste constituents and waste matrix. USEPA has made the treatability variance process available to ensure that LDRs do not unnecessarily restrict the use of alternative and innovative treatment technologies.

In response to ITRC's and California's requests for clarification on USEPA's policy regarding reinjection of contaminated groundwater, Elizabeth Cotsworth, Director of USEPA's Office of Solid Waste, issued on December 27, 2000, an USEPA Guidance Memorandum, *Applicability of RCRA 3020 to In Situ Treatment of Ground Water*, clarifying USEPA's policy on the issue. This memorandum states that reinjection of treated groundwater to promote in-situ treatment is allowed under RCRA 3020(b) as long as certain conditions are met. Specifically, the groundwater must be treated prior to reinjection; the treatment must be intended to substantially reduce hazardous constituents in the groundwater, either before or after reinjection; the cleanup must be protective of human health and environment; and the injection must be part of a response action under CERCLA Section 104 or 106 or a RCRA corrective action intended to clean up the contamination. The memorandum notes that the addition of treatment agents (such as surfactants or nutrients) to extracted groundwater prior to reinjection constitutes "treatment" prior to reinjection. The guidance further states that a commercial chemical or chemical product [such as a surfactant] injected into groundwater also would not be subject to RCRA subtitle C regulations when it is injected into groundwater to treat a type of contamination if it had been proved successful elsewhere in treating such contamination, or if it had been commonly used in other forms of treatment of such contamination, or if it had chemical properties that could legitimately be expected to promote in-situ treatment of that contamination. This memorandum can be viewed on the Guidance Documents page of the ITRC Web site.

7.1.3 Surfactant/Cosolvent Reinjection

Handling and treatment of fluids recovered from surfactant/cosolvent flushing can be a critical component to the success of a surfactant/cosolvent project. In some cases, surfactant/cosolvent flushing may not be economical unless the surfactant can be recovered from the fluids produced and reinjected, along with additional surfactant/cosolvent solution. Although this is a site-specific issue, it is necessary to identify and optimize effective methods for handling and treating produced fluids. In fact, the ability to economically handle fluids produced should be considered and evaluated concurrently with the design of the surfactant/cosolvent solution. Modifications to the solution design may be necessary to develop a system that is economical and effective (AATDF, 1997).

7.1.4 Air Quality

Depending on the nature of the contaminants and the method used to treat produced fluids, it may also be necessary to obtain an air discharge permit. For example, air or steam stripping can be used to separate chlorinated solvents from the surfactant. It may be possible to directly discharge the off-gas from the stripper for a field demonstration if the total mass emitted is small, the duration is short, and the rate of emissions is low. An air discharge permit may be required if the mass emitted is greater than some threshold, typically dictated by the state. Modeling also may be required to demonstrate that air quality at a potential receptor site is not above allowable standards (AATDF, 1997).

Air emissions could be a concern for fuel or hydrocarbon contamination with biological treatment or similar technologies that result in aeration of the produced fluids. Permits and/or off-gas control may be required for these types of facilities (AATDF, 1997).

7.2 Health and Safety Issues

Drilling wells and installing and operating aboveground treatment equipment, piping, and pumps involve some risks to workers during surfactant/cosolvent flushing. Handling of chemicals is a concern since high concentrations of alcohol can be flammable and explosive. Concentrated alcohols should be handled with care to avoid personal injury and damage to the environment during transportation, handling, and injection.

As with any chemical usage, appropriate health and safety measures need to be considered during a surfactant or cosolvent project. Piping, hosing, and other plumbing lines that carry DNAPL-contaminated fluids should be leak-free, and proper safety precautions will be required for handling these fluids during daily operations. Secondary containment of DNAPL storage tanks is necessary. Alcohol drums should be properly grounded to avoid electrical hazards.

Most surfactants and all cosolvents contain alcohol, which can be a concern to all four routes of entry (inhalation, ingestion, skin absorption, and ocular absorption). Based on the level of concentration and type of chemical, required PPE may include anything from Level D to Level B, but in most cases Level C or D, as defined by OSHA, 29 CFR 1910.120 will suffice. Due to

the alcohol content, a protective suit made of natural rubber may be appropriate for dermal protection but only in cases of extremely high alcohol concentrations. If respiratory protection is deemed necessary, a full- or half-face respirator may be used with organic vapor cartridges. Personal protection may be required during chemical injection as well as during contaminant recovery, treatment, and/or disposal. If respiratory protection is deemed necessary, it must be utilized in accordance with OSHA 29 CFR 1910.134.

A Site Safety Plan prepared in accordance with OSHA 29 CFR 1910.120 must accompany any final work plan for surfactant and/or cosolvent flushing. The Site Safety Plan must include the appropriate Material Safety Data Sheets (MSDSs) for all chemicals proposed for use. The Site Safety Plan must identify the proper work zones, contamination reduction zones (if appropriate), and the support zone. It must further identify appropriate methods for isolating and protecting surrounding populations during project activities and details of an emergency response plan in the event of a chemical spill or other accident. The plan must be completed by a health and safety officer or project manager and must include appropriate training for individuals who will handle any hazardous chemicals.

Other safety considerations include

- hearing protection (OSHA 29 CFR 1910.95) when working around any mixing, drilling, or treatment equipment;
- hand protection (29 CFR 1910.138);
- eye protection (29 CFR 1910.133);
- foot protection (29 CFR 1910.136);
- overhead power lines;
- underground utilities;
- trenching safety and shoring requirements (OSHA 29 CFR 1926.650, 1926.651, 1926.652, 1926.653) if horizontal injection wells are specified and placed into trenches; and
- head protection (29 CFR 1910.135).

8.0 STAKEHOLDER/PUBLIC INVOLVEMENT

Stakeholders should be involved at every stage of the evaluation, selection, and permitting (if necessary) of treatment systems. Experience has shown that stakeholder input will benefit the project during this process. While these outreach efforts may go beyond regulatory requirements, they can create a more cooperative partnering between the facility, regulators, and the community. Stakeholder involvement could benefit from the development and implementation of a public involvement plan, public meetings, open houses, and technology working sessions.

Stakeholders could include local, state, and federal government officials, representatives of affected tribes, facility owners and operators, nearby residents, and environmental groups. This outreach should, at a minimum, address the local state and federal statutes, regulation, guidance, and policy provisions for community input. In addition, efforts beyond those specifically mandated may be warranted at individual sites on a case-by-case basis. Such involvement will

lead to better, more defensible solutions and will expedite the cleanup of contaminated sites. One of the objectives of the responsible parties should be to integrate tribes and stakeholders into all of their processes. Stakeholder discussions should clearly define the specific cleanup goals and criteria as explained in detail in Section 7.0.

Since surfactant and cosolvent flushing methods are relatively new technologies, when such technology is being considered for permitting or deployment, stakeholders and tribal representatives should be given the opportunity to comment on it and to make their issues, needs, and concerns known. Information about the technology, including alternatives analysis, should be made widely available for public comment.

Surfactant and cosolvent flushing methods may have the potential benefit of cleaning up a contamination problem quickly and, therefore, may be regarded favorably by tribes and stakeholders. However, since surfactant and cosolvent flushing methods involve the introduction of a chemical(s) into the environment, tribes and stakeholders will have the obvious question “Will it do any harm?” This question must be addressed carefully and honestly.

In some instances, one can cite examples where the technology has been tried before and report on its success or failure in each situation. In the case of an evolving technology, one may be in a situation where one is proposing a solution that is believed to be likely to work but has not been tried previously in a parallel situation. In this situation, accurate and honest information should be given. Explain all of the reasons why the technology is likely to work. Give the details of the possible failure scenarios. How likely is the technology to fail? What damage might be done? Have public discussion about the alternatives. It is possible that tribes and stakeholders will embrace an opportunity to try a new solution to a contamination problem, particularly if there is a good chance that it may succeed where other solutions are likely to fail. Be open about the potential risks and benefits. The affected tribes and stakeholders must be given the opportunity to weigh the potential risks against the potential benefits, since they are often the ones most directly affected by the contamination and by the success or failure of the cleanup technology. In certain cases, they are also the ones who bear the cost of the cleanup; or at the very least, as taxpayers, they serve as the insurer of last resort.

In 1997, the Tribal and Stakeholder Working Group (TSWG), working with the U.S. Department of Energy (DOE) Office of Science and Technology (OST), developed a set of principles for the integration of tribes and stakeholders into the process of evaluating and developing new technologies for the treatment of mixed low-level waste. The applicable TSWG principles and how they apply to a situation where in-situ surfactant/cosolvent flushing is being considered for the remediation of subsurface contamination are discussed below.

1. **Minimize effluents:** Clean up contamination as quickly as possible. Avoid the generation of reaction side products and new contaminants.
2. **Minimize effects on human health and the environment:** Protect present and future drinking water supplies. Minimize the potential for accidents.

3. **Minimize waste generation:** Minimize the production of waste from the cleanup effort.
4. **Address social, cultural, and spiritual considerations:** Minimize land use and habitat destruction in the cleanup process. Discuss the transport of chemical reagents with tribes and stakeholders, and adapt such transport to address their concerns. Respect the social, cultural, and spiritual values of specific sites. Minimize noise and traffic. Protect local vistas. Include the costs of tribal and stakeholder participation in cost estimates and budgets. Include the costs of compliance with intergovernmental agreements in cost estimates and budgets. These cost estimates may also include evaluations of the energy use throughout the remedy's life cycle. If possible, these could include comparative remedy evaluations that are presented at stakeholder meetings.
5. **Provide accurate, complete, and understandable information in a time frame that allows stakeholders to have an impact on the remedy selection process:** Explain the technology screening and evaluation process. Provide information about any previous applications of the technology. Provide information about the potential hazards, risks, and benefits of the remedy. These evaluations could include impacts on local and private wells, transportation, dust, noise, and air buffer zones. Keep the tribal and stakeholder representatives involved and informed throughout the evaluation, selection, permitting, and deployment processes. The senior management staff of the company implementing the remedy needs to understand community concerns and be vested in the remediation process. Independent technical advisory resources should be made available to the tribes and stakeholders whenever feasible.
6. **Incorporate tribal and stakeholder involvement into the responsible parties' procurement process, the permitting process, and the contractor's performance evaluations.**

When an evolving technology such as surfactant and cosolvent flushing is considered for application to a difficult problem such as DNAPL contamination of subsurface water and soil, there may be uncertainties about the efficacy and risks of the technology in a given situation. Public acceptance of a new technology will be more likely if tribes and stakeholders are involved in a timely and meaningful manner in the evaluation process. Such involvement will enable the early identification of significant issues and the joint resolution of these issues. In turn, public involvement will promote faster and more efficacious cleanup of the contamination and will increase public acceptance of novel approaches to such cleanup.

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Appendix A

ACRONYMS

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ACRONYMS

AATDF	Advanced Applied Technology Demonstration Facility
AFB	Air Force Base
ARAR	Applicable or Relevant and Appropriate Requirement
BDAT	Best Demonstrated Available Technology
bgs	below ground surface
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CITT	conservative interwell tracer test
CTL	Cleanup Target Level
cm	centimeter
COC	contaminant of concern
CPT	cone penetrometer testing
DNAPL	dense nonaqueous-phase liquid
DOE OST	U.S. Department of Energy, Office of Science and Technology
DPT	direct push technology
FAC	Florida Administrative Code
FDEP	Florida Department of Environmental Protection
GC	gas chromatograph
GPR	ground-penetrating radar
HPLC	high performance liquid chromatograph
HSA	hollow stem auger
IFT	interfacial tension
ITRC	Interstate Technology & Regulatory Council
LC	liquid chromatograph
LDRs	Land Disposal Restrictions
MSDS	Material Safety Data Sheet
MCL	maximum contaminant level
MEUF	micellar-enhanced ultrafiltration
MPP	macro porous polymer
NAPL	nonaqueous-phase liquid
NAS	Naval Air Station
NAVFAC	Naval Facilities Command Center
NPDES	National Pollutant Discharge Elimination System
O&M	operations and maintenance

PCE	tetrachloroethylene
PITT	partitioning interwell tracer test
POTW	publicly owned treatment works
PV	pore volume
QA	quality assurance
RCRA	Resource Conservation and Recovery Act
SEAR	surfactant-enhanced aquifer remediation
SEAR-NB	surfactant-enhanced aquifer remediation neutral buoyancy
sec	second
SESR	surfactant-enhanced subsurface remediation
TCA	trichloroethane
TCE	trichloroethylene
TSGW	Tribal and Stakeholder Working Group
UIC	underground injection control
UST	underground storage tank
USDW	underground source of drinking water
USEPA	United States Environmental Protection Agency
VOC	volatile organic compound
WWTP	wastewater treatment plant
wt%	percent by weight
XRD	X-ray diffraction

Appendix B

GLOSSARY

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GLOSSARY

alcohol flooding: the injection and extraction of pure alcohol, alcohol-water mixtures, or severe alcohol in water in a contaminated aquifer.

capillary barrier: a geologic unit that impedes the migration of NAPLs because of the small size of its pore spaces. The large capillary forces developed in these small pores must be overcome by larger pressures in the NAPL in order for the NAPL to penetrate a capillary barrier. The concept of a capillary barrier is only valid if the NAPL is nonwetting with respect to the media in the barrier (see wettability).

critical micelle concentration (CMC): the threshold concentration at which micelles begin to form. Above the CMC, any surfactant added to aqueous solution will not increase the number of monomers in aqueous solution but rather will contribute to the formation of additional micelles.

cosolvent flooding: see alcohol flooding definition.

Darcy velocity: refers to volumetric fluid flow rate per unit area of porous media under steady-state, laminar fluid flow conditions.

dense nonaqueous-phase liquids (DNAPLs): organic liquids that have low aqueous solubilities (they are immiscible) and are heavier than water. They are characterized by their component composition, density, viscosity, and interfacial tension with water.

density: mass per unit volume.

DNAPL saturation: fraction of the soil pore volume that is filled with DNAPL.

elutriate: mixture of the injected fluid and contaminant.

geosystem: the sum of all physical/chemical subsurface components that comprise a DNAPL source zone. A geosystem description for a DNAPL site includes the nature of the hydrostratigraphic units and their hydraulic/hydrogeologic properties; the physical and geochemical nature of the groundwater; the chemical composition, physical properties, and spatial distribution of the DNAPL; and the functional relationships controlling multiphase flow.

hydraulic conductivity: describes the rate at which water can move through a permeable medium at unit hydraulic gradient.

interfacial tension: refers to the tensile force that exists in the interface separating two immiscible fluids (e.g., phases).

longitudinal dispersivity: geometric property of a porous medium whereby some of the water molecules and solute molecules travel more rapidly than the average linear velocity and some travel more slowly; spreading of the solute in the direction of the bulk flow.

macroemulsion: physical dispersion of one fluid within the other.

method of moments: a technique for constructing estimates of population parameters from collecting random samples.

micellar solubilization: solubilization (partitioning) of hydrophilic (water-loving) and/or lipophilic (oil-loving) components at the center of a micelle.

micelles: aggregations of surfactant monomers.

microemulsion: thermodynamically stable, swollen micellar solution, i.e., contaminant and water molecules partitioned into the center of a micelle. Should not be confused with macroemulsions but often is.

mobility: “mobility” and “mobility ratio” are multiphase fluid flow concepts used to describe how efficiently one fluid (e.g., DNAPL) can be swept from a porous media by another fluid (e.g., surfactant/cosolvent solution). The mobility of a fluid is defined as the ratio of the relative permeability of the porous medium to the fluid’s viscosity. Therefore, for a fixed relative permeability, a fluid will have high mobility when its viscosity is low and vice versa. Mobility ratio is defined as the ratio of the mobility of the DNAPL to the mobility of the displacing fluid, such as water/surfactant. Since the effect of relative permeability is usually small, the mobility ratio may be approximated as the ratio of water/surfactant viscosity to the DNAPL viscosity. A mobility ratio of greater than or equal to 1 is desirable for effective sweep of the subsurface.

mobility control: a mechanism developed by the petroleum industry to overcome the effects of geological heterogeneities. Traditional mobility control techniques have involved the use of polymer, which increases the viscosity of the injected solutions. The enhanced viscosity of the resulting polymer solutions minimizes the effect of aquifer heterogeneities by promoting strong cross-flow across heterogeneous reservoir units. Another approach to mobility control is the use of injected air to produce foam from previously injected surfactant in the more permeable sedimentary units of the aquifer following their decontamination. Subsequently, injected surfactant is directed into the low-permeability zones.

