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Surfactant-Enhanced Aquifer Remediation (SEAR) Design Manual

Prepared by

Battelle
505 King Avenue
Columbus, OH 43201

and

Duke Engineering and Services
9111 Research Boulevard
Austin, TX 78758

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FIGURES

TABLES

ACRONYMS AND ABBREVIATIONS

ACS	American Chemical Society
AES	alcohol ether sulfate
bgs	below ground surface
BOD/COD	biological oxygen demand/chemical oxygen demand
$CaCl_2$	calcium chloride
CDC	capillary desaturation curves
CEC	cation exchange capacity
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CHC	chlorinated hydrocarbon compounds
CITT	conservative interwell tracer test
cmc	critical micelle concentration
cp	centipoise
CPT	cone penetrometer testing
DE&S	Duke Engineering and Services
DNAPL	dense, nonaqueous-phase liquid
DPT	direct push technology
DSITMS	direct-sample ion-trap mass spectrometer
f_{oc}	fraction of organic carbon
GAC	granular activated carbon
GC	gas chromatograph
GPR	ground-penetrating radar
GUI	Graphical User Interfaces
HAFB	Hill Air Force Base
HSA	hollow stem auger
IDHW	investigation derived hazardous waste
IFT	interfacial tension
IPA	isopropyl alcohol
K	hydraulic conductivity
K_d	distribution coefficient
K_{oc}	organic carbon partitioning coefficients
K_{ow}	octanol-water partitioning coefficients
LIF	Laser Induced Fluorescence
LNAPL	light, nonaqueous-phase liquids
MCB	Marine Corps Base
MCL	maximum contaminant levels
md	millidarcies
MEUF	micellar enhanced ultrafiltration
MLS	multilevel samplers

MPPE	macroporous polymer extraction
MWCO	molecular weight cutoff
NaCl	sodium chloride
NAPL	nonaqueous-phase liquid
NF	nanofiltration
NPDES	National Pollutant Discharge Elimination System
NRMRL	National Risk Management Research Laboratory
NSFO	Naval Special Fuel Oil
O&G	oil and grease
OU-2	Operable Unit 2
PCB	polychlorinated biphenyls
PCE	tetrachloroethylene or perchloroethylene
PID	photoionization detector
PITT	partitioning interwell tracer tests
POTW	public-owned treatment works
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
RAO	remedial action objective
RPM	remedial project manager
SCADA	Supervisory Control and Data Acquisition
SCAPS	Site Characterization and Analysis Penetrometer System
SDWA	Safe Drinking Water Act
SEAR	surfactant-enhanced aquifer remediation
SEAR-NB	neutral buoyancy SEAR
TCA	trichloroethane
TCE	trichloroethylene
TDS	total dissolved solids
ThOD	Theoretical Oxygen Demand
TOC	total organic carbon
TTO	total toxic organics
U.S. EPA	United States Environmental Protection Agency
UF	ultrafiltration
UIC	Underground Injection Control
USDW	underground sources of drinking water
VOC	volatile organic compound
wt%	weight percent
XRD	X-ray diffraction

Section 1.0: INTRODUCTION

1.1 Objectives

This design manual is intended to provide background information and specific guidance for technical personnel who would like to evaluate and apply in situ surfactant flooding or surfactant-enhanced aquifer remediation (SEAR) at sites contaminated with dense nonaqueous-phase liquid (DNAPL) such as chlorinated solvents. SEAR is a source zone remediation technology that may be used as an enhancement to conventional pump-and-treat systems, which often are inefficient for recovering contaminants that are trapped as an immiscible-phase liquid. By promoting the rapid removal of these contaminants, groundwater cleanup goals may be accomplished much more quickly.

This technical document represents the first volume of a two-part series providing practical guidance to support remedial project managers (RPMs) in the application of SEAR. This volume covers feasibility issues and design aspects of the technology and the second volume (Implementation Manual) will cover field implementation including system setup and operations. Some basic technical background in relevant fields (e.g., engineering, geology, hydrogeology, soil science, and chemistry) and some design experience are needed to fully understand and apply the information in this manual.

1.2 Document Organization

The material presented in this design manual is organized into 7 sections, as shown in Table 1-1. The overall SEAR design process includes DNAPL source zone characterization, surfactant selection, SEAR system design and optimization, and wastewater treatment system design. A flowchart of the design process, which mirrors the document organization, is also provided in Figure 1-1.

Table 1-1. SEAR Design Manual Organization

Section	Title	Function
1.0	Introduction	Define the objectives and organization of the SEAR Design Manual. Provide basic design process overview to allow the reader to anticipate/understand materials to be presented in manual. Figure 1-1 is a flowchart of the overall SEAR design process.
2.0	Technology Overview and Feasibility Analysis	Provide a description of the technology and a basic outline of the information needed to conduct a feasibility analysis including measures of effectiveness, implementability, and cost considerations for SEAR.
3.0	DNAPL Source Zone Characterization for SEAR	Define site characterization needs and describe conventional and innovative methods for DNAPL site investigations and aquifer characterization. Accurate characterization is essential to focus the remedial effort on the DNAPL-contaminated areas, predict chemical requirement and the duration of the field effort, and avoid increasing the risk posed by the contamination at the site. Figure 3-1 is a flowchart of the DNAPL site characterization process.
4.0	Surfactant Selection	Provide a basic background in surfactant chemistry and a review of the chemical and physical properties, which control SEAR performance and surfactant selection.

Table 1-1. SEAR Design Manual Organization (Continued)

Section	Title	Function
5.0	Numerical Modeling for SEAR System Design and Optimization	Review SEAR design objectives and approach. The use of field testing and simulation modeling to improve and optimize the preliminary system design is discussed. Full-scale system design is covered including the components required to inject surfactant, maintain hydraulic control, and recover the DNAPL and surfactant solution. Figure 5-1 is a flowchart of the SEAR design/optimization process.
6.0	Wastewater Treatment Unit Process Selection	Present options and rationale for selecting a treatment system that integrates unit processes for removing and concentrating contaminant, cosolvent and surfactant. Figure 6-3 is a flowchart summarizing factors influencing selection of wastewater treatment processes.
7.0	References	Document the information sources used to prepare the SEAR Design Manual.