Péclet number: a dimensionless number relating the advective transport in a system to dispersive transport in that system.

permeability: the ability of a porous or fractured medium to conduct fluid flow. Permeability is a function of the medium only, not the fluids present in the medium.

phase behavior: refers to the behavior of the aqueous-phase DNAPL and microemulsions when a surfactant/cosolvent, water, and DNAPL are mixed and allowed to equilibrate.

phases: defined according to their fluid-mechanical properties. Examples of phases include liquid, gaseous, LNAPL, and DNAPL. Phases do not mix freely with each other and, therefore, exist in the subsurface as separate fluids characterized by their own density, viscosity, and interfacial tensions.

pooled (free-phase) DNAPL: refers to the presence of DNAPL at saturations higher than residual. In contrast to residual DNAPL, which is immobile, pooled DNAPL represents a continuous fluid distribution that is potentially mobile in the subsurface. Pooling of DNAPL occurs due to heterogeneities in the porous medium, e.g., above a capillary barrier.

pore volume (PV): the volume of void space in a region of interest. In the saturated zone, it is usually the volume of water contained within the contaminated zone between injection and extraction wells.

residual (immobile or trapped) DNAPL: refers to the presence of small, disconnected blobs and ganglia of organic liquid that are trapped in the pore spaces of porous media or fractures by capillary forces.

surfactant flooding: refers to the injection, transport, and extraction of surfactants for the purpose of remediating recalcitrant compounds from the subsurface.

sweep efficiency: defined as how uniformly an injected fluid contacts the area contaminated by the DNAPL. Sweep efficiency is affected by aquifer heterogeneity as well as the DNAPL and displacing phase fluid characteristics. Sweep efficiency is generally less in a highly heterogeneous aquifer.

wettability: refers to the affinity of one immiscible fluid for a solid surface in the presence of a second or third immiscible fluid.

viscosity: a measure of a fluid's resistance to flow due to the internal friction of a moving fluid.

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Appendix C

FREQUENTLY ASKED QUESTIONS

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FREQUENTLY ASKED QUESTIONS

1. Q: Can surfactant/cosolvent flushing achieve maximum contaminant levels (MCLs)?

A: Surfactant/cosolvent flushing is an enhanced source-removal technology that is not intended to attain MCL targets in groundwater. This technology is intended to remove NAPL masses from the subsurface and is the first in a series of processes required to remediate a site.

2. Q: What is the difference between various surfactants?

A: Surfactants are industrial chemicals most commonly used in household cleaners and detergents, shampoos, and other cleaning agents. There are thousands of surfactants, but less than 100 have been investigated for use in environmental applications. The biggest difference between the various surfactants that have been injected is their molecular structure and the charge of the surfactant molecule when in solution, which affects their aggregation properties.

3. Q: Why is alcohol used?

A: During surfactant-enhanced aquifer remediation (SEAR), alcohol is used to stabilize the surfactant molecule in solution. If a surfactant precipitates from solution, the resulting gels and crystals will be too viscous to pump through an aquifer.

4. Q: Why is salt/electrolyte used?

A: To vary the properties of charged surfactants to solubilize or mobilize a contaminant.

5. Q: What is surfactant solubilization?

A: This is the mechanism by which surfactants increase the effective solubility of a contaminant.

6. Q: What is surfactant mobilization?

A: This is the mechanism by which surfactants increase the movement of contaminant as a separate phase (as opposed to the dissolved phase which is surfactant solubilization) in the subsurface.

7. Q: What concentrations of surfactants are used?

A: This will vary with the contaminant as well as the objective of the flood but is typically far above the critical micelle concentration (CMC) of the surfactant.

8. Q: How does source-zone characterization for surfactant/cosolvent flushing differ from dissolved-phase plume characterization?

A: Delineating the extent of source-zone contamination is usually far more challenging than the comparable task for the dissolved-phase plume. This is because locating DNAPLs relies on accurate and detailed stratigraphic information and because DNAPLs are typically extremely heterogeneously distributed.

9. Q: How do you know when you've gotten enough surfactant/cosolvent out of the ground to safely terminate a surfactant/cosolvent flood?

A: After a surfactant/cosolvent is used to flood the targeted zone for a period of time, water is used to remove surfactant/cosolvent and contaminant. Generally the ratio of water to surfactant/cosolvent solution flush is 2:1 (the durations are different for different types of geologic settings). Surfactants/cosolvents remaining in the aquifer should be below the CMC.

10. Q: How do you prevent surfactants/cosolvents from escaping the targeted treatment zone during a surfactant/cosolvent flood?

A: By properly selecting injection, extraction, and hydraulic control well locations and flow rates. Extraction rates are typically higher than injection rates, and potable water injection or hydraulic control wells are often used to balance the overall flow rates.

11. Q: Why is modeling needed to select appropriate flow rates for the injection/extraction surfactant/cosolvent flushing system?

A: Modeling is used to design the flood so that it is robust enough to achieve surfactant/cosolvent capture in spite of the subsurface uncertainties that exist at a particular site.

12. Q: Should existing pump-and-treat extraction wells or groundwater monitoring wells be permitted as injection wells for surfactant/cosolvent flooding?

A: The hydraulic efficiency of injection wells is an important element in the surfactant/cosolvent flood design. Proper screen intervals are also required to deliver the surfactant/cosolvent to the proper DNAPL-contaminated zones. If both of these features can be confirmed, such as by examination of the well log and pumping data, these wells should be appropriate. Although permitting is not required, extraction wells used for in-situ surfactant/cosolvent flooding should also meet these criteria.

13. Q: I have 25 mg/l TCE in several wells at my site. Can the use of surfactants/cosolvents help me reach remediation goals?

A: An investigation will be necessary to determine whether there is DNAPL (i.e., a separate phase of TCE) at the site. If so, surfactants/cosolvents can very likely assist in accelerated removal of the DNAPL to achieve total contaminant mass reduction and plume containment goals.

14. Q: Will surfactants/cosolvents inhibit biodegradation following a surfactant/cosolvent flood?

A: Most surfactants/cosolvents will at least temporarily inhibit biological activity. Most surfactants/cosolvents used for in-situ surfactant/cosolvent flooding are food- or cosmetic-grade chemicals. Laboratory studies should be performed to determine how surfactants/cosolvents would impact the growth of microorganisms at the site.

15. Q: Won't surfactants/cosolvents be lost to the soils?

A: A properly chosen surfactant/cosolvent should result in minimal loss to the aquifer.

16. Q: What do you do to dispose of the surfactant/cosolvent that is extracted out of the ground?

A: Surfactants/cosolvents extracted from the subsurface will be significantly diluted and laden with contaminant; thus, the primary task is to separate the contaminant from the surfactant/cosolvent. Gravity separation can be used to remove mobilized DNAPL from the surfactant/cosolvent. Solubilized DNAPL can be removed by a variety of treatment processes depending on contaminant properties. Thus treated, the extracted surfactant/cosolvent may be delivered to a POTW or recycled in the process.

17. Q: I have heavy-metals contamination at my site as well as DNAPL contamination. Can surfactants/cosolvents be used to remove both?

A: Yes. Laboratory studies with site soils are conducted during the design phase to select a surfactant/cosolvent that is appropriate to the contaminants and hydrogeologic conditions at the site.

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Appendix D
CASE SUMMARIES

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ITRC DNAPL TEAM CASE SUMMARY REPORT

MARINE CORPS BASE CAMP LEJEUNE SITE 88 JACKSONVILLE, NORTH CAROLINA

Remediation Technology Surfactant/Cosolvent Flooding

Project Background

Site Description: The Camp Lejeune Base Dry Cleaners is an active facility that has been in use since the 1940s. Varsol™, a petroleum distillate and mineral spirit, was in use as the dry-cleaning solvent at Building 25 from the 1940s through the 1970s.

Site History: Historical operating practices at the dry cleaning facility included disposal of spent PCE into floor drains. At the time the underground storage tanks were removed in 1995, contamination of the soil and groundwater was suspected. The tanks, floor drains, and associated underground pipes may have provided conduits for contamination to reach the subsurface.

DNAPL Source Area: The DNAPL investigations conducted for the surfactant flooding demonstration determined that free-phase and residual PCE are present under and north of Building 25.

Site Hydrogeology

Depth to Water: 7–9 feet below ground surface (ft bgs)

Aquifers: Unconfined aquifer, underlain by the intermediate Castle Hayne drinking water aquifer; groundwater elevation data indicate that the presence of multitudinous hydraulic gradients across Site 88 with the primary hydraulic gradient of concern in the DNAPL source area to the southwest due to disappearance of the underlying clay aquitard.

Lithology: The surficial aquifer at the site consists of fine-grained sand to a depth of 16 to 20 feet bgs with a continuous clay layer as evidenced by the elevation head of 7 ft supported by the aquitard, as well as the presence of pooled DNAPL. The DNAPL zone occurs in a relatively low-permeability layer of silty sediments (hereafter referred to as the basal silt layer) that grade finer with depth at about 18–20 ft bgs, grading from a sandy-silt to clayey-silt until reaching a clay layer at about 20 feet bgs.

Hydraulic Gradient: 0.015 ft/ft
Bulk Hydraulic Conductivity: 1.42 ft/day
Seepage Velocity: 0.071 ft/day (based on effective porosity of 0.3)

Groundwater Geochemistry:

pH: Variable with pumping operations, pH range of 4–6
Temp: Variable across demonstration area, avg. 24° C
Total Alkalinity: ~30 mg/L
Fe²⁺: 6.1–25.8 mg/L
DO: up to 6 mg/L

Contamination

Groundwater

Contaminants Present: PCE, TCE, DCE, and other VOCs and SVOCs (primarily PCE)

Highest Contaminant

Concentrations: Free-phase PCE was recovered from several demonstration area wells.
PCE: Above aqueous solubility limits
TCE: >3,000 µg/l
DCE: >11,000 µg/l

Deepest DNAPL

Contamination: 20 feet bgs (free-phase DNAPL)

Plume Size: ~1 acre (as defined by regulatory MCLs for PCE)

DNAPLs Present: PCE

Soil

Contaminants Present: PCE, TCE, DCE, and other VOCs and SVOCs (primarily PCE)

Highest Contaminant

Concentrations: PCE: 44,352 mg/kg (17.5 ft bgs)
Varsol: 4,900 mg/kg (8–9 ft bgs)
(with methanol preservation of soil samples and estimated 20% soil moisture content)

Demonstration/Pilot Investigation Scenario

Saturated Zone

Cleanup Goals:

Final Residual DNAPL saturation: 0.05%

Percent Recovery of Injected Chemicals: 90%

(Only one portion of the DNAPL source area, outside of the building, could be addressed due to low-permeability soils and low ceiling and subsurface abandoned utility piping issues.)

Remedy Selection:

Surfactant flooding was selected for a pilot study due to technology development funds provided by the Department of Defense Environmental Security Technology Certification Program. The overall purpose was to conduct a demonstration validation project in a more challenging environment than for earlier similar in-situ surfactant flooding projects. Secondly, it was desirable to investigate the potential benefits of surfactant recovery and reinjection. The contamination at Site 88 is shallow, which minimized costs for site characterization (i.e., baseline soil sampling and well installation). Also, the subsurface is relatively homogeneous. While there is a gradient reduction in permeability with depth, there are no intervening clay lenses, which simplifies the test design and maximizes surfactant efficiency. Additionally, there is a thick aquitard underlying the shallow aquifer that serves as an excellent barrier to downward DNAPL migration. While there are some aspects of the site that are not so desirable, such as the low hydraulic conductivity of the aquifer and the bulk of the DNAPL sits in a relatively low-permeability layer, Site 88 provided the most advantages of all the locations explored for the project.

Demonstration Design:

A custom surfactant (propoxylated alcohol ether sulfate) was synthesized for this project to meet the dual objectives of surfactant flooding a PCE-contaminated aquifer and regenerating the surfactant using pervaporation and ultrafiltration membrane processes. A cosolvent was required for optimum surfactant and fluid properties. Calcium electrolyte was also required to maximize solubilization of the DNAPL and to avoid cation exchange with the clay-rich basal sediments.

In a collaborative effort between DoD, USEPA-NRMRL (Ada and Cincinnati laboratories), INTERA (formerly Duke Engineering & Services), the University of Texas at Austin, and the University of Oklahoma at Norman, a pilot study was conducted from April through August 1999.

Injected Surfactant/Cosolvent:

Surfactant: 4 wt% (active) Alforterra 145-4PO surfactant
(C14-15 Guerbet alcohol with an average of 4
propylene oxide groups), 10,000 lbs total
Cosolvent: 16 wt% isopropyl alcohol, 40,000 lbs total
Electrolyte: 0.14 to 0.18 wt% CaCl₂, 400 lbs total
Injection wells: 3
Recovery wells: 6
Hydraulic control wells: 2
Surfactant injection rate: 0.4 gallons per minute (gpm)
Surfactant extraction rate: 1 gpm
Water-flooding injection/extraction rates: 1.5 gpm
Target treatment area: portion of DNAPL source north of (but not
under) the building, approximately 20 ft x 30 ft
Target depth: 16–20 ft bgs
Maximum depth: 20 ft bgs

Surfactant Injection Duration: 38 days fresh surfactant, 20 days
recycled surfactant

Water Flooding Duration: Preflood: 8 days; Postflood including
final partitioning interwell tracer test: 74 days

Total Flooding Duration: 143 days

Results

Pilot Test:

Surfactant flooding removed approximately 76 gallons of PCE from the test zone. Soil-core data indicate that approximately 30 gallons of DNAPL remained in the treated subsurface. Postpartitioning tracer test data could not be used due to interference by the surfactant (thought to be an impurity in the synthesized surfactant mixture) that sorbed during flooding operations. Approximately 88% recovery of IPA and 77% recovery of surfactant was obtained. Following flooding operations, DNAPL appeared in some of the treated zone adjacent to the untreated portion of the source area.

The surfactant recovery processes operated successfully to allow reinjection of 1,806 lbs of surfactant (active). It was observed that calcium electrolyte and residual contaminant (unremoved following pervaporation treatment) became concentrated with the surfactant during ultrafiltration by approximately the same extent. Ninety-five percent contaminant recovery was achieved by pervaporation during 70 days of continuous operation that included just one short-duration shutdown.

Current Status: Quarterly monitoring of select Site 88 wells is ongoing. Periodic sampling of the surfactant demonstration wells and multilevel samplers continues to examine the degradation of residual IPA and chlorinated solvents.

Costs

Pilot test: approximately \$3M, including DNAPL site investigation; surfactant regeneration technology development; and SEAR design, construction, and operation.

Estimated implementation costs of full-scale remediation of Building 25 DNAPL source area are as follows:

Design Cost	\$300,000
Cosolvent Flushing	
Cosolvent System Implementation	\$640,000
Cosolvent Flushing Operation	\$500,000
Performance Assessment Cost (soil borings)	<u>\$103,000</u>
Total:	\$1,543,000

Lessons Learned

1. Surfactant flooding of a DNAPL zone with shallow low-permeability sediments is not cost-effective under gravity-pumping conditions.
2. Alfoterra 145-4PO surfactant may not be the most ideal surfactant for this site, and modifications have since occurred that allow significant reduction of IPA in the surfactant formulation.
3. Mobility-control measures are necessary in order to address permeability heterogeneities, as it is not cost-effective to characterize all of the heterogeneities in the system.
4. With limited postgroundwater monitoring data, bioattenuation has apparently not increased significantly since the termination of flooding operations. However, vacuum-enhanced DNAPL recovery operations conducted since the end of the flooding demonstration may have interfered with bioattenuation of chemicals.

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ITRC DNAPL TEAM CASE SUMMARY REPORT

SAGES DRY CLEANERS JACKSONVILLE, FLORIDA

Remediation Technology Cosolvent Flooding (Ethanol)

Project Background

Site Description:

Sages Dry Cleaners is an inactive dry-cleaning facility in Jacksonville, Florida, that used PCE. It operated from 1968 to 1973 and from 1979 to 1989. The building that formerly housed the operation was razed in 1998. The site is located in a commercial/residential setting in Jacksonville. A drainage canal, which trends roughly south-north, is located approximately 50 feet west of the former building site. The nearest potable well is approximately 1,300 feet to the northeast.

Site History:

Prior to operating as a dry-cleaning facility, an Amoco service station operated at the site from 1953 until the mid to late 1960s. Four 3,000-gallon petroleum underground storage tanks (USTs), a 550-gallon waste oil UST, and approximately 7,500 pounds of contaminated soil were removed in 1990.

DNAPL Source Area:

The DNAPL PCE distribution indicates that a sump beneath the former building location and the area west of the boiler room door were probable locations for PCE releases.

Authorization:

LFR Levine-Fricke was contracted by the Florida Department of Environmental Protection (FDEP) Bureau of Waste Cleanup to conduct assessment and remediation activities as part of the Drycleaning Solvent Cleanup Program. A Contamination Assessment Report was completed in December 1997 and an Addendum completed in February 2000.

Site Hydrogeology

Depth to Water:

8 feet below ground surface (bgs)

Aquifers:

Unconfined aquifer. Groundwater contour data indicate that the flow direction at the site is generally to the west toward the drainage canal and the St. Johns River. Groundwater elevation data indicate that groundwater to the west of the canal is flowing east-northeast toward the canal. A downward vertical gradient also exists at the site.

Lithology: The surficial aquifer at the site consists of fine-grained sand to a depth of 55 to 60 feet bgs, with a discontinuous clay layer approximately 0.5 feet thick encountered at a depth of approximately 35 feet. At approximately 60 feet bgs, site lithology changes to interbedded layers of clay, clayey sand, and silty clay. Clayey silt was encountered from a depth of approximately 120 to 152 feet bgs.

Hydraulic Gradient: 0.002 ft/ft

Hydraulic Conductivity: 10.35 ft/day

Seepage Velocity: 0.23 ft/day

Groundwater Geochemistry:

pH: 3.28 to 9.59

TOC: 16.3 to 57.2 mg/L

Fe²⁺: 0.31 to 1.68 mg/L (pre-pilot test)

ORP: -64.2 to 131 mV (pre-pilot test)

DO: 0.02 to 4.48 mg/L

Contamination

Groundwater

Contaminants Present: PCE, TCE, cis-1,2-DCE, trans 1,2-DCE

Highest Contaminant

Concentrations: Free-phase PCE was recovered from an existing on-site water supply well.

PCE: 930,000 µg/l

TCE: 34,000 µg/l

cis-1,2-DCE: 19,000 µg/l

trans 1,2-DCE: 400 µg/l

Deepest Contamination: 92 feet bgs (PCE at 280 µg/l)

Plume Size: 0.35 acres (as defined by regulatory MCLs)

DNAPLs Present:

In addition to the free-phase PCE detected, high aqueous concentrations (>75% of solubility limit) were detected in groundwater samples, indicating the presence of residual DNAPL.

Soil

Contaminants Present: PCE, TCE, vinyl chloride

Highest Contaminant

Concentrations: PCE: 21,300 µg/kg

Remediation Scenario

Cleanup Goals:

Cleanup Target Levels (CTLs) for groundwater at the site have been identified as the Maximum Contaminant Levels (MCLs) for chlorinated solvents as defined in Chapter 62-782 of the Florida Administrative Code (FAC):

PCE: 3.0 µg/l

TCE: 3.0 µg/l

cis-1,2-DCE: 70 µg/l

trans 1,2-DCE: 100 µg/l

Vinyl chloride: 1.0 µg/l

The Leachability-Based Soil CTLs for chlorinated solvent constituents, as defined in Chapter 62-782 of the FAC, have been identified as the CTLs for the unsaturated zone for this site.

PCE: 30 µg/kg

TCE: 30 µg/kg

cis-1,2-DCE: 400 µg/kg

trans 1,2-DCE: 700 µg/kg

Vinyl chloride: 7 µg/kg

Remedy Selection:

A Remedial Alternatives Evaluation was completed to select the most cost-effective remedial alternative based on site-specific conditions. Soil vapor extraction will be used to remediate vadose zone soil contaminated above the leachability criteria. Groundwater remediation will consist of: 1) in-situ cosolvent flushing with ethanol for the DNAPL source zone; 2) in-situ bioremediation facilitated by residual ethanol for the chlorinated VOC plume above Natural Attenuation Default Source Concentrations (NADSCs) (i.e., 300 µg/l PCE); and 3) monitored natural attenuation for the plume below NADSCs.

Remediation Design:

Full-scale in-situ remediation of groundwater will be conducted via cosolvent flushing. Injection of ethanol into an aquifer reduces the polarity of the aqueous phase, resulting in a significant increase in the rate of interfacial mass transport between DNAPL and the aqueous phase (groundwater) and an increase in the solubility of nonpolar compounds (in this case, PCE) in groundwater.

In a cooperative effort by FDEP, LFR Levine-Fricke, USEPA-TIO, and the University of Florida, a pilot study was conducted in August 1998 using the following design:

Injected Cosolvent:

Volume: 9,000 gallons

Cosolvent: 95% ethanol/5% water

Injection wells: 3

Recovery wells: 6

Injection rate: 0.8 gallons per minute (gpm) in two wells and 1.4 gpm in the third well for 2.5 days

Extraction rate: 8 gpm for 8 days

Treatment area: 24 ft by 9 ft elliptical DNAPL source area

Target depth: 26 to 31 ft bgs

Maximum depth: 35 ft bgs

Ternary mixture of PCE, ethanol, and water was treated with Akzo Nobel Macro Porous Polymer (MPP) system for removal of PCE, and approximately 160,000 gallons of ethanol/water mixture was disposed of off site as nonhazardous liquid waste.

Results

Pilot Test:

Cosolvent flushing removed approximately 43 L of PCE from the test zone (62% removal effectiveness). These results were in agreement with soil-core data that indicated approximately 65% removal and a postflushing partitioning tracer test that indicated approximately 26 L of PCE remained (63% removal). Postflushing groundwater concentrations of PCE were an average of 92% lower than preflushing values at 21 of 35 multilevel sampling locations, but the combined effects of residual ethanol and incomplete flushing likely resulted in artificially elevated postflushing PCE concentrations at the other 14 locations.

The pilot test demonstrated that enhanced dissolution, solubilization, and recovery of PCE were achievable through cosolvent flushing. Hydraulic containment was successful in maintaining capture within the test zone, and the system effectively removed PCE from the recovered ternary mixture. Periodic monitoring also indicated that enhanced biodegradation is occurring as a result of residual ethanol remaining in the aquifer.

Current Status:

Postpilot test monitoring is continuing. A full-scale cosolvent flushing and SVE Remedial Action Plan has been approved by FDEP, and implementation is anticipated to occur by August 2003.

Costs

Pilot test: approximately \$440,000 including design, construction, and operation.

Estimated implementation costs of full-scale remediation are as follows:

Design and RAP Development	\$40,000
Cosolvent Flushing	
Cosolvent System Implementation	\$300,000
Cosolvent Flushing Operation	\$275,000
SVE System Implementation	\$80,000
SVE System Operation, Maintenance, and Monitoring (1 Year)	\$35,000
Groundwater Monitoring (2 Years)	<u>\$110,000</u>
Total:	\$840,000

Lessons Learned

1. Cost savings could be realized through alcohol reuse by limiting the total amount of alcohol necessary to complete flushing activities and decreasing disposal costs for wastewater with a high alcohol concentration.
2. Residual ethanol remaining after cosolvent flushing has significantly enhanced in-situ biological dechlorination processes for natural attenuation of the contaminant mass.
3. Contractor believes that flushing would be more cost-effective if injection and extraction systems and treatment system were trailer-mounted, similar to the MPP system but including reuse of processing equipment as necessary.

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ITRC DNAPL TEAM CASE SUMMARY REPORT

HILL AIR FORCE BASE OPERABLE UNIT 2 OGDEN, UTAH

Remediation Technology Surfactant/Cosolvent Flooding

Project Background

Site Description: Operable Unit 2 at Hill AFB was the site of a chemical disposal trench where waste solvents and degreasers used in aircraft maintenance were disposed of.

Site History: The site (formerly designated Chemical Pit #3) was used continuously from 1967 until 1975 for basewide disposal of spent degreasing fluids and other solvents at Hill AFB. The area was identified as a contaminated site during a basewide environmental investigation (the Installation Restoration Program or IRP) in 1981. The site was designated Operable Unit 2 in 1991 under the Federal Facilities Act. A subsequent remedial investigation found DNAPL pooled within the topographic lows of a clay aquitard at OU 2. A source-recovery system (SRS) was installed to recover the DNAPL in 1992. Subsurface characterization continued through 1996 when a slurry wall was constructed around the site. The Air Force Center for Environmental Excellence hosted a demonstration of surfactant-flood technology at OU 2 in 1996. Five partitioning interwell tracer tests (PITTs) were conducted to further characterize the DNAPL distribution in 1998. Full-scale remediation by surfactant flooding commenced in 1999. One surfactant and two surfactant-foam floods have been conducted at OU 2 through 2002.

DNAPL Source Area: The length of the source area is 600 ft along the bottom of a paleo-channel with an average width of 50 ft. The initial DNAPL saturations (after pump and treat but before surfactant flooding) were in the range of 11% to 0.3%.

Site Hydrogeology

Depth to Water: 25 ft below ground surface (bgs)

Aquifers: Unconfined aquifer, underlain by a thick uniform clay layer. The Provo alluvium extends from the surface to the Alpine clay layer.

Lithology: The DNAPL source zone exists in a fluvial paleo-channel scour feature incised in lacustrine clay deposits. The fluvial deposits consist of sands and gravelly sands in a fining upward sequence of stacked channel deposits. The fluvial deposits are highly heterogeneous. The confining clay layer is continuous throughout the area.

Hydraulic Gradient: A slurry wall was installed around the site in 1996 to isolate the source, resulting in no discernable hydraulic gradient under static conditions.

Bulk Hydraulic Conductivity: 17 ft/day to 146 ft/day

Seepage Velocity: 0.28 to 0.85 ft/day (based on effective porosity of 0.27)

Groundwater Geochemistry:
pH: ~7
Temp: 11 °C
Total Alkalinity: NA
Fe²⁺: NA
DO: NA

Contamination

Groundwater Contaminants Present: PCE, TCE, TCA, DCE, trace heavy metals

Highest Contaminant Concentrations: Free-phase DNAPL was recovered from source-zone area wells. TCE >1,100,000 µg/L

Deepest Contamination: 45–50 ft bgs (free-phase DNAPL)

Plume Size: The dissolved-phase plume emanating from the OU 2 source has an areal extent of approximately 1,054,944 square feet. Based on the 1999 plume dimensions, it is estimated that approximately 340 kg (750 lbs) of TCE is dissolved in 83,652,815 liters of groundwater in the OU 2 plume.

DNAPLs Present: DNAPL is composed of approximately 70% TCE, 10% PCE, 5% TCA with other minor volatile organic constituents. In addition, there is a significant oil and grease fraction entrained in the DNAPL. Approximately 49,000 gals of DNAPL were initially present in the aquifer. Of this amount, approximately 44,000 gals have been recovered by extraction (pumping of free-phase DNAPL), water flooding, a steam-flooding demonstration, two

surfactant-flood demonstrations, and three full-scale surfactant floods.

Soil

Contaminants Present: TCE, PCE, TCA, DCE, CFC 113, some heavy metals

Highest Contaminant

Concentrations: TCE: 149,716 mg/kg (50 ft bgs)
PCE: 9,092 mg/kg (50 ft bgs)
TCA: 5,660 mg/kg (50 ft bgs) (with methanol preservation of soil samples in the field)

Demonstration/Pilot Investigation Scenario

Saturated Zone

Cleanup Goals: Final Residual DNAPL saturation: 0.05%
Percent Recovery of Injected Chemicals: 90%

Remedy Selection: Surfactant flooding was selected for a pilot study as recommended in the ROD. The pilot demonstration recovered ~98% of the DNAPL from the test zone. Verification of demonstration results was provided by partitioning interwell tracer tests (patented by INTERA, Inc.) and additionally confirmed by soil sampling.

Demonstration Design: The demonstration area was developed during the spring of 1996 by installing a set of three injection wells and three extraction wells in a 3 x 3 line-drive geometry. This well field also contained one hydraulic control (injection) well and one interwell monitor well. The distance between injectors and extractors was 20 feet; the distance between individual injectors and individual extractors was ten feet; the water table depth was approximately 25 feet below ground surface; and there was a four-foot-thick zone of free-phase and residual DNAPL approximately 45 feet below ground surface. The screened intervals of the injectors and extractors were completed in this DNAPL zone and extended some distance above it. Prior to the demonstration, some 500 gallons of free-phase DNAPL was pumped from the recently installed well field and sent for incineration.

The demonstration was conducted in two phases. The first of these phases comprised a partitioning interwell tracer test (PITT) followed by a DNAPL solubilization test, both of which were conducted in May and early June 1996. The PITT determined the spatial distribution and volume of DNAPL in the test zone of the alluvial aquifer. The solubilization test verified the efficiency of the selected surfactant, determined whether the surfactant would cause the deflocculation and mobilization of fine-grained particles

resulting in a reduction in permeability of the aquifer, and also addressed the issue of the effect of the surfactant-rich effluent on the efficiency of the steam-stripping system at the site. This test involved the injection of an 8% surfactant solution into one injection well at two gallons per minute (gpm) for 0.6 days, producing an interfacial tension of 0.1 dynes/cm between the surfactant solution and the OU2 DNAPL.

The PITT indicated that there was a total of 346 gallons of DNAPL in the four-foot-thick test zone with an average residual DNAPL saturation of 20%, or approximately 4% when measured over the whole 20-foot-thick swept volume of the aquifer. The solubilization test showed that the selected surfactant was effective and that there was no significant head loss due to mobilization of fines across the line-drive test zone.