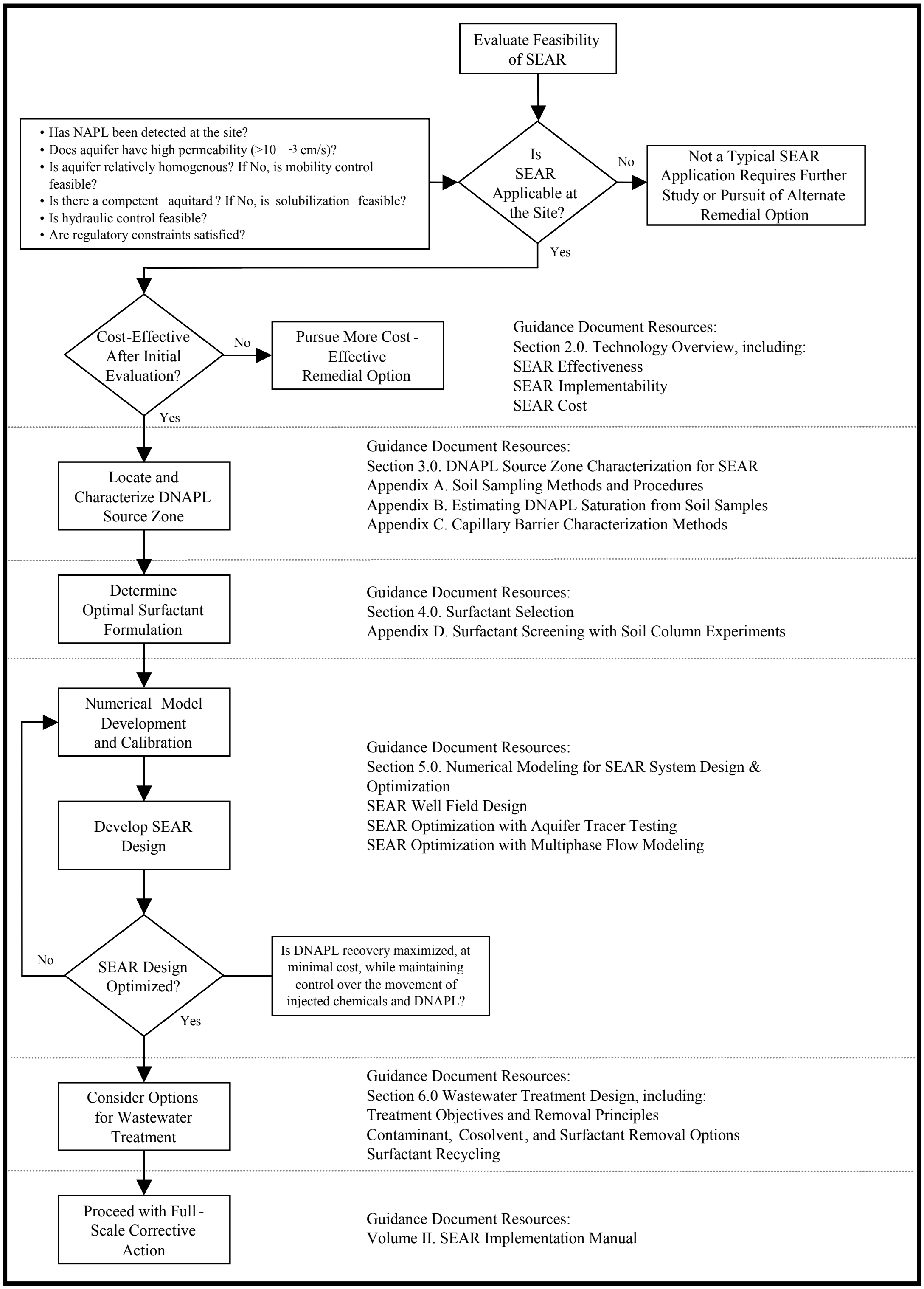


Figure 1-1. SEAR Project Flowchart

Section 2.0: TECHNOLOGY OVERVIEW AND FEASIBILITY ANALYSIS

This section provides a basic description of SEAR technology, along with an overview of factors affecting the selection and design of SEAR including effectiveness, implementability, and cost. These factors correspond to the main criteria used for an evaluation or feasibility analysis of remedial options as conducted under the corrective action requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Resource Conservation and Recovery Act (RCRA).

2.1 Technology Description

Pumping groundwater for aboveground treatment is a standard remedy for groundwater contamination. However, remediation with pump-and-treat methods can require periods of years to decades to reach treatment goals due to persisting sources of contamination (MacKay and Cherry, 1989). These persistent sources were determined to be NAPLs, which are undissolved organic contaminants that become trapped in the subsurface due to capillary forces. Many NAPLs have low aqueous solubilities and are biologically recalcitrant; therefore mass removal from the dissolved phase is slow. SEAR was developed as a method to increase the solubility and mobility of NAPL and enhance the removal rate achievable with pumped groundwater. Surfactants are surface active agents that have two different active sites, a water-liking (e.g., hydrophilic) head and a water-disliking (e.g., hydrophobic) tail. Thus, they exhibit solubility in both water and oil and help to improve NAPL recovery. SEAR technology can be used to clean up a wide variety of NAPL contamination. Over the past few years, the greatest demand for the SEAR technology has been for remediating chlorinated hydrocarbon DNAPLs such as trichloroethylene (TCE) and tetrachloroethylene (PCE). This is due to their prevalence as groundwater contaminants, the risk associated with their presence in the subsurface, and the lack of other established remedial alternatives. Industrial solvents were often released to the environment as spent solvents laden with oily contaminants. SEAR has been used to remove these variable density contaminant mixtures and contaminants such as creosote, gasoline, jet fuels, and polychlorinated biphenyls (PCBs) (Lowe et al., 1999a).

SEAR can be considered a chemical enhancement to pump and treat in which a surfactant solution is pumped through a contaminated zone by introduction at an injection point and removal from an extraction point. To cover the entire contaminated zone, a number of injection and extraction wells are used; the well configuration is determined by the subsurface distribution of DNAPL and the hydrogeologic properties of the aquifer. A conceptual picture of SEAR application is shown in Figure 2-1. Application of SEAR technology removes the contaminant source by removing the residual DNAPL contamination that dissolves to form the groundwater plume. Once the DNAPL sources impacting a particular groundwater plume are entirely removed, an intermediate and long-term reduction in dissolved-phase contaminant concentrations will occur through natural attenuation. Thus complete delineation of the existing DNAPL sources is requisite to effective management of source control removal measures such as SEAR.

At suitable sites, a water flood is applied first to remove any easily recoverable mobile DNAPL. The more tightly held, residual DNAPL is then removed through injection of the surfactant solution into the DNAPL source zone. A post surfactant-injection water flood is conducted to recover injected chemicals and solubilized or mobilized DNAPL remaining in the aquifer. The extracted fluids are then treated above ground to remove free-phase (i.e., separately mobile phase) and dissolved-phase contaminants and any other constituents necessary to meet disposal requirements. The surfactant can be recovered for reinjection, if desired. The primary difference between a SEAR system and a pump and treat system is the importance placed on maintaining hydraulic control over the injected fluids and contaminants. To this end, a SEAR wellfield consists of closely spaced injection and extraction wells and often includes hydraulic control or tap water injection wells to prevent the escape of injected chemicals and solubilized/mobilized contaminant. As shown in Figure 2-1 below, injected fluids and contaminants are captured at extraction wells screened within the DNAPL-contaminated zone.

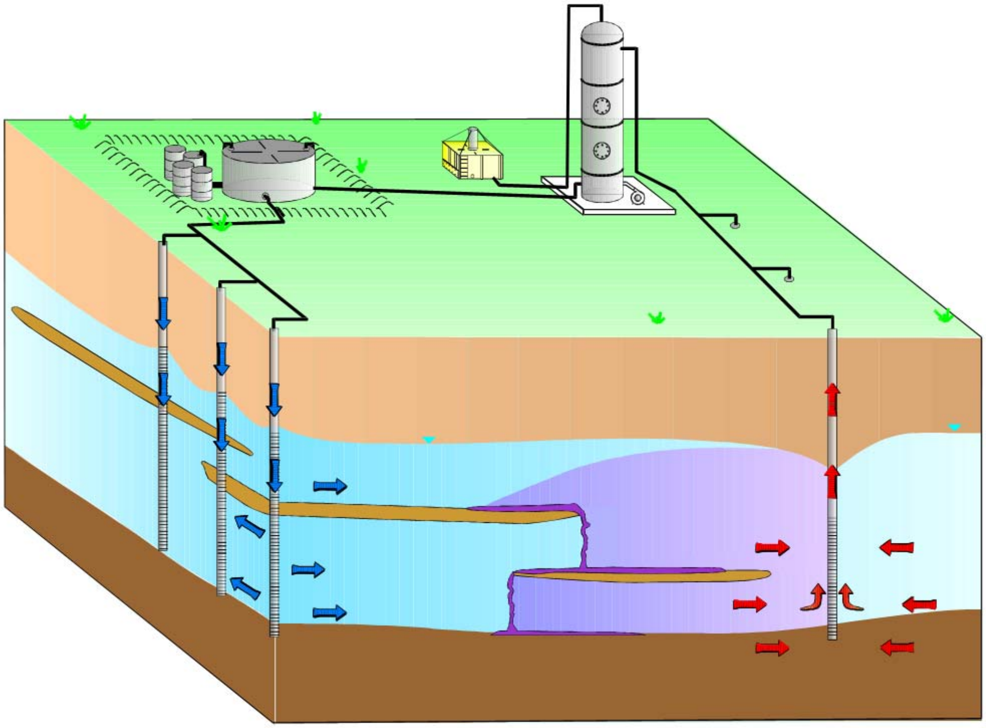


Figure 2-1. Conceptual Design for a SEAR Application

SEAR works by (1) increasing the effective solubility of DNAPLs in water for DNAPL removal by enhanced solubilization, and (2) further reducing the interfacial tension (IFT) between the DNAPL and water phases for DNAPL removal by mobilization. (IFT is the force existing where two fluids meet that keeps them as separate fluids.) SEAR application uses the properties of surfactants to remove contaminants either primarily by solubilization or primarily by mobilization (see Section 4.0 for more detail on solubilization and mobilization processes). Surfactant induced mobilization can remove greater amounts of DNAPL in less time; however, there is greater risk of uncontrolled downward movement of DNAPL, as DNAPL is being physically displaced by the surfactant solution. Thus, to conduct a mobilization flood, it is necessary to have a competent aquitard as a barrier to prevent vertical DNAPL migration. Where there is no clay barrier underlying the contaminated zone, or a thin and/or discontinuous one, the surfactant flood must be designed only to solubilize contaminant. (Solubilization increases the density of the contaminant-loaded surfactant solution by only several weight percent (wt%) compared to mobilization, which involves a much more dense, moving front of DNAPL.) It is important to identify from the outset whether solubilization or mobilization of DNAPL is desired, because not all surfactants can accomplish the low IFT necessary to conduct a mobilization flood.

The surfactant solution formulated for a SEAR application typically consists of water and surfactant, plus additives such as an electrolyte (i.e., dissolved ionic salt) and a cosolvent. The surfactant must be able to efficiently remove the DNAPL and be compatible with the soils and groundwater.