The results of the Phase I field operations were used to finalize the design of the Phase II surfactant flood. The Phase II flood was preceded and followed by PITTs so that the performance of the flood could be assessed. The surfactant flood consisted of the injection of a solution of 8% surfactant, 4% isopropyl alcohol, and 0.7% NaCl, producing an interfacial tension of 0.02 dynes/cm. The Phase II field operations lasted for 30 days, of which surfactant injection at 7.5 gpm accounted for three days (i.e., 2.4 pore volumes); the follow-up water flood lasted 5.5 days, and the final PITT took six days. The final PITT indicated that the average residual DNAPL saturation over the 20-foot-thick swept zone of the aquifer had been reduced from 0.036 in early May to 0.0004 in late August in a swept volume of approximately 15,000 gallons. Therefore, the PITTs had shown that the two surfactant floods had recovered 341 of the 346 gallons of DNAPL within the test zone of the OU2 alluvial aquifer.

Injected Surfactant/Cosolvent:

Surfactant: Aerosol MA-80I (CYTEC Industries) 8 wt%

Cosolvent: 4 wt% isopropyl alcohol

Electrolyte: 0.07 to 0.12 wt% NaCl

Injection wells: 3

Recovery wells: 6

Hydraulic control wells: 2

Surfactant injection rate: ~11 gallons per minute (gpm)

Surfactant extraction rate: ~12 gpm

Water-flooding injection/extraction rates: ~12 gpm

Target treatment area: approximately 20 ft x 30 ft

Target depth: 3–5 m bgs

Maximum depth: 5 m bgs

Results

Pilot Test: The pilot test resulted in the removal of 98% of the residual DNAPL. Pretest pumping recovered some 500 gallons of free-phase DNAPL before the surfactant flood and, therefore, prior to the DNAPL's dissolution and subsequent downgradient extraction and treatment, resulting in a cost savings of approximately \$15 million to USAF.

Current Status: Full-scale remediation of the source zone by surfactant flooding has recently been completed (Summer 2002).

Costs The cost of the pilot test was \$1,200,000 or about \$1,800/gallon of DNAPL. This can be compared with the original USAF estimate for cleanup of the DNAPL that used the traditional time frame of 30 years with a recovery cost now running at over \$32,000/gallon for pump and treat.

Lessons Learned

1. The cost savings underline the importance of source-zone removal prior to natural attenuation of aqueous plumes.
2. The regulatory community can derive encouragement from the success of the PITTs in detecting and characterizing a DNAPL zone in terms of its spatial distribution and total volume.
3. The two surfactant floods demonstrated the technical practicability of removing >99% of DNAPL from alluvium, provided the site is well characterized and an exhaustive design protocol is followed.

Contact

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References

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ITRC DNAPL TEAM CASE SUMMARY REPORT

ALAMEDA NAVAL AIR STATION ALAMEDA, CALIFORNIA

Remediation Technology Surfactant Flooding (Ultrasolubilization)

Project Background

Site Description:

The Alameda Point site is located on the San Francisco Bay in Alameda, California. The purpose of the study was to demonstrate enhanced dense nonaqueous-phase liquid (DNAPL) removal at the selected site. After preliminary site investigation, the selected test location is on the east side of Building 5 in IR Site 5. Building 5 lies in the middle of the former Naval Air Station (NAS) Alameda Point Complex. No operations are currently ongoing in Building 5.

Site History:

Building 5, which covers over 1 million square feet, began operation in 1942. It housed shops used for cleaning, reworking, and manufacturing metal parts, tool maintenance, plating, and painting operations. Processes in the plating shop included degreasing, caustic and acid etching, and metal stripping and cleaning, along with chrome, nickel, silver, cadmium, and copper plating. Prior to 1972, the wastewater from operations in Building 5 was discharged without pretreatment to the San Francisco Bay via the industrial sewers, the bulk of which emptied into the Seaplane Lagoon. From 1972 until 1991, the wastewater from the plating shop was split into two waste streams, one from the alkaline tanks and one from the cyanide tanks. The wastewater streams were kept separate until the cyanide stream was treated in a cyanide destruction unit. The two waste streams were then routed together to a treatment plant.

DNAPL Source Area:

Site investigation conducted for the surfactant-flushing demonstration determined that a high concentration DNAPL plume, consisting primarily of 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), 1,1-dichloroethene (DCE), 1,1-dichloroethane (DCA), and vinyl chloride (VC), was discovered at the east side of Building 5. The DNAPL occurred as trapped oil droplets and free-phase liquids in the sands above the lower confining layer (Bay Mud; 17 feet below ground surface). The site investigation also showed that the DNAPL plume extended outside the test area on all sides. In addition, free product was observed in the recovery and injection wells prior to the test.

Site Hydrogeology

Depth to Water: 7 feet below ground surface (bgs)

Aquifers: The hydrological units of primary importance to the SESR study are the Merritt Sand, the Holocene Bay Mud, and the overlying artificial fill material. These units make up the shallow aquifer. The shallow aquifer has two primary water-bearing zones. The first zone is above the Holocene Bay Mud in the fill material (referred to as the “first water-bearing zone”). The second zone is below the Holocene Bay Mud in the Merritt Sand (referred as the “second water-bearing zone”). The Holocene Bay Mud has been found to contain higher percentages of silt and sand in the western portion of the base and is discontinuous in the southeastern portion of the base.

Lithology: The lithology at IR Site 5 is characterized by a fill layer between 0 and 17 feet deep, which consists of interbedded fine sands (well sorted), silty sands (moderately well sorted), and gravelly sand. Below the fill, the native soils consist of the Holocene Bay Mud deposits. These deposits are primarily a lower permeability mixture of silty clay to sandy clay, with occasional sands, silts, and shell fragments. At IR Site 5, the Bay Mud layer is approximately 15 to 20 feet thick.

Hydraulic Gradient: 0.0015 ft/ft

Bulk Hydraulic
Conductivity: 10 ft/day

Seepage Velocity: 0.043 ft/day (based on effective porosity of 0.35)

Groundwater Geochemistry:
pH: 6.8–8.4
Temp: 21–24 °C
Total Alkalinity: ~272 mg/L
Fe²⁺: 106.1–317 µg/L
DO: up to 6 mg/L

Contamination

Groundwater
Contaminants Present: TCA, TCE, DCE, DCA, and VC

Highest Contaminant Concentrations: Free-phase TCA+TCE was recovered from few demonstration area wells.
TCA: 580 mg/L
TCE: 150 mg/L
DCE: 37 mg/L
cis-DCE: 100 mg/L
DCA: 110 mg/L
VC: 19 mg/L

Deepest DNAPL Contamination: 17.5 feet bgs

Plume Size: ~ 1.4 acres (estimated)

DNAPLs Present: TCA, TCE, DCE, and other VOCs

Soil Contaminants Present: TCA, TCE, DCE, and other VOCs

Highest Contaminant Concentrations: TCA: 32,000 mg/kg (17 ft bgs)
TCE: 17,000 mg/kg (17 ft bgs)

Demonstration/Pilot Investigation Scenario

Saturated Zone

Cleanup Goals: DNAPL mass removal: 95% (from the soil)
Determine the effectiveness of the treatment system to remove chlorinated solvent mass that cannot be removed using conventional pumping techniques.
Determine the efficiency of surfactant recovery from the test area.

Remedy Selection: The Navy (Engineering Field Activity West) requested Tetra Tech EM, Inc. to conduct a surfactant-enhanced subsurface remediation treatability study at Alameda Point. The purpose of the study was to demonstrate enhanced dense nonaqueous-phase liquid (DNAPL) removal at the NAPL-impacted site. This NAPL acts as a continuous source of groundwater contamination. Surfactants can greatly enhance the solubility of the chlorinated hydrocarbons, thereby increasing the removal of DNAPL constituents from the soil matrix. Because of the nature of the behavior of the chlorinated solvents in the groundwater, a bench-scale study alone was not sufficient to provide conclusive evidence regarding the

effectiveness of the technology. Therefore, an in-situ pilot-scale study was performed.

Demonstration Design:

A mixture of two anionic surfactants was used to provide an ultrasolubilization capacity of NAPL without mobilization. Use of the mixed surfactant system also eliminated any adverse phase behavior (such as gel or liquid crystal) without adding the cosolvent (e.g., isopropyl alcohol). Addition of cosolvent tends to increase the difficulties and the cost of aboveground treatment systems for the waste fluid. Sodium and calcium electrolytes were added to maximize solubilization of DNAPL.

Surbec-ART Environmental, LLC was selected to complete the treatability study, with Levine-Fricke-Recon (LFR) and the University of Oklahoma as subcontractors. The pilot study was conducted from January through September 1999.

Injected Surfactant:

Surfactant: 2 wt% (active) Aerosol MA-80I (sodium dihexyl sulfosuccinate) and 5 wt% Dowfax 8390 (diphenyl sulfonate derivative). 1,045 gallons of AMA and 1,540 gallons of Dowfax were used.

Cosolvent: None

Electrolyte: 3 wt% NaCl, 5,120 lbs total; 1% CaCl₂, 3,440 lbs total

Injection wells: 2

Recovery wells: 4

Hydraulic control wells: 2

Surfactant injection rate: IW1: 1.91-2.06 gallons per minute (gpm)
IW2: 0.45 to 2.03 gpm

Surfactant extraction rate: total: 3.65 to 8.31 gpm

Water-flooding injection/extraction rates: 4.8 to 7.8 gpm

Target treatment area: east side of Building 5 approximately
20 ft x 20 ft

Target depth: 13.5–17.5 ft bgs

Maximum depth: 17.5 ft bgs

Surfactant Injection Duration: 1.5 days fresh surfactant, 16.5 days recycled surfactant

Water Flooding Duration: Preflood: 7 days; Postflood including final partitioning interwell tracer test: 23 days

Total Flooding Duration: 48 days

Results

Pilot Test:

Surfactant flooding removed approximately 80 gallons of DNAPL from the test zone. Soil-core data indicate that less than one gallon of DNAPL remained in the treated subsurface, as compared to 34 gallons of the pretest value (estimated). A 97% reduction of NAPL mass was observed in the demonstration cell after the surfactant flood, based on soil-boring data. Prepartitioning tracer test gave an estimate of 100 to 169 gallons of DNAPL in the treatment zone. Postpartitioning tracer test indicated that less than 3 gallons of NAPL were left in the treatment zone (> 99% reduction). The final groundwater concentrations within the cell boundary showed an 80% decrease in the mass of TCA and a 56% decrease in mass of TCE. This study demonstrated that proper design of SESR could significantly reduce the contaminant concentrations of soil and groundwater. The total mass recovery of Dowfax and AMA from the subsurface was 117% and 90%, respectively, as compared to the surfactant mass injected.

Current Status:

Demonstration completed. Site further plan unknown.

Costs

Pilot test: approximately \$658K, including DNAPL site investigation and SEAR design, construction, and operation.

Estimated implementation costs of full-scale remediation of Building 5 DNAPL source area (based on 60,000 ft² & 44,444 yd³ assumption & '99 values) are as follows:

Installation	\$90,000
Equipment Rental	\$444,000
Surfactant Cost (capital cost)	\$1,572,000
O&M (1.8 yr)	<u>\$845,000</u>
Total:	\$2,951,000
Cost per yard ³ :	66*

*Note: This cost estimate (in 1999) should be further reduced based on Surbec's recent low surfactant concentration approach (Surbec, 2002).

Lessons Learned

1. Surfactant flood cost analyses indicate that SESR costs are 1/3 the cost (\$2.9M vs. \$10M) of the traditional pump-and-treat technology. In addition, SESR technology implemented at the site would require a significant less amount of time to remediate the site as compared to the traditional pump and treat.
2. Full-scale application could utilize most of the same infrastructure used in the treatability study. As a result, scalability of the technology is practical for the site.

3. Results of the estimated NAPL volumes in the cell based on the soil coring and partitioning tracer data were somewhat different in this study. While these assessment techniques provided a useful tool to quantify the NAPL volume, interpretation of these data requires care. Therefore, performance assessment of SESR should probably rely on multiple parameters, such as soil coring, groundwater concentration, and PITT, if available to provide more accurate estimation.

Contact

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ITRC DNAPL TEAM CASE SUMMARY REPORT
SPARTAN CHEMICAL COMPANY SUPERFUND SITE
WYOMING, MICHIGAN

Remediation Technology Surfactant Flooding (Mobilization/Ultrasolubilization)

Site Description The Spartan Chemical Company Superfund Site is located in the southeast quarter of Section 9, Township 6 North, Range 12 West, as observed in the Grand Rapid West USGS quadrangle. The address of the site is 2539 28th Street, which is situated approximately one block northwest of the intersection of Byron Center Avenue and 28th Street in Wyoming, Kent County, Michigan. The Spartan Chemical Company site is located on the northeastern edge of an industrial/commercial area but is bordered by a school to the east and adjacent residential areas further eastwardly. The site occupies an approximate two-acre land area. The facility is currently closed, and no commercial operations are active at the site.

Site History: From 1952 to 1992, Spartan Chemical Company operated as a bulk chemical transfer, blending, and repacking plant. During its operation, Spartan Chemical Company handled a variety of chemicals, including aromatic solvents, naphthas, alcohols, ketones, ethers, chlorinated solvents, and lacquer thinners. The company filed for bankruptcy in 1992; the site has been vacant since that time. There are no other known responsible parties on record for this Superfund project. On September 8, 1983, Spartan Chemical Company was added to the National Priorities List (NPL) of Superfund sites, which names hazardous waste sites that are eligible for further study and remediation under the federal Superfund program. Spartan Chemical Company signed a consent order with the Michigan Department of Environmental Quality (MDEQ) on September 20, 1984, to conduct an investigation and cleanup of groundwater contaminated by activities that had transpired at the site.

DNAPL Source Area: According to the findings of Malcolm Pirnie Engineers LLP's remedial investigation and MDEQ's interpretation of available data, source areas were concluded to be in the vicinities of the aboveground storage tanks (ASTs), former USTs, and the loading dock areas where spills have reportedly occurred. High concentrations of VOCs and inorganic compounds are present throughout the unsaturated soil column, particularly near the ground surface around the surface areas. Concentrations of VOCs

that exceed Michigan's Generic Residential Cleanup Criteria (GRCC) include BTEX compounds, trichloroethene, and tetrachloroethene.

Site Hydrogeology

Depth to Water:

5 to 18 feet below ground surface (bgs)

Aquifers:

The aquifer is an unconfined water-bearing unit present in the sand/gravel material super-positioned above the bottom confining clay layer. As a result, the aquifer has a reported thickness ranging from 15 to 80 feet. Changes in aquifer thickness are primarily due to the configuration of the clay surface relative to the generally flat ground surface topography. The underlying clay unit is at least 5 feet thick and has been reported to serve as a local aquitard. Downward vertical contamination migration has not been documented in the clay layer.

Lithology:

The unconsolidated material at the site is composed of fine-to-coarse sand with fine-to-coarse gravel from the ground surface to depths ranging from 17 to 95 feet below ground surface (bgs). Gray silty clay (glacial till) of undetermined thickness underlies the unconsolidated sand/gravel material. The clay surface in the general area of the Spartan site appears to slope to the south; however, this sloping feature of the clay is thought to be part of a large basin-like structure. A trough-shaped topographic structure in the clay is evidenced in an area between the Spartan Chemical Company site and the west-abutting Ambassador Steel building. There is concern that this variation in the clay surface may cause nonaqueous-phase liquids (NAPLs), if present, to migrate locally in a direction different from the northwestern direction of the regional groundwater flow. Gravel zones are present in the unsaturated soil column, as well as in the aquifer. The high permeability of these zones may provide preferential pathways for contamination migration.

Hydraulic Gradient:

0.0025 ft/ft

Bulk Hydraulic
Conductivity:

30 to 60 ft/day

Seepage Velocity:

0.2 to 0.43 ft/day (based on effective porosity of 0.35)

Groundwater Geochemistry:

pH: 6
Temp: 15 °C
Total Alkalinity: 656 mg/L
Fe²⁺: 9637 µg/L
DO: up to 5 mg/L

Contamination

Groundwater

Contaminants Present: acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), methylene chloride (MC), TCE, BTEX

Highest Contaminant

Concentrations: Acetone: 560 mg/L
MEK: 200 mg/L
MIBK: 120 mg/L
MC: 32 mg/L
TCE: 7.3 mg/L
Toluene: 58 mg/L

Deepest Contamination: 92 feet bgs

Plume Size: unknown

DNAPLs Present: unknown

Soil

Contaminants Present: acetone, MEK, MIBK, MC, TCE, BTEX

Highest Contaminant

Concentrations: Acetone: 61 mg/kg (86.5 ft bgs)
MEK: 167 mg/kg (86.5 ft bgs)
MIBK: 17 mg/kg (86.5 ft bgs)
MC: 3 mg/kg (86.5 ft bgs)
TCE: 0.77 mg/kg (86.5 ft bgs)
Toluene: 6.7 mg/kg (86.5 ft bgs)

Demonstration/Pilot Investigation Scenario

Saturated Zone

Cleanup Goals: Determine the effectiveness of the SESR DNAPL treatment system to remove chlorinated solvent mass that cannot be removed using conventional pumping techniques.
Determine the physical properties of the porous media within the study area, including the hydraulic and sorption properties of the aquifer material.

Determine the optimal surfactant mixture for DNAPL removal.
Determine the efficiency of surfactant recovery from the study area.

Remedy Selection:

MDEQ requested Snell Environmental Group, Inc. (SEG) to conduct a surfactant-enhanced subsurface remediation (SESR) treatability study at the Spartan Chemical facility in Grand Rapids, Michigan. The purpose of the treatability study was to demonstrate enhanced removal of dense nonaqueous-phase liquid (DNAPL) at the selected test site. Surbec-ART Environmental LLC (Surbec-ART) was selected to complete the treatability study. Due to the complex nature of the behavior of chlorinated solvents, petroleum hydrocarbons, and ketones in groundwater, a bench-scale study alone was not sufficient to provide conclusive evidence regarding the effectiveness of the technology. Therefore, an in-situ pilot-scale treatability study was performed.

Demonstration Design:

Laboratory screening tests were conducted to select the optimal surfactant system for application at the site. Since a site-specific NAPL sample was not available, two synthetic NAPL mixtures were used to perform NAPL/surfactant phase behavior studies. The selected surfactant system consisted of 4wt% AMA, 4.5% alkylated naphthalene sulfonate (SMDNS), and 2% NaCl. The optimal surfactant system was selected based on the assumed contaminant concentration of synthetic NAPL2 (MeCl₂, 44%; acetone, 25%; TCE, 17%; toluene, 14%), which displayed favorable phase diagram. The optimal Winsor Type III (middle-phase) microemulsion was selected to both mobilize and solubilize the contaminants.

Injected Surfactant:

Surfactant: 4 wt% (active) Aerosol MA-80I (sodium dihexyl sulfosuccinate) and 4.5 wt% alkylated naphthalene sulfonate (SMDNS). 8,607 lbs of AMA and 9,682 lbs of SMDNS were used.

Cosolvent: None

Electrolyte: 2 wt% NaCl, 4,303 lbs total

Injection wells: 1

Recovery wells: 2

Hydraulic control wells: 2

Surfactant injection rate: IW1: 10 gallons per minute (gpm)

Surfactant extraction rate: RW-1: 16.75 gpm; RW-2: 13 gpm

Water-flooding injection/extraction rates: 10 gpm

Target treatment area: approximately 20 ft x 20 ft

Target depth: 87–92 ft bgs

Maximum depth: 92 ft bgs

Surfactant Injection Duration: 2 hours fresh water, 34 hours surfactant

Water Flooding Duration: Preflood: 27 hours; Postflood including final partitioning interwell tracer test: No

Total Flooding Duration: 63 hours

Results

Pilot Test:

Contaminant mass removal was calculated for acetone, MeCl₂, MEK, TCE, MIBK, and toluene for the time period during the surfactant injection. The total mass recovered from RW-1 and RW-2 was 42.5 kg (93.6 lbs). The dissolved contaminant enhancement was clearly observed at two monitoring wells, MW-1D and MW-4D located between the injection and extraction wells. The average enhancement factors (ratio of highest concentration detected vs. the background) of the individual compounds ranged from 4 (TCE) to 62.8 (acetone). Based on the monitoring well data, it is anticipated that the predicted mass-removal enhancement should increase at least several fold by surfactant injection, as compared to the water-only flushing. However, the high pumping rates used at RW-1 and RW-2 (a total of 30 gpm) probably mitigated the impact of the total enhancement due to the dilution effect. Based on the mass recovery in the conservative tracer test (35.7 kg) and surfactant flood (42.5 kg), 46% of NAPL mass was recovered during the preflood operations in this study.

Current Status:

Demonstration completed. Site plan unknown.

Costs

Pilot test: approximately \$143K, including DNAPL site investigation and SEAR design, construction, and operation.

Lessons Learned

1. Initially, water flooding was effective in removing a large amount of the more soluble contaminant mass; however, after several days of pumping, the rate of mass removal dropped substantially.
2. Concentrations of the highly water-miscible contaminants, acetone, MEK, and MIBK, also showed significant increase during the surfactant injection phase. Greater enhancement was observed in the downgradient direction of the flow in the cell. Hence, a line drive in the direction of flow may be the optimal injection recovery configuration.

Contact

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References

Surbec-ART Environmental. *Surfactant/Cosolvent Enhanced Subsurface Pilot-Scale Remediation at Spartan Chemical, Wyoming, Michigan*. Submitted to DLZ Corp/Snell Environmental Group, Inc., 1425 Keystone Avenue, Lansing, Michigan 48911, November 2001.

Shiau, B.J., M.A. Hasegawa, J.M. Brammer, T. Carter, M. Goodspeed, J.H. Harwell, D.A. Sabatini, R.C. Knox. "Field Demonstration of Surfactant-Enhanced DNAPL Remediation: Two Case Studies." *Chlorinated Solvent and DNAPL Remediation: Innovative Strategies for Subsurface Cleanup*. S.M. Henry and S.D. Warner (Eds.). American Chemical Society Symposium Series 837, ACS, Washington, D.C., 2002, pp. 51–72.

Appendix E

RESPONSES TO COMMENTS

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Suresh Rao

1. *A more consistent use of terminology is needed to avoid confusion. Much of the text in the report is heavily biased toward surfactant flushing; a careful editing to use more generic terminology (e.g., chemical flooding?) and concepts (e.g., solubilization, mobilization) applicable to both surfactants and cosolvents is needed. Otherwise, the title should be changed to just focus on surfactants (which I do not recommend, however).*

We agree. The document has been revised to be more specific in referring to either specific technologies (i.e., surfactant flushing only) or in referring to a more generic flushing process.

The use of a more generic term such as “chemical flooding” could also cause confusion since this could also include other chemicals such as oxidants; therefore we decided not to use this term.

2. *It is important to point out that if DNAPL mobilization is the desired approach, control of the DNAPL bank is extremely difficult and requires very careful monitoring. If I were a state regulator, I would be very nervous unless it can be shown that (1) an aquitard of substantial thickness and integrity underlies the target flushing zone; and (2) the added surfactants or cosolvents do not depress the DNAPL entry pressure for the aquitard.*

We agree, and have identified both horizontal and vertical control of mobilized DNAPL as a critical factor. We attempted to bring forth this issue in the document (Sections 2.4, 2.4.3, 3.1, 3.2, and 4.1.2), but it was not sufficiently emphasized. Section 2.1 was modified to identify this as a critical issue.

3. *For an enhanced solubilization approach, I would want to be assured of hydraulic control of the injected and extracted fluids and would require that density-viscosity differentials in the injected and extracted fluids be carefully considered in the design.*

We agree. This issue is identified in Sections 2.4, 2.4.1, 3.2 (Table 3-1), and 4.1.2 of the document; however, to further emphasize this point, Section 2.1 has been modified.

4. While enhanced solubilization of DNAPLs using surfactants (one or more) is the result of micellar solubilization, addition of cosolvents produces “true” solutions (in a thermodynamic sense). Surfactants and small amounts of cosolvents are used to produce stable microemulsions and macroemulsions; in the latter cases, the small amount of alcohol is used as a cosurfactant to stabilize the microemulsion, but not as a cosolvent. Cosolvent flushing can also be used for either enhanced solubilization, or microemulsification, or mobilization, although most field tests have involved only the first type of application. At least one field test examined a combination of mobilization and solubilization for LNAPL source-zone remediation [see Falta RW et al., 1999, Field test of high molecular weight alcohol flushing for subsurface nonaqueous phase liquid, WATER RESOURCES RESEARCH, 35 (7): 2095-2108]. Phase-diagram approach is also used for selection of cosolvents to optimize the mixture composition [see Falta, RW. 1998, Using phase diagrams to predict the performance of cosolvent floods for NAPL remediation, GROUND WATER MONITORING AND REMEDIATION, 18 (3): 94-102].

This comment appears to relate to insufficient attention to cosolvent flooding and clarifies fundamental differences between surfactants and cosolvents. The excerpts from the comment provided by Dr. Rao have been added to Section 2.1. Some of the comments provided by Dr. Rao are very technical in nature and may be more appropriate for a design manual.

5. Section 3.3.2 covers some of the traditional applications of CPT for hydrogeologic characterization and only briefly mentions (one sentence) innovative applications for DNAPL characterization. Perhaps an expanded discussion of some of these methods (with citations to references to published papers and reports for details) would be useful. CPT-based methods provide “local” or “point” measurements, much the same as soil borings or multilevel samplers. Groundwater wells provide depth-integrated values but still are considered to be “local” values. Certain geophysical methods (cross-borehole tomography techniques) and interwell partitioning tracer techniques provide properties “integrated” over much larger aquifer volumes. This section should discuss the reliability of these DNAPL characterization methods and point out the level of accuracy and certainty that is desired (or required) to make reliable site management decisions. That is, how good an estimate of DNAPL volume is needed? Is it enough if we can provide an estimate within 50%, or is something better needed?

We agree and have attempted to provide insight with respect to innovative characterization techniques. However, this topic is extremely broad, and a separate ITRC document could be developed on this topic alone. This document does identify “integrated” characterization methodologies (i.e., interwell tracer tests).

Section 3.3.2 has been modified to better clarify “point vs. local” measurements.

6. Section 3.5.4 covers the topic of PITTs for DNAPL source-zone characterization, and most of the citations to the papers published by the UT-Austin and INTERA groups. Others who have evaluated PITTs for pre- and postflood characterization – and have expressed concerns over various limitations – should also be cited..

The following references have been included in the document:

Annable, M.D., P.S.C. Rao, W.D. Graham, K. Hatfield, and A.L. Wood. 1998. “Use of Partitioning Tracers for Measuring Residual NAPL: Results from a Field-Scale Test.” *Journal of Environmental Engineering*, 124(6): 498–503.

Brooks M.C., M.D. Annable, S.C. Rao, K. Hatfield, J.W. Jawitz, W.R. Wise, A.L. Wood, and C.G. Enfield. 2002. “Controlled Release, Blind Tests of DNAPL Characterization Using Partitioning Tracers.” *Journal of Contaminant Hydrology*, (59): 187–210.

Istok J.D., J.A. Field, M.H. Schroth, B.M. Davis, and V. Dwarakanath. 2002. “Single-Well “Push-Pull” Partitioning Tracer Test for NAPL Detection in the Subsurface.” *Environmental Science and Technology*, 36(12): 2708–2716.

James, A.I., W.D. Graham, K. Hatfield, P.S.C. Rao, and M.D. Annable. 1997. “Optimal Estimation of Residual NAPL Saturations Using Partitioning Tracer Concentration Data.” *Water Resources Research*, 33(12): 2621–2636.

Jin, M., R.E. Jackson, and G.A. Pope. 2000. “The Interpretation and Error Analysis of PITT Data.” *Treating Dense Nonaqueous-Phase Liquids (DNAPLs): Remediation of Chlorinated and Recalcitrant Compounds*. G.B. Wickramanayake, A.R. Gavaskar, and N. Gupta (Eds.), Battelle Press, Columbus, Ohio, pp. 85–92.

Lee, C.M., S.L. Meyers, C.L. Wright Jr., J.T. Coates, P.A. Haskell, and R.W. Falta, Jr. 1998. “NAPL Compositional Changes Influence Partitioning Coefficients.” *Environmental Science and Technology*, 32 (22): 3574–3578.

Nelson, N.T., M. Oostrom, T.W. Wietsma, and M.L. Brusseau. 1999. “Partitioning Tracer Method for the In Situ Measurement of DNAPL Saturation: Influence of Heterogeneity and Sampling Method.” *Environmental Science and Technology*, 33 (22): 4046–4053.

Wise, W.R., D. Dai, E.A. Fitzpatrick, L.W. Evans, P.S.C. Rao, and M.D. Annable. 1999. “NAPL Characterization via Partitioning Tracer Tests: A Modified Langmuir Relation to Describe Partitioning Nonlinearities.” *Journal of Contaminant Hydrology*, 36(1-2): 153–165.

7. Section 4.1.2 deals with various aspects of subsurface design that are important in ensuring that hydraulic control is maintained over the injected fluids and complete capture is achieved. While in some cases natural geologic features help (e.g., Hill OU2 site) in simplifying the design, at other sites (e.g., Jacksonville drycleaner site) complete hydraulic capture can also be achieved without physical barriers (slurry walls, sheetpile walls).

We agree, and this point has been emphasized in Section 4.1.2.

8. *One topic I did not see discussed in the report is "Design & Decision Tools". A discussion is needed on how a surfactant and cosolvent flood can be designed at a site -- based on simulation models such as UTCHEM or others -- and how the design and decisions on the cost effectiveness of the source-zone remediation can be optimized. If such models and tools are not readily available, the report should identify that need and argue for their development.*

We agree, and a section on numerical design simulations has been added to Section 4.0.

9. *The other topic that receives too little of attention is a summary of performance at several DNAPL sites (using various metrics) and an assessment of "success" or "failure" of the technology to meet the remedial objectives. I am assuming that the report's primary audience is your "clients" (i.e., state and federal regulators), but the members of the regulated and academic communities read the ITRC reports and pay a great deal of attention to what you have to say. Your report does not need to duplicate the technical details documented elsewhere. But, if economic factors (e.g., cost-benefit analyses), uncertainties in performance predictions (e.g., models and design), and lack of consensus on performance metrics or remedial endpoints (e.g., MCL vs. mass depletion vs. flux reduction) are limiting testing and adoption of the DNAPL remediation technologies, who better than ITRC to make a statement of support or concern?*

We agree. This is an important issue that has broad implications encompassing all remediation projects. The DNAPL Team is in the planning stages of developing a new document covering this issue. It will address performance assessment methods for all types of DNAPL source removal technologies, including surfactant/cosolvent flushing.