Surfactant selection begins by examining the performance of the surfactant with the contaminant and proceeds with experiments conducted using soils and groundwater from the site. Typically, negatively charged (anionic) surfactants are used for subsurface flooding, as their negative charge repels the negatively charged clay surfaces to minimize surfactant loss due to sorption on the soil. The solubilization properties of an anionic surfactant can be adjusted and optimized by varying the electrolyte concentration; thus, the surfactant formulation typically includes an electrolyte (e.g., chloride and calcium chloride [$CaCl_2$]). A cosolvent, such as isopropyl alcohol (IPA), often is added to improve the solubility of surfactant in water, so that the resulting surfactant-DNAPL solution (microemulsion) 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 cosolvent complicates wastewater treatment, ongoing technology development has focused on surfactants that have no or minimal cosolvent requirements, as well as on cosurfactant substitutes to cosolvents. Further discussion on selection of the optimal surfactant solution formulation is provided in Section 4.0. Identifying an appropriate surfactant for a variety of DNAPL contaminants should be feasible due to the wide range of commercially available surfactants and the existing knowledge base for synthesizing custom surfactants for environmental application.

The most economical application of SEAR is in a relatively homogeneous and highly permeable subsurface ($K \geq 10^{-3}$ cm/s). As the permeability of soils decreases and/or the heterogeneity increases, remediation project costs will increase. A surfactant flood recently completed in a low permeability, shallow aquifer at Marine Corps Base (MCB) Camp Lejeune, NC, determined that SEAR application is expensive at sites with permeabilities equal to or less than 10^{-4} cm/s (ESTCP, 2001). The shallow low permeability aquifer at the site significantly increased the flushing time required and reduced surfactant performance (e.g., lower DNAPL removal than expected). Heterogeneities caused by subsurface layers with permeabilities varying over an order of magnitude also affected the sweep efficiency of the surfactant. Design of the injection and extraction system and surfactant solution can accommodate heterogeneities if the depth of contamination is sufficient, but the cost of SEAR application typically is driven by the lowest permeability contaminated strata at the site.

Each step in the SEAR design process must take into account the remedial action objective (RAO). The RAO for SEAR is to maximize DNAPL recovery, at minimal cost, while maintaining control over the movement of injected chemicals and DNAPL. Because it is impossible to fully characterize the variations in aquifer properties over the treatment zone, numerical modeling is used to simulate system response to the expected range of variation in hydrogeologic conditions. The accuracy of the model (and therefore the effectiveness of the SEAR design) is limited by the accuracy of the parameters used to define site conditions and surfactant flow properties. It is essential to collect complete and accurate field and laboratory data in order to conduct a reliable feasibility analysis and to develop a satisfactory design basis (see Section 3.0).

2.2 Effectiveness

Effectiveness is a measure of the extent to which a remedial option can eliminate significant threats to human health and the environment through reduction of the toxicity, mobility, or volume of contaminants at a site. Effectiveness includes both short-term and long-term effectiveness and scope of the remedy. There are several factors that impact SEAR effectiveness including aquifer heterogeneity, aquifer permeability, capillary barriers, and contaminant properties.

2.2.1 Aquifer Heterogeneity. All chemical flooding technologies, including SEAR, are constrained by aquifer heterogeneities. These include not only variations in aquifer permeability, but also in DNAPL contaminant levels. Aquifer heterogeneities can cause significant channeling of the injected fluids and bypassing of contaminated zones, causing poor surfactant sweep of the area targeted for remediation. The success of SEAR depends upon an accurate characterization of not only the aquifer lithology, but also the DNAPL saturation and its spatial distribution in the aquifer.

High heterogeneity in aquifer soils is indicated by a one order of magnitude or greater contrast in hydraulic conductivity between hydrostratigraphic units. In a geology with low permeability layers or lenses interspersed with higher permeability zones, fluid flow tends to bypass the lower permeability zones. Flow bypassing limits the ability of the surfactant solution to reach contaminants and reduces the performance of surfactant flooding. A more uniform surfactant sweep may be induced by mobility control using either polymer or surfactant foam addition. Where it can be implemented, mobility control should be considered as it can greatly improve the performance and cost effectiveness of SEAR. Mobility control fluids increase surfactant contact with lower permeability zones of a heterogeneous aquifer, however are subject to certain constraints. Overall forced hydraulic gradients will increase due to the higher viscosity of the polymer used in the surfactant formulation, and surfactant foam propagation may be limited by the air injection pressure. Under shallow conditions (<25 ft to the aquitard), the minimum bulk hydraulic conductivity necessary for implementing mobility control anticipated to be 10^{-3} cm/s. For lower bulk hydraulic conductivities (~10^{-4} cm/s), a minimum depth of approximately 50 ft is suggested for SEAR application.

2.2.2 Permeability Considerations. In general, a low absolute formation permeability is less constraining compared to high heterogeneity. The challenge of low permeability environments is less flexibility in adjusting system operating parameters such as flowrates to optimize SEAR performance. In low permeability formations, a high-induced gradient will be required to propagate surfactant solution flow, which may or may not be feasible in shallow subsurface formations. The low permeability will also decrease the maximum allowable flowrate and thereby greatly increase the duration of surfactant flooding. Low permeability soils can be treated more effectively if the aquifer is deep (>50 ft to the aquitard) allowing higher induced gradients.

2.2.3 Capillary Barrier Considerations. A capillary barrier is usually a formation of hydraulic conductivity (< 10^{-6} cm/s) which is low enough to prevent downward migration of DNAPL. DNAPL tends to form pools on top of capillary barriers. The type of surfactant flooding that can be implemented at a given site will be determined by the presence or absence of a capillary barrier and the structure of the capillary barrier (e.g., fractures, thickness, discontinuities, etc.). Therefore detailed information about the capillary barrier is necessary in the design of a SEAR system.

At a site with an excellent capillary barrier such as Hill Air Force Base (HAFB) Operable Unit (OU-2) (hydraulic conductivity < 10^{-9} cm/s), a mobilization type surfactant flood is preferable as the mobilized DNAPL will not penetrate formations with such low conductivity. A mobilization flood for DNAPL removal generally uses a surfactant that has ultralow IFTs than can induce ultrahigh contaminant solubilization and mobilization of DNAPL. Such surfactants can minimize the surfactant requirement to 1-2 pore volumes (defined as the aquifer treatment volume multiplied by porosity) and therefore lower operating costs. More pore volumes of surfactant flooding may be required at less optimal sites with preferential flow that cannot be addressed with mobility control fluids, with complex contaminants (i.e. mixtures of contaminants with widely varying physico-chemical properties), and/or with high DNAPL saturations.

The absence of a capillary barrier necessitates the use of a surfactant that will solubilize DNAPL with no downward mobilization. Some practitioners have suggested 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 is based on the premise that high concentrations of alcohol and viscosity controls can offset the DNAPL density and recover the contaminant by solubilization alone.

However, using this method, more surfactant may be required in comparison to a mobilization flood and high alcohol concentrations will increase SEAR effluent treatment costs.

2.2.4 Contaminant Viscosity. The most effective remediation method will also depend upon physico-chemical properties of the NAPL such as viscosity. For highly viscous NAPLs such as coal tars, creosotes, and Naval Special Fuel Oil (NSFO), recovery by mobilization may not be feasible, as the high gradients required to mobilize these NAPLs may not be sustainable for a given aquifer. In addition, the low viscosity of the water and surfactant solutions compared to the NAPL will result in the formation of viscous and hydrodynamic instabilities that will lead to fingering and bypassing of NAPL-contaminated zones. This may be alleviated by the use of a viscosifier such as xanthum gum polymer. The higher viscosity of the polymer will mitigate viscous fingering and also aquifer heterogeneities and provide better sweep of the contaminated zones. If the NAPL viscosity is extremely high, on the order of 1,000 cp, heating of the surfactant solution may be necessary. Duke Engineering and Services (DE&S) conducted such a heated solubilization flood to recover the highly viscous NSFO (viscosity ~1,029 cp) at Pearl Harbor, Hawaii (Ooi et al., 1999).

2.3 Implementability

Implementability is a measure of the technical and administrative feasibility of installing, operating, monitoring, and maintaining a remedial option. Technical challenges to successful implementation of SEAR include accurately determining the DNAPL distribution, finding the optimum surfactant solution for a given DNAPL composition and soil type, and fully characterizing the hydraulic properties of the aquifer, particularly the heterogeneities typically present in the subsurface environment. Administrative factors related to implementability are discussed below and include technology maturity and regulatory and permitting issues. The implementability of SEAR will depend on site-specific regulations and subsurface environments.

2.3.1 Technology Maturity and Prior Applications. SEAR is considered an innovative technology, but acceptance of this technology by the regulatory community as a viable remedial alternative continues to grow as successful pilot and field-scale applications are completed. Information to guide decisions on the selection of SEAR are available from a number of pilot-scale tests and field applications of SEAR technology. Some recent large-scale demonstrations and full-scale applications are summarized in Table 2-1.

2.3.2 Regulatory/Permitting Issues. Injection wells are regulated by the underground injection control (UIC) program under the federal Safe Drinking Water Act (SDWA). The purpose of the UIC program is to protect underground sources of drinking water (USDWs). Under the UIC program, injection of any fluid into a well is prohibited, except as authorized by permit or rule. Injection wells incidental to aquifer remediation and experimental technologies are distinguished from hazardous waste injection wells and are designated as Class V wells under the UIC program. Class V wells covered by the federal UIC program are authorized by rule and do not require a separate UIC permit. A Class V well regulated by a state may require a permit. Application of UIC requirements depends on the regulatory framework controlling the cleanup with fewer restrictions expected for cleanup activities conducted under CERCLA authority (United States Environmental Protection Agency {U.S. EPA}, 1995). UIC requirements typically are applicable to RCRA corrective action cleanup projects, but may not be applicable or relevant or appropriate to CERCLA sites.

The U.S. EPA recently reviewed state policies controlling injection of surfactants, cosolvents, and nutrients for groundwater to promote aquifer remediation (U.S. EPA, 1996). This review determined that 11 states have allowed surfactant injection, mostly for the enhancement of existing pump-and-treat systems. Most of these approvals were for application to CERCLA sites. No state has a direct regulatory

Table 2-1. Summary of SEAR Case Studies

Date, Site Name and Location	Test Scale	Contaminants	Surfactant Solution	Contact
Alameda Naval Air Station, CA (1999)	Field pilot	TCA and TCE	5% Dowfax surfactant + 2.5% AMA surfactant + 3% NaCl + 1% $CaCl_2$	Surbec-Art Environmental, Norman, OK
Bachman Road Site, Ann Arbor, MI (2000)	Field pilot	TCE, PCE, and 1,2-DCE	Tween 80[(a)]	University of Michigan, Ann Arbor, MI
Borden, Ontario, Canada (1997)	3-m by 3-m test cell	PCE	1% Nonylphenol ethoxylate phosphate and 1% nonylphenol ethoxylate	University of Waterloo and State University of New York, Buffalo, NY
Camp Lejeune Marine Corps Base, NC (1999)	Field pilot	PCE and Varsol (as a secondary nontarget contaminant)	4% Alfoterra 145-4PO Sulfate™ surfactant + 16% IPA + 0.16 to 0.19% $CaCl_2$	Duke Engineering & Services, Austin, TX
Commercial site, Fredericton, NB, Canada (1993)	Full-scale	Diesel fuel oil	Ivey-sol™ proprietary compound	Ivey Environmental Services, Fredericton, NB
Corpus Christi, TX (1993)	Field pilot	Carbon tetrachloride	1% Witconol followed by 1.9% Tegitol	State University of New York, Buffalo, NY
Hill Air Force Base, Layton, UT (1999-ongoing)	Full-scale	Spent TCE with some PCE and 1,1,1-TCA	Aerosol MA-80I, IPA + NaCl [(b)]	Duke Engineering & Services, Austin, TX
Lake Charles, UT (1997)	Field pilot	1,2-DCA	Linear Alkyl Benzene Sulfonate[(a)]	IT Corporation, Lake Charles, LA; State University of New York, Buffalo, NY
Millican Field, Pearl Harbor, HI (1999)	Field pilot	Petroleum hydrocarbons (Navy Special Fuel Oil)	4% Alfoterra 123 $(PO)_{7.7}$ sodium ether sulfate™ surfactant + 8% sec-butyl alcohol + 1100 mg/l $CaCl_2$ heated to 50°C	Duke Engineering & Services, Austin, Texas
Paducah Gaseous Diffusion Plant, KY (1994)	Field pilot	TCE	1% Sorbitan monooleate	University of Texas, Austin, TX; State University of New York, Buffalo, NY; Intera, Austin, TX
Piketon DOE facility, OH (1996)	Field pilot	Mostly TCE with some PCBs and other chlorinated solvents	4% Sodium Dihexyl Sulfosuccinate, 4% IPA, and 2% electrolyte (1:1 NaCl and $CaCl_2$)	University of Texas, Austin, TX; State University of New York, Buffalo, NY; Intera, Austin, TX
Shawnee, OK (1996)	Field pilot	Gasoline	4% Dowfax 8390	Surbec-Art Environmental, Norman, OK; Oklahoma University, Norman, OK
Tinker Air Force Base, OK (1998)	Field pilot	Mixed nonchlorinated solvents (mostly toluene)	4% Dowfax 8390	Surbec-Art Environmental, Norman, OK; Oklahoma University, Norman, OK

(a) Formulation not specified.

(b) Formulation has been varied over the interim.

Adapted from: Lowe et al., 1999a; Strbak, 2000; Jafvert, 1996.

prohibition on injection technologies for treating contaminated aquifers. Prior to 1995 a few states prohibited the use of injectants, either through bans on new Class V injection wells or prohibition of injectants that did not meet groundwater quality criteria. Currently, exceptions are made for Class V remediation wells, and the states that prohibit injection of fluids that do not meet groundwater standards allow the use of site-specific criteria for contaminated aquifers. It is essential that the injection permit documentation list both principal compounds and any unreacted compounds or impurities. One example of this point is the use of sodium chloride (NaCl) as an electrolyte. Most sources of NaCl (including food grade material) will list arsenic as a potential impurity. Hence, the potential arsenic concentration in the injectate must be considered.

Should it prove economical to recycle compounds such as the surfactant and alcohol, regulatory permission for reinjection must be gained. The recycling process involves concentration of components to be reinjected and the simultaneous concentration of undesirable compounds, such as contaminants, is frequently an issue. The feasibility of surfactant reuse is strongly dependent on site-specific regulations, as contaminant removal to maximum contaminant levels (MCLs) prior to surfactant reinjection is cost-prohibitive. Recently completed surfactant floods at Alameda Point, CA, and MCB Camp Lejeune, where surfactant reinjection was accomplished with contaminants exceeding MCLs indicates that the reinjection of surfactants may gain regulatory acceptance. As regulatory interpretations allowing the use of injectants have recently become more lenient, it is possible that a similar trend will follow for the reinjection of SEAR process chemicals.

In addition to UIC permitting requirements, permitting requirements for wastewater handling and discharge should also be addressed. Conducting SEAR requires recovery of the injectate containing high concentrations of dissolved or mobilized contaminant. The extracted groundwater must be treated and appropriately discharged, usually to a public-owned treatment works (POTW). If a POTW is not available, on-site treatment can be used to comply with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit. On-site treatment of the extracted groundwater typically is needed to reduce contaminant concentrations to levels consistent with the permit requirements of the POTW and possibly to recover chemicals (e.g., surfactant or cosolvent). Management of other waste streams resulting from wastewater treatment (e.g., DNAPL separated by decanting or air discharged from a stripper) must comply with all applicable federal, state, and local requirements.

2.3.3 Health and Safety Issues. Drilling wells and installing and operating aboveground treatment equipment, piping, and pumps involves some risks to workers during SEAR application. The toxicity of the DNAPL contaminants typically is high and requires design and operating features to minimize exposures to the workers and off-site populations. The chemicals used in the surfactant solution typically have very low toxicity (e.g., food grade surfactants) and do not significantly increase hazards at the site. However, because alcohol is flammable and explosive, mixtures with high alcohol content should be transported, stored, and handled with the proper safety precautions. The risks involved with a SEAR application are within the norm for standard industrial activities.

2.4 Cost

SEAR costs need to be evaluated against the risk posed by the persisting DNAPL source and the costs and feasibility of alternative remedial methods. The risk may be an exposure hazard (e.g., when the contamination is located in or near a drinking water aquifer), and/or an environmental hazard (e.g., continued migration of DNAPL to less accessible regions of the aquifer). If one or both of these hazards exist, it may be necessary to remove DNAPL quickly. This cannot be accomplished using pump and treat or natural attenuation processes. If the contamination is located under an occupied facility, neither in situ thermal treatment nor a heat-generating chemical oxidation process may be implementable. Thus, the cost-effectiveness of SEAR application for a given DNAPL site needs to be evaluated on an site-by-site basis.

The primary cost elements in a SEAR application are as follows:

Design Costs

- Source zone characterization specifically for SEAR application
- Subsurface tracer tests or other site assessment tests
- Surfactant selection studies
- Simulation modeling.