10. *The schematics will need some improvement; they are either too simplistic or they seem to perpetuate the textbook "myths" about DNAPL source zones. DNAPL distribution (i.e., "architecture") within the source zones tends to be much more complex (more sparse distribution, with large volume fraction being uncontaminated). This is one of the primary factors contributing to low contact (or sweep) efficiencies of chemical floods of DNAPL source zones. An understanding of this architecture is also very important in designing the chemical flood and forecasting the benefits (e.g., decrease in resident concentration or contaminant flux) from source-mass depletion.*

We agree. This comment seemed to focus on Figure 2-1, the schematic related to the depiction of subsurface conditions. Figure 2-1 has been replaced.

Missouri

1. *The success metric presented in the short descriptions of the case studies focuses only on gallons (or mass) of DNAPL waste recovered. Unless this number is placed into the context of how much waste DNAPL was originally present and how much was left, the metric of gallons removed does not convey the success of this technology.*

Agreed. That is why time and money should be spent on characterizing the DNAPL zone and determining how much DNAPL is originally present and how much is left.

2. *The explanation of the physical limitations fails to convey well the limited set of circumstances where this method will result in substantial cleanup. The document tends to leave one with the impression that soil materials with a 1×10^{-4} hydraulic conductivity can be treated if adequately characterized. The truth is soil materials this low in permeability are not likely to be dominated by drainable porosity. The method will not treat more than a few percent more total porosity than the drainable porosity. Simple water injection and withdrawal will remove most of the contaminants without solvents or surfactants from the drainable porosity.*

We do not agree. If pump and treat (and water flooding) remediated our DNAPL sites, we wouldn't need aggressive technologies like surfactant/cosolvent flushing. The goal of surfactant/cosolvent flushing is to remove the DNAPL that doesn't drain.

3. *The presentation of dual-phase flow fundamentals does not convey the issue adequately, and it is the understanding of dual-phase flow and pore entry pressure that allows good understanding of the difference between drainable and undrainable porosity, the distribution of this contrast, and the consequences for remediation effort.*

The comment that the document does not address “dual-phase flow fundamentals” (this is actually multiphase instead of dual phase) “adequately” may be correct for a limited audience. It was intentionally left out because it was not deemed appropriate for the targeted reader.

The terms “drainable” and “undrainable” porosity are unclear whether the commenter is referring to a dual porosity system (i.e., matrix and fractures), in which we don't advocate the use of surfactant/cosolvent flushing, or whether the commenter is referring to the concept of saturation (volume of NAPL/volume of available pore space), in which case the whole goal of surfactant/cosolvent flushing is to remove the NAPL phase that doesn't drain without reducing interfacial tension (i.e., immobile at “irreducible” or residual saturation). It is this common situation (DNAPL at residual) that represents the recalcitrant source term at most DNAPL-contaminated sites.

4. *In general this technology would not be effective or applicable in the state of Missouri. The majority of the geology in the state is composed of tight confining clays associated with karstic features. The ability of the surfactant to disperse within an area of contamination under naturally occurring conditions would be limited to the fractured structure within the confining clays. Injection of surfactants or solvents into an aquifer would not be permitted by state regulation.*

It is agreed that surfactant/cosolvent flushing may not be practical or implementable when a lot of clay is present. However, in the last two years, some limited success has been observed using surfactant flushing for NAPL free product recovery at low permeability zones, such as silty clay materials ($k=1.5 \times 10^{-4}$ cm/sec). This limited success is site-specific and depends on how complex the DNAPL distribution at the site is and the cost.

Oregon

1. *UIC Rules. In Oregon if the technology is part of a cleanup under EPA or DEQ CERCLA/RCRA action and meets CFR 144.23(C), then injection is allowable. The owner/operator would need to meet the substantive rule requirements by filling out registration forms and providing a map of injection points and a summary of the remediation plan. The state's UIC staff would issue a letter authorizing the action, and copy the agency cleanup project manager so they are aware that registration has occurred. When cleanup is complete, a decommissioning form would be completed to remove the site from the database. One concern for Oregon cleanup sites utilizing injection schemes is that sites in the Voluntary Cleanup Program and the Independent Cleanup Program (specific to Oregon) would have a lesser degree of agency oversight; therefore, these sites would need to take additional steps to be rule-authorized for injection. Surfactants and cosolvents would be allowed in Oregon as long as they were used in a controlled manner. This means injected fluids would need to be hydraulically controlled with no impact to any nearby wells. Monitoring would be required.*

No response required for this comment.

2. *Goals, page 2, second paragraph. These goals seem to read the same, to reach protective concentrations, but imply that there is less expected from cleanup of DNAPL areas. The common understanding that DNAPLs may not be practicable to clean up to protective levels is changing, and it may not be best to continue to suggest a lower expectation for DNAPLs.*

The comment above appears to be in reference to the following statement: “While appropriate remedial goals for the aqueous contaminant plume are the prevention of further migration (plume containment) or restoration of the maximum areal extent of the aquifer to cleanup levels appropriate for its beneficial use (aquifer restoration), these are usually not appropriate goals for the DNAPL source zone.” We agree with the comment, and this sentence has been rewritten to state: “While appropriate remedial goals for the aqueous contaminant plume are the prevention of further migration (plume containment) or restoration of the maximum areal extent of the aquifer to cleanup levels appropriate for its beneficial use (aquifer restoration), the DNAPL source zone may require a staged treatment train approach to meet these stringent goals.”

3. *Flushing versus Flooding. These terms are interchanged throughout the document, which can be confusing. If these terms are synonymous, then it would be helpful to include a statement up front to this effect.*

We agree. A statement has been added to the Introduction, making clear that the term “flushing” and “flooding” are synonymous and interchanged throughout the document.

4. *Section 3.3.3, page 16, first paragraph. The outside-in approach for characterizing DNAPL source zones is recommended. This should be stated as a site-specific judgment. There may be a need to do some characterizing near the DNAPL release point early on to determine how deep the outside-in characterization should go.*

Agreed. This has been modified in the document.

5. *Page 23, 4th line of first paragraph. There seems to be a word missing - move?*

The missing word was “flow” and it has been added.

6. *Page 23, second to last sentence. This sentence suggests that groundwater samples collected prior to remediation can be compared to postremediation concentrations to assess long-term natural attenuation. It would seem like you would need data collected immediately after remediation to compare to long-term data to assess this.*

Agreed. Postremediation samples would provide better assessment of long-term attenuation.

7. *Page 24, first sentence. Using the terms “complex” and “complicated” is redundant.*

We agree. The correction has been made.

8. *Section 5. This section is hard to follow. The bullets in Section 5.0 do not correspond to the sections that follow, and some of the sections seem to cover the same topic. The difference between Section 5.1.4, Monitoring Wells, and 5.2, Groundwater Quality Monitoring, is not clear. Should injection/extraction flow rate monitoring in Section 5.3 be discussed in section 5.1?*

Section 5.1.4 was written to describe the specific role of monitoring wells in the flushing process. Section 5.2 was written to target overall process monitoring during a flood. It is very important to monitor not only contaminants, but also chemical parameters in recovered water and monitoring wells.

9. *Table 5-1. While this table indicates frequency of monitoring is site-specific, it would be useful to have some general guidelines or considerations with the table.*

We agree. Whether to include specific guidelines in this table or not was discussed. Due to the substantial variability in sampling frequency, it was excluded from the document. The frequency of sampling is usually based on the expected breakthrough curve during flooding (as determined in pilot tests and modeling) and then set to ensure that the frequency is sufficient to adequately document and monitor progress. An absolute minimum would be enough sampling points to clearly define the breakthrough of surfactants and contaminants (20–30 sampling events). A sentence was added to the document to include this minimum.

10. *Section 5.1.1. More frequent monitoring might be needed during startup to assess the amount of surfactant needed or changes to other parameters.*

We agree.

11. *Section 5.1.2. This section references surfactant-surfactant mixtures, but there does not seem to be an earlier discussion of this, which should include when you might want to use two different surfactants.*

The surfactant formulation is quite complex and usually consists of a surfactant-cosurfactant and salt. Due to the complexity of this issue and the scope of this document, the details with respect to surfactant mixtures were kept to a minimum.

12. *Page 39, second to last sentence. There seems to be a word or two missing.*

The sentence has been revised.

13. *Section 8.0, second paragraph, third line. "Statues" should be "Statutes".*

The correction has been made.

14. *Question 1, Appendix C. The answer given does not really answer the question.*

The answer to Question 1 was enhanced to more clearly define the role of surfactant flushing as one step in an integrated process.

15. *Question 2, Appendix C. The word "a" is missing from the second sentence in the answer.*

The correction has been made.

Virginia

1. *The surfactant/cosolvent flushing of DNAPL has potential for use on sites in Virginia. If this technology is used in Virginia, the specific site needs to be thoroughly assessed to evaluate feasibility.*

We agree.

2. *The flushing system needs to be designed so that contaminants are completely hydraulically contained so that no significant surfactants or cosolvents are left in the ground and DNAPL, surfactants, and cosolvents do not migrate to uncontaminated groundwater zones.*

Agreed.

3. *The use of low toxicity chemicals only for flushing is recommended.*

We agree. Although there are several hundred surfactant products available for different applications, most surfactants applied for environmental cleanup are either direct food additives or indirect food additives, as specified by U.S. Food and Drug Administration (FDA). Typically, these food-additive surfactants represent surfactants with no or low toxicity below specific dosage under the FDA guideline. In addition, the selected food-grade surfactants should be much more easily biodegraded as compared to other industrial or nonfood grade surfactants. Most surfactant flushings are designed to flush the surfactant out after the remediation. The postflushing residual surfactant concentrations in the subsurface should be around low part per million (ppm) range and eventually be degraded by microorganisms.

4. *When the project is proposed by a responsible party, that party needs to get the proper permit or approval from the UIC program of EPA.*

Agreed.

California

General Note: We appreciate the thoughtful comments below and the detailed review that Mr. Wesnousky performed. Many of the comments were incorporated into the document, and we believe the document quality was improved by Mr. Wesnousky's efforts. Most of the comments that were not incorporated dealt with requests for more detailed information than was intended by the authors of this document.

1. *The document provides an overview of the technology and generally discusses the major factors that need to be addressed but mainly defers the technical details to the experts (or to selected reference documents), rather than providing the appropriate analytical tools needed to implement/evaluate the technology.*

The reviewer had expectations of the document that the authors did not intend. A lot of the specific comments made by the reviewer are requesting more technical information outside the scope of the document. There are other documents in existence that contain a greater degree of technical detail that can (and should) be used, and these are included in the reference section.

A statement has been added in the Introduction to more clearly address the intent and use of the document.

2. *Concerning the selected reference documents, there should be some statement as to what aspects of these documents are being partially or fully endorsed.*

ITRC does not endorse documents written by others but includes pertinent references to aid the reader in further research.

3. *The metrics listed for evaluating performance appear appropriate, but details on procedures to collect the necessary data to apply the metric are not provided. A critical performance metric that should be added is containment, how well hydraulic controls prevent the migration and spread of injection material and contaminants. Metrics related to risk reduction are important and would apply to virtually any source-control technology. However, providing guidance on how to apply this metric is a separate project onto itself. Consideration should be given to covering this major issue in a separate guidance document.*

A statement on hydraulic control (containment) as a performance metric has been added to Section 6.0.

The DNAPL Team is in the planning stages of developing a new document on performance assessment. It will address performance assessment methods for all types of DNAPL source-removal technologies, including surfactant/cosolvent flushing.

4. *The number of sites where this technology could be effectively applied may be very limited. In California, application of this technology would be very limited due to the heterogeneous, fine-grained sediments typically encountered in the near subsurface geology. At deeper sites, even as shallow as 50 feet, there is a major concern in the ability to control the flushing solution, as well as the large expense to monitor adverse migration (vertical and horizontal).*

The implementation of this technology in California, as well as its implementation elsewhere, requires that site-specific needs be thoroughly assessed to evaluate feasibility.

There are advantages associated with flushing deeper sites, including less interference from surficial processes (e.g., tidal fluctuations) and the ability to apply greater hydraulic pressures (see Section 2.4.2 of the document). Although additional costs may be incurred to access the deeper subsurface, these are typically relatively minor components of the total project cost.

5. *The guidance document is very general in providing recommendations and does not provide specifics to a project manager on how the technology should be applied. For example, the guidance calls for the development of a “geosystem model” to address an extensive list of input parameters but offers no recommendations on which models might be appropriate or what minimum level of data is necessary to support the many input parameters. How to evaluate the appropriate surfactant or cosolvent is generally deferred to laboratory tests that are only mentioned. The statement, “...each site requires a tailored design, what worked at one site will lead to failure at another,” speaks to the difficulty in developing useful guidance on how to apply this technology. The guidance leaves the user to turn elsewhere for technical guidance and leaves the reader with the sense that application of this technology is extremely complex and site-specific with a high risk of problems or failure.*

A section on using multiphase simulators to model a geosystem for design purposes has been added to the document. The recommendations in the document are very general by design due to the extremely site-specific nature of the problem and due to the complexity of the technology. A geosystem model as defined and discussed in Section 3.2 is simply a description of the pertinent subsurface attributes that comprise the DNAPL zone (similar to a conceptual site model) and as such is independent of numerical or analytical simulators.

We agree that in-situ flushing projects are extremely complex and should be designed and implemented by experts.

6. *On regulatory requirements, the guidance describes generally what regulations might apply in terms of UIC, RCRA, CERCLA, etc. For example, under the federal UIC program, injection wells used for aquifer restoration are Class 5 wells, authorized by rule and not requiring a permit unless authorized states require otherwise. It would be beneficial to provide examples on how an in-situ flushing technology is regulated in different states. As this is an ITRC document, it was our expectation that such examples would be provided, that the representatives of respective states involved in developing this document provide this information for their respective states. Of interest would be the specific citations on regulations that are applicable, and how these are applied and limit application of this in-situ technology in specific states.*

The state members of the DNAPL team are not aware of any specific regulatory barriers that would prevent the use of this technology. The regulations that may apply were mentioned only to direct the reader to consideration of any pertinent regulations that may apply within his/her state. If the document is updated in the future, consideration will be given to including more detailed regulatory information.

7. *Executive Summary: This section misrepresents the status of the technology from what is presented in the body of the report. Statements such as, “Environmental applications have become more numerous in recent years,” and “has shown to be effective for several DNAPL types” imply that the technology has been successfully developed and applied at many sites. This is not quite true. The Executive Summary needs to more accurately reflect the current status of the technology, potential environmental risks versus benefits, and the fact that in-situ flushing is more of an emerging technology that has been applied to full-scale cleanup at few sites. The Executive Summary reads more like a vendor marketing a technology.*

The statements are correct and are not meant to convey any special meaning. The technology of recovering nonaqueous liquids was developed in the field of petroleum engineering, and as such, it is arguably more mature than other technologies utilized in environmental remediation. The most important flushing mechanisms and processes utilized in enhanced oil recovery are essentially the same as those utilized in environmental remediation. The Executive Summary was revised to remove unnecessary adjectives and verbiage such that it reads less like an advocate position. The statement regarding environmental applications was revised to read “Environmental applications are relatively new but have increased in recent years.”

8. *Introduction: The statement, “Surfactant/cosolvent flushing of DNAPLs is an emerging technology with limited cost and performance information,” is very accurate. Consider including this statement in the Executive Summary.*

The sentence “Environmental applications are relatively new but have increased in recent years” was placed in the Executive Summary.