Capital Costs

- Injection/recovery wells and pumps
- Effluent treatment equipment
- Monitoring wells, samplers, and equipment

Operating Costs

- Surfactant/cosolvent chemicals
- Monitoring labor
- Chemical analyses
- Utilities

The capital and operating costs associated with subsurface treatment will be lower at sites with high permeability, homogenous aquifers. The pattern of DNAPL mass distribution may also be relevant to costs. For example, remediating 1,000 lbs of DNAPL distributed over a 5-ft thickness of aquifer would be less costly compared to the same quantity of DNAPL distributed over a 100-ft thickness of aquifer (assuming the contaminated area is the same at both sites). In addition to higher remediation costs at the latter site, locating DNAPL over a greater thickness of aquifer would require a greater investment. Costs for implementing SEAR tend to be decreased by the following factors:

- High soil permeability
- Low hydrogeologic complexity
- Homogeneous pattern of contaminant distribution
- Extensive site characterization data on hydrogeologic conditions and DNAPL distribution and boundaries
- Availability of wastewater treatment facilities capable of processing the extracted groundwater.

Capital costs for a SEAR system can be significantly reduced by the presence of existing wastewater treatment facilities on site such as an air stripper or steam stripper (e.g., from an operating pump-and-treat system) that can be adapted to handle a more concentrated waste stream that contains surfactant and alcohol. If on-site waste treatment facilities are not available, it may be cost-effective to recover surfactant. The use of high cosolvent concentrations with surfactant, i.e., above 4 wt%, can be expensive if the contaminants are not strippable. Surfactant recycling can reduce operating cost if the site is sufficiently large that the cost of the surfactant can justify the capital cost of recovery equipment or if adequate facilities to process the extracted groundwater are not available at the site. Surfactant recycling first requires efficient contaminant separation from the extraction well effluent. The DNAPL concentration must be sufficiently reduced to meet regulatory standards after concentration of surfactant for reinjection. Removal of dissolved contaminants from the effluent may be done using methods such as air stripping (Section 6.3.1.2), macroporous polymer extraction (Section 6.3.1.3), and pervaporation (Section 6.3.1.5). Once the contaminants are removed, the surfactant may be reconcentrated using methods such as micellar enhanced ultrafiltration (MEUF) (Section 6.3.3.1) or nanofiltration (NF) (Section 6.3.3.2) techniques. Alternative approaches for wastewater treatment are discussed further in Section 6.0.

Estimated costs for SEAR application for high- and low-permeability cases with three different contaminated areas were recently reported (ESTCP, 2001). The site conditions for the estimate were as follows:

- Contaminant – PCE
- Depth to aquitard – 20 ft bgs
- Saturated thickness – 11 ft bgs
- Contaminated thickness – 5 ft bgs
- Permeability – 5×10^{-2} to 10^{-3} cm/s (high-permeability case) or 5×10^{-4} to 10^{-5} cm/s (low-permeability case)
- Heterogeneous aquifer with permeability decreasing near the aquitard
- Swept pore volume ~ 6000 gallons
- Average DNAPL saturation ~ 2% of the pore volume

The costs for the high-permeability case are summarized in Table 2-2. SEAR is most cost-effective at sites with relatively homogeneous formations with hydraulic conductivities on the order of 10^{-3} cm/s. The remediation costs for projects at low permeability sites are estimated to be over twice as high per acre ($13 million versus $4.5 million) and may limit the cost-effectiveness of SEAR at such sites. The costs provided were estimated assuming conventional wastewater treatment with disposal of the treated water to a POTW. The potential cost saving by using surfactant recovery is summarized for the high permeability case in Table 2-3. With respect to capital expenses for surfactant recovery, lease costs were assumed for the smallest scale (1 panel) and the 0.5 acre scale, while purchased equipment costs with 50% salvage value were assumed for the 1.0 acre scale.

Table 2-2. Estimated SEAR Application Costs (High Permeability Case)

Cost Element	**Item Cost ($) for 3333 sq. ft. (1 panel)**	**for 0.5 acre**	**t ($) for 1.0 acre**
Preconstruction Cost	$237,400	$627,000	$1,012,100
Construction Cost	$492,100	$829,300	$1,234,000
Operations and Maintenance Cost[(b)]	$209,500	$958,100	$1,884,700
Performance Assessment Cost	$103,700	$177,300	$324,700
Full-Scale SEAR System Total Cost	$1,042,700	$2,591,700	$4,455,500

(a) Source: ESTCP, 2001.

(b) These costs assume the use of polymer for mobility control.

Table 2-3. Cost and Savings Estimates for Surfactant Recovery (High Permeability Case)[a]

Cost and Savings	High Permeability		
	1 Panel	0.5 Acre	1.0 Acre
Cost of Recovery Technologies[b]	($82,400)	($252,400)	($381,900)
Cost of Additional Equipment, Labor, and Chemical Analyses	($10,430)	($30,520)	($58,340)
Value of Recovered Surfactant	$33,600	$224,200	$493,200
Credited Cost[c]	$90,200	$92,400	$95,100
Total Net Cost Savings	$30,970	$33,680	$148,060

(a) Source: ESTCP, 2001.

(b) Lease costs were assumed for the smallest scale and 0.5 acre scale.

(c) This credits the cost of the air stripper off-gas treatment unit associated with the conventional wastewater treatment system.

Section 3.0: DNAPL SOURCE ZONE CHARACTERIZATION FOR SEAR

This section focuses on DNAPL behavior in the subsurface and the development and use of a conceptual site model or geosystem model to guide the site characterization process and eventually the full-scale SEAR system design. The recommended methods and procedures for DNAPL source zone identification and characterization will also be reviewed.

Locating and accurately characterizing the DNAPL source zone is a key step in gaining a sufficient understanding of in situ conditions to support SEAR system design. Complete site characterization often is difficult because DNAPL transport characteristics can cause complex DNAPL distribution in situ. DNAPL is heavier than water and migrates downward through the saturated zone until it is trapped as residual saturation or encounters a confining, low permeability layer. DNAPL also spreads laterally along paths of higher permeability. The DNAPL source zone characterization program has the following two purposes:

- ☐ To determine how the DNAPL is distributed in the subsurface, and
- ☐ To quantify aquifer properties that will affect the application and control of SEAR fluids in the subsurface.

Figure 3-1 provides a summary of the major steps involved in the site characterization process.

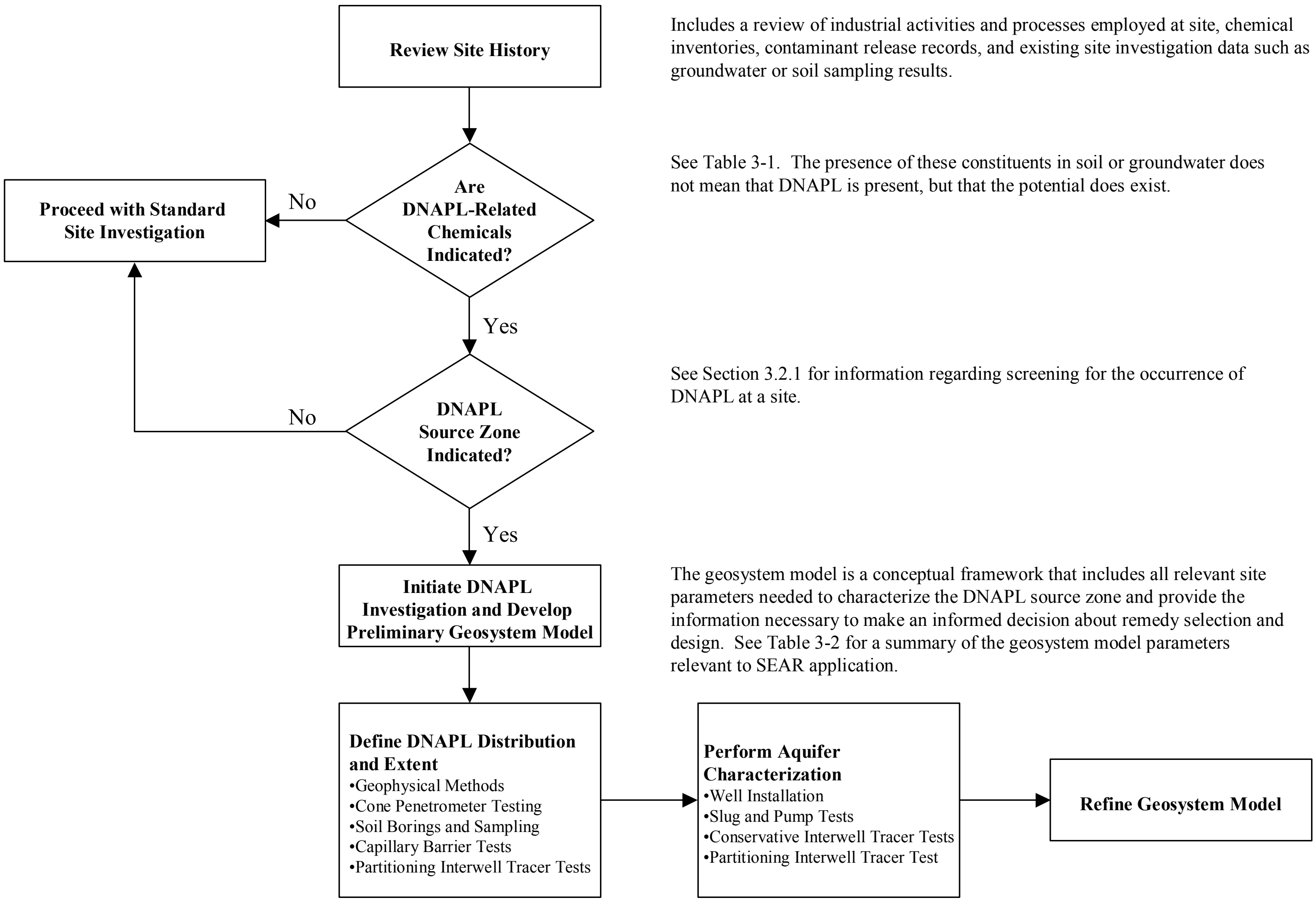
3.1 Target Treatment Area Definition

The target treatment area is the in situ volume where SEAR application will provide the most effective recovery of DNAPL. This section describes DNAPL behavior in the subsurface and general concepts related to expected contaminant distribution to clarify the types of contaminant distributions that can be encountered. Developing and using a geosystem model to guide site characterization and selection of the target treatment area also is discussed.

3.1.1 DNAPL Contaminant Distribution Concepts. DNAPL can consist of either a single chemical component or a mixture of chemical components. The most commonly encountered DNAPLs at contaminated sites are chlorinated solvents, wood preservative wastes, coal tar wastes, and pesticides (see Table 3-1). Once a spill occurs and DNAPL reaches the saturated zone, it can act as a continuous source of contamination through gradual dissolution into groundwater. In order to make an informed decision about the risks of DNAPL at a site, the typical behavior of DNAPL in the subsurface must be understood. DNAPL migration in the subsurface is a complex, multiphase flow process, which is affected by many factors including the following:

- ☐ Location and area of DNAPL infiltration or entry point,
- ☐ Estimated volume and duration and/or history of DNAPL release,
- ☐ Physical and chemical properties of the DNAPL,
- ☐ Physical and chemical properties of the soil and groundwater, and
- ☐ Subsurface stratigraphy or geologic layering.

DNAPL distribution in the subsurface is characterized by a parameter called saturation, which is defined as the fraction of the soil pore volume that is filled with DNAPL (see Figure 3-2). Depending on the degree of saturation, DNAPL will exist in situ as either free-phase DNAPL or as residual DNAPL. Free-phase or mobile DNAPL exists when the saturation is high enough to form



Includes a review of industrial activities and processes employed at site, chemical inventories, contaminant release records, and existing site investigation data such as groundwater or soil sampling results.

See Table 3-1. The presence of these constituents in soil or groundwater does not mean that DNAPL is present, but that the potential does exist.

See Section 3.2.1 for information regarding screening for the occurrence of DNAPL at a site.

The geosystem model is a conceptual framework that includes all relevant site parameters needed to characterize the DNAPL source zone and provide the information necessary to make an informed decision about remedy selection and design. See Table 3-2 for a summary of the geosystem model parameters relevant to SEAR application.

Figure 3-1. DNAPL Site Characterization Process

Table 3-1. List of DNAPL-Related Constituents

Halogenated Volatile Compounds	Nonhalogenated Semivolatiles	Halogenated Semivolatile Compounds	Miscellaneous
Chlorbenzene	2-Methyl Napthalene	1,4-Dichlorobenzene	Coal Tar
1,2-Dichloropropane	o-Creosol	1,2-Dichlorobenzene	Creosote
1,1-Dichloroethane	p-Creosol	Aroclor 1242, 1254, 1260	
1,1-Dichlorethylene	2,4-Dimethylphenol	Chlordane	
1,2-Dichloroethane	m-Creosol	Dieldrin	
Trans-1,2-Dichloroethylene	Phenol	2,3,4,6-Tetrachlorphenol	
Cis-1,2-Dichloroethylene	Napthalene	Pentachlorophenol	
1,1,1-Trichloroethane	Benzo(a)anthracene		
Methylene Chloride	Fluorene		
1,1,2-Trichloroethane	Acenapthene		
Trichloroethylene	Anthracene		
Chloroform	Dibenzo(a,h)anthracene		
Carbon Tetrachloride	Fluoranthene		
1,1,2,2-Tetrachloroethane	Pyrene		
Tetrachloroethylene	Chrysene		
Ethylene Dibromide	2,4-Dinitrophenol		

Note: Table reproduced from EPA, 1992.
Many of these chemicals are found in mixtures.

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 a small 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 imposed hydraulic gradients.

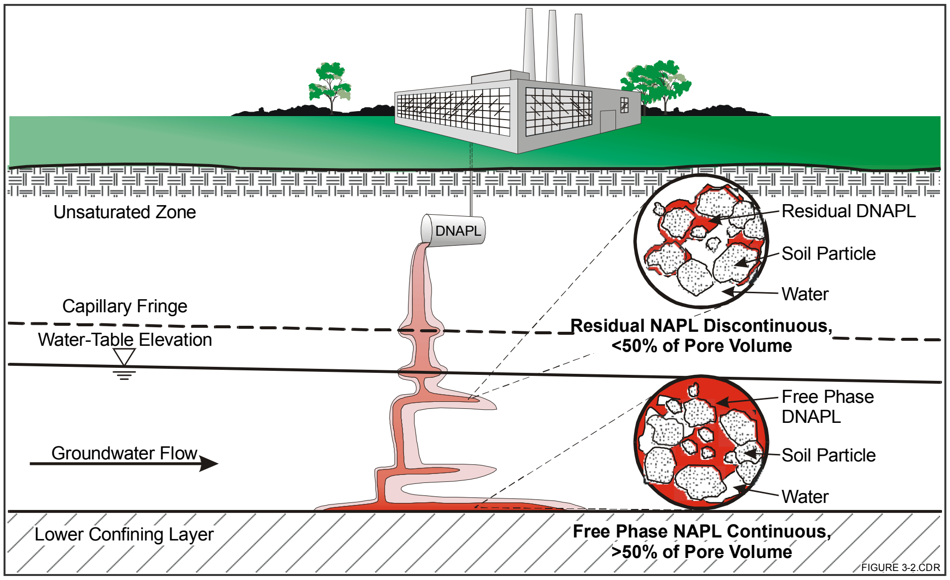
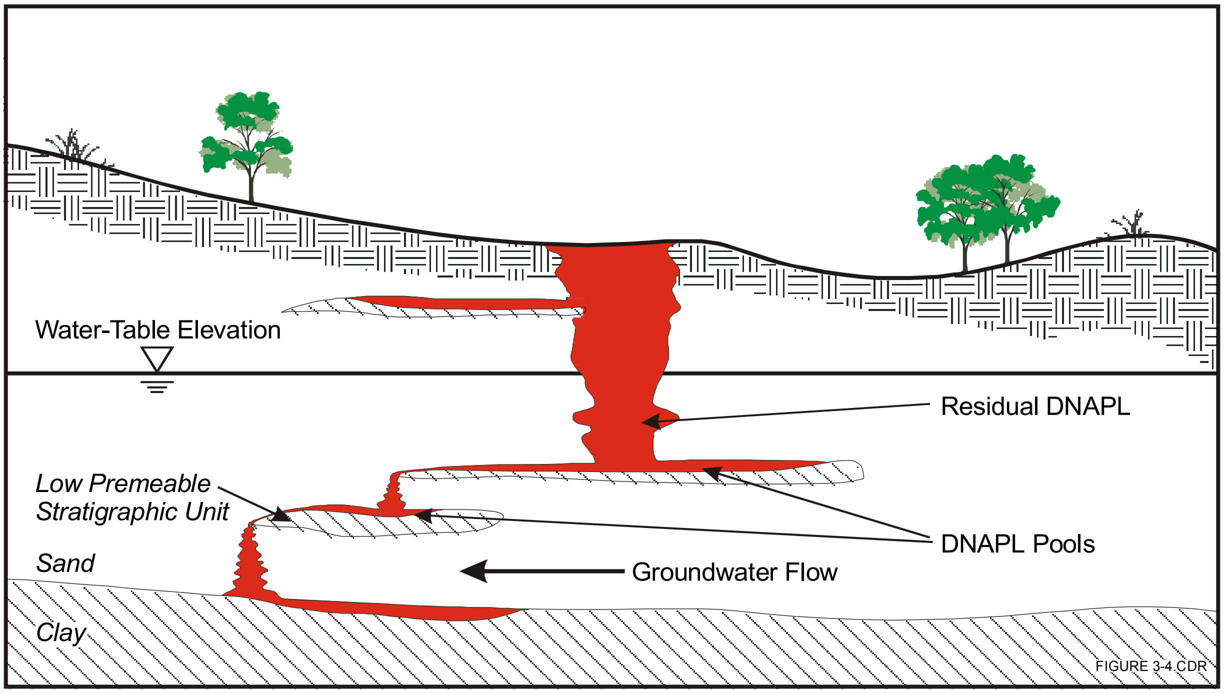