9. *“There are other documents in existence that contain a greater degree of technical detail and can be used as a design manual.” If this is the case, what is the purpose of the ITRC guidance? The scope statement is vague and limited: A summary of the information “needed by regulators to select and evaluate design and implementation workplans...” More than summary information is required for regulators and decision makers. Also, the scope of the guidance should go beyond review of the workplan, and include data evaluation and performance assessment.*

The scope statement for the document has been revised. The authors understand the need for regulators and decision makers to have the information necessary to properly evaluate and assess a particular remediation technology. However, the intent was to keep the document manageable in terms of readability and size. This technology is well documented in the peer-reviewed technical literature and in technical design manuals, both of which are referenced in this document.

10. *Policy Implications. The statement that DNAPL mass removal in many cases will significantly shorten the cleanup duration is not based on existing data. Recommend deleting “in many case,” and rewording to “can potentially shorten.”*

The sentence was reworded per this suggestion.

11. *Technology Description and Status, Section 2.1. An explanation of the term “water-wet” would be useful.*

A definition of the wetting fluid in a multiphase fluid has been added to the text.

12. *Technology Description and Status, Section 2.2. This section may be misleading. Language such as “applications have become more numerous” and “for a large number of those sites” need to be supported with documented numbers. How many actual full-scale cleanup projects are known to have been implemented? How many of these were pilot projects that did or did not go to full scale? Five projects are discussed as examples or cases following a statement that the technology “has been shown to be effective.” The performance parameter for these examples appears to be total gallons of DNAPL removed. Although gallons removed is important, by itself it does not indicate whether the technology was effective or contributed significantly to site cleanup. Parameters to assess performance are discussed in Section 6.0, Performance Assessment, and if possible these parameters should be applied to the examples/cases and discussed. If it is not possible to apply these parameters to a given example(s) due to data limitations or for some other reason, then this should be indicated.*

The text has been revised to reflect which of the case studies are pilot scale and which are full scale.

13. *Of the five examples presented, only one includes a full or large-scale application, the Hill AFB project that was completed last year. The case summary presented in Appendix D, however, provides detail only on the pilot study at the Hill AFB and not on the full-scale application. The remaining four examples given were pilot-scale demonstrations. For one of the sites (Sages Dry Cleaner) a full-scale application is anticipated; for three sites a follow-on full-scale application was either not planned or uncertain; and in one case (Camp Lejeune), the pilot determined the technology would not be effective at that site. Overall, the case summaries do not provide convincing data that surfactant or cosolvent flushing is a very developed technology or that the technology is effective. For example, in two cases, removal efficiencies are reported to be 46% and 62%, meaning that a large percentage of DNAPL was left behind. Additional comments and concerns regarding the five examples are provided in comments on the case summaries section.*

Please see the response to Comment #12. The Hill Air Force Base Case Study has been revised to include more information on the full-scale implementation. Mass removal efficiencies should be evaluated in terms of the site-specific remedial objectives, which may not be the nearly complete removal of DNAPL. Reducing the mass flux emanating from a source zone to a level appropriate for source-control purposes may not require extremely high removal efficiencies, although these have been achieved in several flushing applications.

14. *Section 2.3. Applicability. The technology is very limited by site hydrogeology and is best applied at shallow sites with relatively homogenous and higher permeability sediments. These conditions are not all that common at California hazardous waste sites, where subsurface geology is typically heterogeneous, and sediments are intermixed layers of clays, sands, silts, and gravels. The generalized advantages listed in this section would be best placed under the technology description section.*

This technology was successfully applied at Alameda Point, California in heterogeneous sediments with relatively low permeability. We do not agree with the reviewer's conclusions.

15. *Section 2.4. Limitations. The list of technology limitations presented appears appropriate and provides useful guidance on the many limitations and substantial risks in applying this technology. There is a limitation with respect to the depth of contamination; application at deeper sites is more problematic in terms of controlling the surfactant flush and monitoring. In addition, cost of implementation greatly increases with the depth of contamination. One of the listed limitations, "Long-term post-treatment data are currently not available to evaluate rebound effects and the ability of the technology to meet MCLs" (or other established goals?), relates to the status of the technology and should also be discussed in that section. Regulations may limit the application of the technology but are not technology limitations.*

We do not agree that depth is a technology limitation. Although cost is always an issue with remedial technologies, it is not a technical limitation; and although the depth of contamination can increase cost, it is a relatively minor component of the total project cost.

Long-term post-treatment data are generally lacking for all aggressive source-removal technologies. This technology is designed to target DNAPL and remove it from the subsurface. Attaining MCLs in the subsurface with one unit process is not a realistic goal. The authors are not aware of any case where regulations have prevented the application of this technology.

The generalized guidance provided on the primary limitation/concerns in applying the technology (sections on heterogeneity, low permeability, migration, and DNAPL properties) is beneficial. All these limitations are significant challenges to an effective application. The complexity involved in effectively applying this technology cannot be overstated. Geologic faulting (prevalent in California) and fractures are heterogeneities also of concern.

We agree.

16. Section 2.4.1. Heterogeneity. It states that mobility controls (foaming agents, polymers to effect viscosity changes) can overcome heterogeneities. The only example given where mobility control may not work is where “the aquifer cannot support hydraulic gradients,” and this is unclear. Since most or many sites exhibit heterogeneity, a technical discussion on mobility control, how it is applied, and its limitations should be included. Although there is some discussion on mobility control elsewhere in the guidance, it is quite limited. Improper application of foaming agents or polymers could result in contaminant spreading, formation plugging, or other problems.

The example has been clarified to state that the gradients required to propagate polymers across the zone of interest in a timely fashion may not be achievable in some shallow aquifers. The discussion of mobility control has been expanded as suggested. Because formation plugging by mobility control is transient and not permanent, it is not considered a serious risk.

17. Section 2.4.2. Permeability. The statement, “relatively low permeability sites have been effectively remediated at depths as shallow as 15 feet (Surbec-ART, 2002),” appears to be a vendor’s conclusion and, if so, inappropriate. The term “effectively remediated” suggests that the site has been remediated to some cleanup goal; this statement however is unsupported with a case study or data.

The USEPA and the Oklahoma Corporation Commission were involved in the project cited in Section 2.4.2 and conducted the postflushing performance assessment. Since the site in question is a site with a tight formation impacted by free product gasoline, not DNAPL, the reference to this site has been removed.

18. *Section 2.4.3. Migration. To control and prevent vertical migration, a competent aquitard barrier of substantial thickness and $k < 10^{-6}$ cm/sec is recommended. What is the minimum recommended thickness? One case summary suggests a discontinuous 0.5 feet thick clay layer may be acceptable. How a stratum is evaluated as an adequate “capillary barrier” in terms of the chemical/physical properties of DNAPLs is not provided. How does a surfactant or cosolvent affect the properties of an aquitard as a capillary barrier? What types or properties of the clays composing an aquitard might be affected and why? Section 3.3.6 discusses how a capillary layer might be characterized. Several methods are identified, but a specific approach, or specific laboratory method is not recommended. The laboratory methods listed are “experimental.” Unless the impermeable layer is very thick (e.g., >20 feet), there is always a concern about the competency of a stratum to act as a true barrier. Pump tests can be used to determine if there is any hydraulic connection between zones above and below the aquitard. The statement that, “it should be assumed that an aquitard can permit downward migration of DNAPL through localized areas through fractures unless it can be proven otherwise through a field investigation,” is sound, but no field investigation methodology is provided for this purpose. A monitoring and sampling program can assess what fraction, if any, of the contamination has migrated into or beyond the identified aquitard or capillary barrier but only after the system has been installed and operated, and a problem has occurred.*

The wording of the text has been revised to state that “an aquitard of appropriate thickness is usually needed...” The aquitard thickness required is a function of the site-specific hydrogeology (and its heterogeneity) and the character of the aquitard itself. References to evaluation criteria have been added to the text.

Specific approaches for characterizing capillary barriers in Section 3.3.6 are not provided because these are strongly dependent on the specific site conditions encountered. The word “experimental” has been removed from the text (this term was meant to convey the fact that these were procedures conducted in a laboratory and was, therefore, redundant). The laboratory methods listed are in fact well established and standardized, having been used in the petroleum industry for decades.

At many sites, characterization of aqueous contaminant concentrations below an aquitard can indicate how competent an aquitard is prior to system installation and operation. At other sites, the competency of the aquitard is demonstrated by the fact that a significant thickness of mobile DNAPL has accumulated on the barrier with no indication of DNAPL migration from the stratigraphic trap.

19. *Section 2.4.4. DNAPL Properties. Technical guidance on the physical/chemical properties of DNAPLs would be appropriate here. The specific chemicals known to have been treated and those that potentially could be treated should be included. It would be useful to present a table detailing the specific DNAPLs, their relevant physical/chemical properties, and appropriate surfactants, cosolvents, or mixtures, along with their limitations with respect to site geology/geochemistry and other factors. There is some discussion on difficulty with highly viscous DNAPLs. Highly viscous petroleum hydrocarbons may be better addressed with steam injection technology. Problems with cosolvent flushing of lower molecular weight DNAPLS are*

also mentioned. Again, only generalized information is presented, rather than technical criteria to enable the user to evaluate the acceptability of a proposed approach as opposed to relying on the technology developer or other “experts.”

The authors agree it could have been beneficial to add this information to the document. If the document is updated in the future, consideration will be given to including this information.

20. Section 3.2. Geosystem Model. This section indicates what must be considered in developing a model, but no guidance on what constitutes an acceptable model is provided. Table of data that needs to be incorporated into a model is useful.

The term “model” in this context refers to a coherent description of the parameters needed to fully describe a design basis for a remedial action and does not refer to a mathematical model simulated numerically (much like a conceptual site model does not refer to a mathematical model). Ultimately, however, the geosystem should be compiled into a numerical model so that predictive simulations can be used to assist the in-situ flushing design process. The text has been revised to clarify this.

21. Section 3.3. DNAPL Source Characterization. The information in this section is very general and may be redundant with other ITRC guidance (developed?) on DNAPL characterization. The exception to this might be Section 3.3.6, Characterizing Capillary Barriers. This section also is summary information and does not provide specific recommendations.

No response required for this comment.

22. Section 3.5. Aquifer Characterization. Conservative tracer tests are clearly important in assuring that all injected materials can be recovered by the extraction well system. How swept pore volume, hydraulic properties, heterogeneity, etc. can be determined from this test is not clear (method of moments). Also not clear are the accuracy, precision, or pitfalls of using these indirectly derived numbers.

References to technical papers describing the use of moment analyses to determine swept pore volume and other hydraulic properties have been added to the text so that interested readers can research this mathematical tool. One of the most useful aspects of a tracer test is that the tracers have passed through the zone of interest, giving us direct estimates of swept pore volume, etc. The accuracy and precision of these tests are no more or less affected by measurement uncertainties than other direct environmental measurement techniques (e.g., uncertainty in flow rate measurements and tracer concentration chemical analyses).

23. *Section 3.5.4. PITTs. Heterogeneities and consequent preferential flow-paths, along with partitioning or interferences with tracers, can give inaccurate results. The risk is that the PITT results may indicate most of the DNAPLS have been removed when a large fraction actually remains. PITT test results should be viewed qualitatively and with caution. Technical guidance on how to avoid “PITTfalls” and misleading results would be useful.*

Technical guidance on reducing the uncertainty in PITT results has been added to the text. The risk of a PITT providing an indication that DNAPL has been removed when a “large fraction” still remains is less than for remediation performance assessments based on conventional soil and groundwater sampling.

24. *Section 3.6. Characterizing Groundwater. One example is given on how a surfactant addition might affect cation exchange, mobilize fines, and plug an aquifer. No other information is provided on groundwater quality parameters and formation conditions that are problematic.*

Potential cation exchange concerns are specific to the site’s geochemistry and to the particular surfactant being utilized. We know of no other groundwater quality issues that may be described as problematic due to the use of surfactants.

25. *Section 4.0. System Operation Consideration. The introductory paragraph to this section, below, is excellent and should be highlighted in the Executive Summary and Introduction (technology description) of the report.*

“Designing and implementing a DNAPL source-removal operation is with few exceptions an intrinsically complex and complicated endeavor. Chemical flushing activities (and any other aggressive source-removal technology) must be designed in such a way that uncontrolled vertical and horizontal migration of contamination is avoided. A comprehensive understanding of the subsurface environment, multiphase fluid flow, and the physical processes being employed is required to prevent remediation failure and avoid contaminating previously uncontaminated portions of the aquifer. ”

This paragraph has been added to the Executive Summary, as requested.

26. *Section 4.0. System Operation Consideration. Most of the information presented under this section of the report is very general information. Designing an in-situ flushing technology is considered so site-specific that the technical issues/analyses are deferred to other reference documents or to the “technical experts” (e.g., the consultants or technology developers/vendors). Some useful cautionary information and examples are presented in these sections, but no technical tools are provided one can use to evaluate the adequacy of a design (even at a screening level). Section 4.0 is more a primer than a technical guidance.*

As with many technically complex processes (e.g., the chemical synthesis of pharmaceuticals), the expertise required to evaluate a flushing design at the level that the reviewer requests is not possible to impart in a document of this type. The technical guidance in Section 4.0 is intended to allow the reader to understand the components of the system so that an evaluation can be conducted of the overall process system with respect to achieving the treatment goals.

Where is the “numerical simulation phase” described in any detail (referred to in Section 4.1.2).

A section on numerical design simulations has been added to Section 4.0.

27. Section 5.0. Process Monitoring. Again, everything is considered so site-specific that detailed technical guidance is not provided. There should be mention of sampling the “capillary barrier” and any underlying aquifer to confirm vertical migration has not occurred.

See response to Comment #26. A sentence about monitoring aquifers uncontaminated with DNAPL has been added to the section on groundwater monitoring. Sampling the capillary barrier is part of the performance assessment and not a process-monitoring task. A statement suggesting that in some cases the capillary barrier may require sampling has been added to the performance assessment section.

28. Section 5.0. Process Monitoring. This section has a number of statements, such as “typical flushing project” and “in many cases” incorrectly inferring the technology is further developed than it is.

The authors respectfully disagree with the reviewer’s assessment.

29. Section 5.0. Process Monitoring. The statement, “In many cases, small fluctuations in surfactant/cosolvent concentrations or ratios can have a profound effect on the performance of the technology,” should be further explained. What are the acceptable ranges, examples of profound effects? This appears problematic since subsurface heterogeneities cause variations in dilution as well as absorption as the injected solutions travel through the target treatment zone.

The statement has been revised to state that in some cases (e.g., Type III or ultralow interfacial tension floods) small fluctuations in electrolyte concentrations or ratios can have a profound effect on the performance of the technology because the chemical system can be pushed into unfavorable phase behavior. Subsurface heterogeneity does not create significant dilution effects in a well-designed flood using mobility control since the surfactant injection is typically on the order of multiple treatment zone pore volumes. Adsorption of injected solutions will be negligible if the proper chemical formulation is selected.

30. *Section 5.0. Process Monitoring. How does one assess whether “false partitioning” of the tracers has occurred or not? Vendors/developers have presented PITT results to demonstrate the effectiveness of the technology at a site. What other data needs to be provided to confirm the validity of such results.*

The requested explanation has been added to the text. Such partitioning should be investigated during the bench-scale testing phase of an in-situ flushing project by conducting a preflood PITT and then a surfactant flood in a column filled with field soil and contaminated with DNAPL from the site. Once the column has been surfactant flooded, a postsurfactant flood PITT should be conducted to provide an independent mass balance (in addition to volumetric measurements) and to determine if the surfactant remaining in the column interferes with the partitioning tracers.

The reviewer is referred to the papers on PITTs in the references section.

A conservative tracer test should be used in all cases to validate hydraulic capture effectiveness.

The authors agree that the CITT is a powerful tool for verifying that hydraulic capture can be achieved. However, not all sites require a conservative tracer test to achieve this verification of hydraulic capture.

31. *Section 5.0. Process Monitoring. In California, a carbon filter or other treatment device would likely be required to treat VOC emissions from an air stripper.*

A statement to this effect has been added to the text.

This is the first mention of a “24-hour prestabilized pumping period.”

The text has been revised to reference a presurfactant water flood in place of the phrase “24-hour prestabilized pumping period.”

Are there known interferences with certain surfactant or surfactant mixtures that interfere with VOC analyses using approved analytical methods?

If direct injection for the GC analysis is used, most surfactants used will interfere with the VOCs readings. However, one can use indirect injection (e.g., purge-and-trap pretreatment) or direct injection with glass wool packed in-line injector to eliminate the interferences.

32. *Section 6.0. Performance Assessment. This section is quite important. A list of approaches is provided with no specific recommended metric(s). Should all of the listed metrics be applied? It would be a difficult task to assess the impact of the DNAPL source-zone removal on the overall site cleanup in terms of risk reduction. Discussion on performance metrics related to risk reduction might best be deferred to another guidance document on that issue. The metrics (items*

1, 2, and 3) related to DNAPL removed and remaining, and contaminant flux are appropriate. The summary statement is made, “In all cases, the risk of unremoved DNAPL and the reduction of risk due to removed DNAPL should be considered in assessing technology performance.” How is this accomplished? In any case, this section offers no specific guidance or criteria on how risk reduction due to a source-removal action might be evaluated.

The requested information is beyond the scope of this document. A reference to the planned ITRC performance assessment case history document and the technical and regulatory guidance on performance assessment has been added to the text.

Item (4), “the percentage of injected chemicals” is unclear in terms of a performance metric.

The text has been clarified to explain that this item refers to the percent of injected chemical recovered at the extraction wells as a measure of the adequacy of hydraulic control during the flood.

“Exit criteria” are mentioned but not explained. Guidance on appropriate exit criteria would be useful.

The authors agree it could have been beneficial to add this information to the document. If the document is updated in the future, consideration will be given to including this information.

One needed performance metric is the containment of DNAPLs and injection solutions within the target treatment volume (i.e., the extent to which DNAPL contaminants and injected materials were contained and not spread outside the treatment zone).

See comment above on recovery of injected chemicals.

33. Section 7.0. Regulatory. FDA food-additive status does not necessarily mean that the proposed amendment (e.g., surfactant) doesn’t pose other environmental hazards, such as a problem for aquatic life. I think this is indirectly addressed, but it could be more clearly stated.

What specific types of recovered “fuels” could be recycled at a blending facility (gasoline and diesel are not DNAPLs)?

The reference to fuel blending has been removed.

The site owner and waste generator would have responsibility and ultimate liability for proper management of any hazardous wastes generated in an in-situ flushing operation.

We agree. Although there are hundreds of surfactant products available for different applications, most surfactants applied to environmental cleanup are either direct food additives or indirect food additives, as specified by U.S. Food and Drug Administration (FDA). Typically, these food-additive surfactants represent surfactants with no or low

toxicity below specific dosage under the FDA guideline. In addition, the selected food-grade surfactants should be more easily biodegraded as compared to other industrial or nonfood-grade surfactants. Most surfactant flushings were designed to flush the surfactant out after the remediation. The postflushing residual surfactant concentrations in the subsurface should be low and eventually be degraded by microorganisms.

34. *Case Summaries. All case summaries presented involve pilot studies. In one case, a follow-on full-scale implementation was apparently completed last summer, but information on that application is not provided (Hill AFB). In one other case, the full-scale application of the technology has been approved and is expected to be implemented this year. Following are notes and questions concerning the five case summaries presented:*

a. *Sages Dry Cleaner, Jacksonville, Florida (Pilot Study). Is removal of 10 gallons of PCE when injecting 8900 gallons of a cosolvent in a permeable unconfined sand aquifer considered to be effective? Based on soil and PITT, 62% total percent of the DNAPL source was removed. What were the results at the 14 of 35 sampling locations where contamination levels weren't 92% lower? Deepest groundwater contamination was found at 92 feet bgs. Maximum depth of injection was 35 feet, underlain by 0.5 feet thick discontinuous clay at 35 ft. 160,000 gallons of wastewater had to be disposed. What percent of cosolvent was recovered versus lost (given geology this is a concern!)? Was contamination spread deeper? What monitoring was done to ensure capture containment and that contamination wasn't spread horizontally or vertically? A full-scale project is planned for 8/2003.*

Regarding the effectiveness of the pilot study, the Florida Department of Environmental Protection (FDEP) was very concerned with losing hydraulic control of the pilot test area; therefore, the design of the pilot test system was very conservative. Because of this conservative design, a lot of efficiency was lost. Based on the pilot test data, numerous improvements were made to the design of the full-scale system. It is believed that the full-scale system will remove greater than 85 percent of the DNAPL PCE at the site.

Regarding the issue on percent of cosolvent recovered versus lost, 1 percent of the cosolvent (ethanol) in the source area was intentionally left to enhance the bioremediation process. The residual alcohol significantly enhanced the bioremediation process.

Regarding the potential for contamination having been spread deeper, there was contamination below this thin discontinuous clay layer prior to the pilot test. In fact, it is believed that the clay layer does not exist at the site.

Multilevel samplers (MLS) and monitoring wells were installed above the discontinuous clay layer. Monitoring wells were also installed beneath the clay layer.

A full-scale project is planned for August 2003.

- b. *Camp Lejeune Base Dry Cleaners, Jacksonville, Florida (Pilot Study)*. 76 gallons were recovered from a shallow aquifer: clay at 20 feet, aquifer 16–20 ft bgs; DNAPLs located in lower permeability 0.0001 cm/sec silt layer and 0.005 cm/sec sand layer. PITT results problematic due to interference with surfactant. 88% recovery IPA, 77% recovery surfactant. What happened to 23%, 12% not recovered? Lesson learned: not cost-effective due to lower permeability silt layer. Soil sampling indicated 30 gallons remained (soil results typically underestimate).

At this site, the surfactant apparently degraded and/or had an impurity that sorbed and behaved as contaminant. Surfactant still degrading, IPA mostly removed with vacuum extraction activities conducted by on-site contractor to remove free-phase DNAPL still in the treated zone at the site.

- c. *Hill AFB (Pilot Study)*. DNAPL layer 45 to 50 ft. bgs; 0.01 to 0.001 cm/sec high permeability zones. 4,9000 gallons DNAPL initially present at site; 45,000 gallons (91%) removed by extraction pumping; water and steam flooding; surfactant flooding demonstrations; and three full-scale surfactant floods. Pretest pumping in pilot recovered 500 gallons of free phase; two surfactant floods removed 341 gal in pilot test with claim of 98% residual removal determined by PITT; residual-removal claim apparently confirmed with soil sampling results. How were displacement or off-site migration of contaminants to adjacent areas evaluated? What is the basis of the 49,000 gallons DNAPL initially present?

Confirmation borings with soil samples and sentinel wells were used to evaluate the containment of the contaminants. The solubilized component was also evaluated by measuring the percent recovery of the injected chemicals and by maintaining hydraulic gradient control during the flood. The estimate of DNAPL initially present was determined by soil sample data and PITT studies.

In a full-scale application after the pilot, 1,750 gallons were removed by three large-scale surfactant floods. Note that no information is provided on the full-scale application other than to say the project was completed summer 2002. A full-scale application is a significant accomplishment, and its case summary should be presented. It would be useful to know the percent of residual DNAPL removal that was determined for the full-scale application, versus the 98% determined for the pilot.

The Hill AFB full-scale application data is still being evaluated. Preliminary estimates indicate that approx 90% of the DNAPL was recovered. A report dealing with mass flux will be prepared by ESTCP, and this report is expected to contain more detailed estimates of the amount of DNAPL removed.

Surfactant flushing removed 2,091 gallons of DNAPL and accounted for about 4.6% of the 45,000 gallons DNAPL, or about 4.2% of the estimated 49,000 gallons DNAPL initially present. The effectiveness of in-situ flushing at Hill AFB may be difficult to evaluate since pilot and full-scale applications were conducted in conjunction (and possibly concurrently) with an extraction program at the same location. About 4,000 gallons of residual DNAPL

apparently still remain. An explanation and supporting data/results on what actually remains and why would be useful in evaluating the overall effectiveness of the full-scale application.

There cannot be a direct comparison between SEAR and extraction because they both target a different objective. It is much more cost-effective to remove DNAPL via extraction and water flooding than with SEAR (or another aggressive mass-removal technology). However, the endpoint achieved with extraction/water-flooding operations is limited to the flowing DNAPL phase, and the remaining residual phase continues to present a very large source term that can be targeted by SEAR. SEAR is a tertiary recovery technology and should be applied only after more cost-effective techniques have been utilized to recover as much mass as possible, a strategy analogous to enhanced oil recovery in the petroleum engineering.

- d. Alameda Naval Air Station, California (Pilot Study): A shallow site with maximum depth of 17.5 ft. DNAPLS present in a silt/sand/gravel fill material overlying bay muds. A 97% DNAPL mass reduction “observed” based on prepartitioning tracer estimate of 100 to 169 gallons in the treatment zone. The low range of mass recovered based on the 35 gallons of DNAPL reported to have been recovered would be $35/169 * 100\%$ or 21%; 35% would be the high range. Why the large discrepancy using these figures versus solely the pre/post PITT result? The 35-gallon number is reported in the February 3, 2000 SESR DNAPL Removal Treatability Study Results Report at Alameda Point. The case summary indicates 80 gallons of DNAPL was removed from source zone, or 47% to 80% versus the stated 97%. How was the 80 gallons calculated? The 2/3/00 report (Section 4.4) indicates a range of 65 gallons (based on measured concentrations times volumes recovered to 35 gallons, based on a direct measurement of DNAPLs recovered by the MPP unit (macroporous polymer liquid/liquid extraction). Figure 4-15 of that same report indicates the MPP removal efficiency for TCE +TCE was generally around 95%; and during a period of several days during the initial portion of the 18 days, surfactant flooding was as low as 76%. Using 76% and assuming 24% was not directly recovered would indicate the system recovered 46 gallons, or from 27% to 46% of the 100 to 169 gallons that the PITT estimated to be present. The most direct measurement, the 35 gallons actually recovered, should tie well with other calculated values presented but does not. Pilot test cost \$658K/35 gallons recovered or \$18.8K per gallon.*

The 35 gallons of DNAPL were collected from the aboveground waste treatment system, the MPP unit. This MPP system was used to separate the VOCs from the recovered surfactant waste stream. Among the aboveground treatment processes (e.g., between the recovery wells, oil/water separator, and the MPP unit), significant VOCs were volatilized and lost in the air. Therefore, the DNAPL collected from the MPP unit represented only part of the DNAPL recovered (or underestimated the actual DNAPL recovered). As indicated in the report, it was documented that an estimated 80 gallons of DNAPL was recovered based on the measured TCA+TCE concentrations observed in the recovery wells and the flow rates of each well. The 80-gallon DNAPL value was calculated from a total of 69 gallons of TCA+TCE-only detected in the recovered well samples plus an estimated 10% to 20% of additional contaminants, like DCE and DCA. According to the report, this estimation was based on the TCA+TCE concentrations, which averaged 80% to 90% of total VOCs observed at the site.

PITT was one of the tools selected to assess the performance of the surfactant flushing in the demonstration. Though PITT is a very good tool for estimating DNAPL volume, it has limitations. Based on the soil-coring results, most postflushing DNAPL concentrations in the aquifer material were much lower compared to the pretest samples, except in the Bay Mud samples (one or two located at 17', most Bay Mud started at 19'). The post-PITT results indicated that less than one gallon of DNAPL was left in the treated zone. Compared to 100 to 169 gallons, this is more than 99% reduction of DNAPL as a result of surfactant flushing. The results of the contaminants in pre- and postsoil samples, in the groundwater, and the PITT data, all indicated significant reduction of DNAPL (> 97% based on the soil-coring data) in the treated area.

Not mentioned in the case summary are boring-sample results taken after treatment from the underlying "aquitard," all of which indicated contamination ranging from 520 mg/kg to 15,730 mg/kg TCE and TCA. These results were apparently excluded from the removal-effectiveness calculation because the samples were collected outside the treatment cell. Results were not available to assess the mass of contamination both before and after treatment (i.e., Did treatment mobilize contaminants into the underlying aquitard?)

Pre- and post- multilevel samplers at 22' deep into the Bay Mud zone, located in the center of the treated area, were monitored. Results indicated no evidence of increasing VOCs and surfactant concentrations into the Bay Mud zone or any mobilization of the DNAPL. This confirmed laboratory column results indicating that no mobilization of DNAPL was observed using the selected surfactant system (via the ultrasolubilization mechanism) in the Alameda sand-packed column.

- e. Spartan Chemical Co. Superfund Site, Wyoming - (Pilot Demonstration): 46% DNAPL mass recovered in preflood; less than 10 gallons recovered with 4,000 lbs. electrolyte, 1,8000 lbs surfactant. Deeper site, 87–92 feet bgs; \$143K/10 gallons contaminant removed; ~ \$14,000/gal; not enough known about site! underlying clay 5ft. thick; aquifer thickness 15 to 80 feet thick. Why such large variation in thickness? How are conservative tracer test results used to predict percent mass recovery? Summary does not indicate amount recovered via surfactant injection after the preflood, only that certain contaminants showed increases. Not clear what is meant by background concentration in the context of "enhancement factor." Is background the concentration in recovered groundwater upon termination of the preflood? Not clear what monitoring or sampling was conducted to ensure that vertical or off-site migration outside the treatment cell did not occur. Uncertain if technology is being considered at the site for full-scale application.*

The changes in the aquifer thickness at the Spartan site are primarily due to the configuration of the clay surface and changes to ground surface topography. Due to project budget constraints during the pilot study, no further investigation regarding the thickness of the clay layer was conducted.

The purpose of the conservative tracer test was to show hydraulic capture of injected fluids. Hydraulic capture indicated that all surfactant injected during the surfactant-injection phase would not leave the test cell area and could be recovered by the surfactant flushing well. In this study, hydraulic capture was observed during the second conservative tracer.

Maine

1. *The document is very well written and easy to follow. Also, this time we gave credits to the sources of information and authors.*

No response required for this comment.

2. *On page 16, I would like to see a short description of the Rotosonic drilling method. The average PM would not understand the term, and it may not be best to continue to suggest a lower expectation for DNAPLs.*

A short description of the Rotosonic method has been provided.

3. *I think a short QA/QC section would be useful. At least a system QA/QC should be added. The analytical QA/QC is usually provided with the method; therefore, we do not have to be concerned with that. However, the system and other aspects of the processes should have a QA/QC plan. The QA/QC could be generic, but you have to point out the QA/QC issues we must watch for when we use the process.*

The authors agree it could have been beneficial to add a QA/QC section to the document. However, the authors did not feel it was pertinent to the overall theme of the document. If the document is updated in the future, consideration will be given to including a QA/QC section.

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Appendix F

**DNAPLS TEAM CONTACTS, ITRC FACT SHEET,
ITRC PRODUCT LIST, AND USER SURVEY**

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