Figure 3-2. Schematic Diagram of Residual Versus Free-Phase Saturation

Based on past field experience, the majority of mass at most DNAPL sites is at residual saturation. Residual saturations typically do not exceed 15 to 20%, while average DNAPL zone saturations typically range from a few tenths of a percent to less than 3%. Figure 3-3 illustrates the effect of heterogeneity with low-permeability layers on DNAPL distribution in the subsurface. The free-phase or mobile DNAPL migrates from the vadose zone downward through the saturated zone until a confining or low permeability stratigraphic unit is encountered. An accumulation or pool of DNAPL then builds up on top of the clay lens or aquitard. Other more complicated DNAPL distributions are found at sites with fractured bedrock or fractured clays present in the subsurface.

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 void spaces in the porous geologic media. Fluid properties that influence capillary forces include the surface tension of the DNAPL and interfacial tensions between the DNAPL and water. 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. These basic concepts of multiphase flow, along with knowledge of typical DNAPL behavior from field observations, can be used in the assessment of DNAPL fate and transport at a given site. Generally, DNAPL will be found in low permeability sediments, which will retard further downward movement of DNAPL due to the smaller pore size and higher capillary forces.



Source: EPA, 1992

Figure 3-3. DNAPL Pools and Effect of Low Permeability Units

3.1.2 Geosystem Model Development. The primary objective for DNAPL source zone characterization activities 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 and adequately detailed to ensure efficient and cost-effective design, installation, and operation of the remedy. Site investigation data is organized to develop an evolving conceptual model of the site or geosystem model. Formulated early in the source zone investigation program using available site data to build a foundation 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 should be continuously updated throughout the duration of the project. The endproduct is a model that reflects those properties of the aquifer and its fluids that may influence surfactant flow through a contaminated subsurface. Table 3-2 summarizes the elements of a geosystem model that are collected during DNAPL site investigations and laboratory testing for SEAR design. Ultimately, this data is used as input to a numerical simulations model, along with surfactant phase behavior data, to simulate surfactant injection and extraction operations for SEAR design. SEAR design simulations are discussed further in Section 5.0.

Table 3-2. Site Data Incorporated into the SEAR Geosystem Model

SITE HISTORY	
Site plans	Review existing site data, including any groundwater modeling documentation, to determine which site parameters have been properly defined and which still need to be evaluated. 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.
Chemical inventory records	
Contaminant release records	
Previous site investigation reports	
PHYSICAL SETTING	
Utilities, pipelines, and other subsurface structures	Information about subsurface structures should be obtained as these may offer conduits for DNAPL migration. Location of these structures should also be known to avoid interference with installation of soil borings and groundwater wells.
SITE GEOLOGY/HYDROGEOLOGY	
Stratigraphy/Hydrostratigraphy	Document 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.
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.
Hydraulic conductivity	A coefficient which describes the rate at which groundwater can move through the subsurface.
Hydraulic gradient	A measure of the driving force for groundwater flow.
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 fate and transport evaluated.

Table 3-2. Site Data Incorporated into the SEAR Geosystem Model (Continued)

GROUNDWATER CHARACTERISTICS	
Nature and extent of dissolved-phase plume	Interpretation of dissolved phase contaminant plume data to obtain contaminant concentration gradients in groundwater and biodegradation data, in conjunction with aqueous solubility information can be used to indicate the presence of hot zones (see Section 3.2.1). Use EPA SW-846 Methods for volatile organics 8260, semivolatile organics 8270, and pesticides/PCBs 8080.
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. SEAR performance must be optimized for this temperature.
SOIL CHARACTERISTICS (Continued)	
DNAPL saturation	Measure the contaminant concentration present in each major hydrostratigraphic unit and use the organic partition coefficient, solubility data, soil porosity and fraction of organic carbon data to estimate the local DNAPL saturation.
Geochemistry	Obtain information on soil mineralogy, soil structure, clay content, and pH.
Grain size distribution	Grain size distribution provides information about site stratigraphy. Generally, the less permeable stratigraphic units will be more poorly sorted and have smaller average grain sizes than more permeable units. ASTM Method No. D422.
Porosity	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. ASTM Method No. D5084. F_{oc} is the fraction of soil that consists of organic matter. ASA Method No. 29-3.5.2.
Fraction of organic carbon (f_{oc})	
DNAPL CHARACTERISTICS	
Density	Mass per unit volume of a substance. Measured with a pyncometer. ASTM Method No. D1217 or D1480.
Viscosity	A physical property of a fluid that characterizes its resistance to flow. ASTM Method No. D445.
Chemical composition	The constituents of concern detected on site should be reviewed. Categorize all detected constituents as DNAPL-related or not DNAPL-related (see Table 3-1). Use EPA SW-846 Methods for volatile organics 8260, semivolatile organics 8270, and pesticides/PCBs 8080.
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 Cayias 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 should be used.
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 should be used.

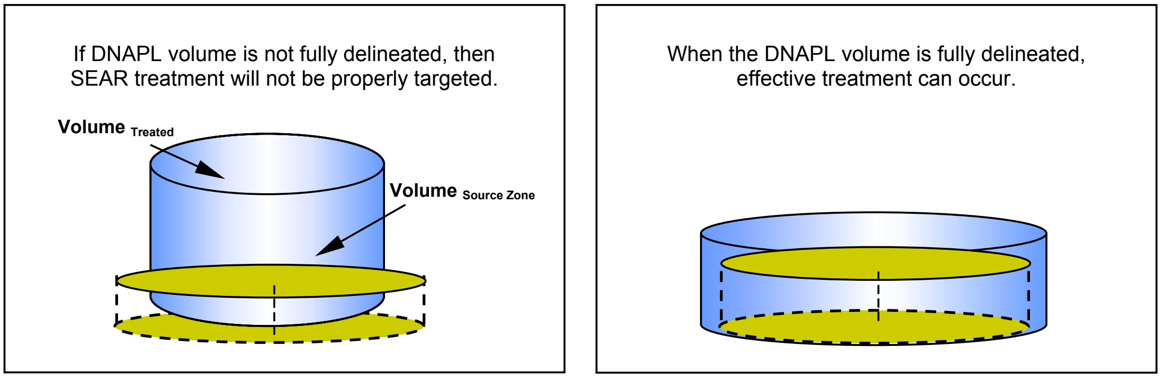
The most important information in the geosystem model is the nature, distribution, and extent of the DNAPL. The primary objective of any DNAPL site investigation program should be to locate the source zone and then define an appropriate target treatment area. At a site where DNAPL has not been located, site historical information, dissolved-concentration plume data, and DNAPL property data will assist in defining the initial investigation areas. Geophysical data can further identify the likely migration pathways for DNAPL for a more focused DNAPL investigation. As Figure 3-4 shows, proper site characterization will ensure that the SEAR design targets the correct subsurface volume ensuring safe and cost-effective technology implementation (i.e., allowing maximum surfactant contact with DNAPL zones without inducing unintended mobilization).

Aquifer characterization is also an important part of developing a good geosystem model. Adequate data is needed to design a system to deliver the correct amount of surfactant to the right location while mitigating the risk of surfactant or DNAPL loss by maintaining hydraulic control over the injected fluids. Several aquifer characteristics (e.g., hydraulic conductivity(ies), static hydraulic gradient(s) and aquitard topography) need to be defined to ensure that DNAPL removal and hydraulic control will be effectively accomplished. Detailed information concerning the depth and thicknesses of low permeability and relatively impermeable units is necessary to identify where DNAPL is likely to become trapped.

All DNAPL remediation technologies (not just SEAR) will require detailed site characterization and it is important to have adequate site data before moving forward with the selected remedy. It is important not to mobilize DNAPL beyond the targeted treatment zone. Remediation system failures often can be attributed to poor site characterization and incomplete laboratory feasibility studies, so great care should be taken in the development of the geosystem model. The steps and methods for identifying and delineating the DNAPL source zone are discussed in Section 3.2. Techniques for aquifer characterization are discussed in Section 3.3.

3.2 Identifying and Delineating DNAPL Source Zones

This section will review general strategies and methodologies for detecting and locating the boundaries of the presence of DNAPL at a given site. The recommended approach to site investigation will be covered including subsurface investigation methods and procedures, capillary barrier characterization, and studies of DNAPL fluid properties.



If DNAPL volume is not fully delineated, then SEAR treatment will not be properly targeted.

When the DNAPL volume is fully delineated, effective treatment can occur.

(a) Poor Site Characterization Leads to Poorly Designed and Ineffective Remediation

(b) Successful Site Characterization Leads to Well-Designed Remediation

Figure 3-4. Target Treatment Area Selection

3.2.1 DNAPL Occurrence. Locating DNAPL source zones is a process that involves culling available site information and then using screening methods and technologies at existing sampling points to progressively narrow the target search area. Once this is done, conventional technologies may be used to delineate the source area. Information sources to be gathered and consulted for determining the occurrence of DNAPL is provided below.

☐ **Review Site History -** The history of the site should be thoroughly investigated to provide information about the waste mixtures spilled, volumes introduced into the subsurface, and potential entry locations. Interviews with the personnel involved in operations potentially related to the contamination are valuable. Understanding the mechanics of the processes that generated the DNAPL (e.g., vapor degreasing, dry cleaning) provides additional helpful information (e.g., volumes, types of products used, etc.).

☐ **Use of Direct Observations** – DNAPL may be found in existing groundwater monitoring wells or recovered from extraction wells in a pump-and-treat system. Groundwater wells should be checked with a NAPL/water interface probe and by bailing or pumping fluid from the bottom of the well for inspection. Several methods can be used to enhance inspection of the recovered fluid including: (1) Use of a centrifuge to separate groundwater and DNAPL due to density differences and (2) Use of brightly colored, hydrophobic dyes (such as SUDAN IV™) which preferentially adhere to or color the DNAPL making it distinctly visible.

☐ **Use of Groundwater Plume Data** – As groundwater contaminant concentrations will be elevated around the source area, the groundwater data that defines the dissolved-phase plume can be used to detect the source. This concept gave rise to the rule of thumb that states that DNAPL is indicated if groundwater concentrations of DNAPL chemicals are greater than 1% of their pure phase solubility (U.S. EPA, 1992). However, it is important to note that because of mass-transfer limitations between DNAPL and groundwater, this screening guideline should be viewed only as a potential indication of DNAPL presence, not as an exact means to locate the source zone. Plume data is usually too sparsely distributed to indicate the location of the source, however, it can be used to narrow the search to a general area of the site. If measurable contaminant degradation products exist within the plume, their spatial distribution may serve to further define the potential source area. A groundwater screening program, using direct push technology (DPT), may be able to rapidly delineate the “halo” these daughter products form around the source zone, thereby further reducing the targeted area. One advantage to sampling groundwater with a DPT platform is that the short screen length minimizes dilution effects and therefore provides much better resolution of concentrations that emanate from a DNAPL zone.

☐ **Use of Geological Data** – Well-defined site stratigraphy data obtained from soil borings, cone penetrometer surveys, or geophysical methods is often necessary in guiding the search for DNAPL source zones. Conducting geological investigations in areas adjacent to the suspected DNAPL zones can provide valuable information on site hydrogeology and stratigraphy. Detailed geologic data can help define the extent of vertical heterogeneity at a site and aid in the location of general areas where DNAPL is likely to be trapped including topographic low spots on the surface of fine-grained, relatively impermeable units. Methods of obtaining stratigraphic data are described further in Section 3.2.2.

☐ **Use of Soil Sampling Data** – Historically, locating DNAPL source zones through drilling and soil sampling has been one of the most commonly applied, although frequently arduous approaches. This is primarily because in the absence of a narrow or targeted site investigation area, these samples do not have volumes that are representative or large enough to effectively investigate the heterogeneous system in which the DNAPL resides. However, for general screening purposes, the presence of DNAPLs can be indicated, if DNAPL chemicals are present at levels greater than 10,000 mg/kg (U.S. EPA, 1992). Methods to enhance the visual detection of DNAPLs in soil samples are discussed in Table 3-3. The use of DPT for soil sample collection can be more effective than drilling for fine-grained and shallow aquifers.

Soil sampling approaches for use in a known DNAPL zone are discussed in more detail in Section 3.2.3.

Table 3-3. Visual Examination of Subsurface Samples for DNAPL

Methods to detect DNAPL in wells:

- NAPL/water interfaces probe detection of immiscible phase at base of fluid column.
- Pump from bottom of fluid column and inspect retrieved sample.
- Retrieve a transparent, bottom-loading bailer from the bottom of a well and inspect the fluid sample.
- Inspect fluid retrieved from the bottom of a well using a mechanical discrete-depth sampler.
- Inspect fluid retained on a weighted cotton string that was lowered down a well.

Methods to enhance inspection of fluid sample for DNAPL presence:

- Centrifuge sample and look for phase separation.
- Add hydrophobic dye (such as Sudan IV or Red Oil) to sample, shake, and look for coloration of DNAPL fraction.
- Examine UV fluorescence of sample (fluorescing compounds tend to be associated with DNAPL if present)

Assess density of NAPL relative to water (sinkers or floaters) by shaking solution or by using a syringe needle to inject NAPL globules into the water column.

Methods to detect DNAPL in soil and rock samples:

- Examine UV fluorescence of sample (fluorescing compounds tend to be associated with DNAPL if present)
- Add hydrophobic dye and water to soil sample in polybag or jar, shake, and examine for coloration of the DNAPL fraction.
- Conduct a soil-water shake test without hydrophobic dye (can be effective for NAPLs that are neither colorless nor the color of the soil)
- Centrifuge sample with water and look for phase separation.
- Perform a paint filter test, in which soil is placed in a filter funnel, water is added, and the filter is examined for separate phases.

Source: EPA, 1992

- **Other Methods** – There are relatively few methods for directly detecting DNAPL in the subsurface. A number of direct NAPL detection tools have recently been developed for the DPT platform (or are still undergoing development). These include a flexible inverted membrane and hydrophobic dye combination (FLUTe™), Laser Induced Fluorescence (LIF), and other optical methods. Although FLUTe™ allows for direct detection of DNAPL, the device does not allow for the estimation of saturation, but simply a positive or negative test for the presence of DNAPL. In addition, those tools that depend on optical fluorescence are appropriate only for NAPLs that contain petroleum hydrocarbon constituents (common chlorinated solvents do not fluoresce). However, organic matter or co-contaminants that do fluoresce can leach preferentially into DNAPL. Thus in limited cases, fluorescence can be used to infer the presence of DNAPL. Also under development is the Navy's Site Characterization and Analysis Penetrometer System (SCAPS) system with a membrane interface probe (MIP) coupled with a direct-sample ion-trap mass spectrometer (DSITMS). The Navy SCAPS system can be used to complete near real-time, in situ surveys to screen for volatile organic compounds (VOCs). The system has been certified for analysis of TCE, PCE, carbon tetrachloride, and other VOCs. Currently, the only method capable of directly detecting DNAPL in permeable materials at large scales of investigation (many thousands of cubic feet of aquifer) is the partitioning interwell tracer test (PITT), the use of which is described in detail in Section 3.3.4.

3.2.2 Subsurface Geologic Investigation Methods. The section discusses in additional detail technologies that are recommended for obtaining stratigraphic information to identify DNAPL migration pathways. Obtaining information in suspected DNAPL zones through invasive methods such as cone penetrometer testing, DPT and conventional drilling must be done carefully to avoid the risk of spreading the contaminant or creating pathways for continued vertical migration. The methods for resolving geologic/hydrogeologic units are presented in order of implementation during a characterization program:

- **Geophysical Methods** - 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 DNAPL zone hydrostratigraphy. 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. Geophysical data provides information that can guide more expensive and invasive investigation techniques. 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) necessary for SEAR 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. For example, at HAFB OU-2, a GPR survey was used to map the contact between the clay aquiclude and the overlying DNAPL-contaminated aquifer. The results of the GPR survey were used to guide subsequent cone penetrometer and drilling tasks to cost-effectively delineate the DNAPL zone (USAF, 1999). Another recommended geophysical method is downhole natural gamma logging. This instrument measures the natural gamma decay count of subsurface soils. Since the natural gamma activity is markedly higher in clays than in sands, gamma logging is useful for locating the contacts between clays and sands more accurately (to within a tenth of a foot) than possible with a drill rig (typically ±0.5 ft or more). Other logging tools include electric resistance tomography, thermal-neutron tools, cross-hole radar, and emerging acoustic impedance methods. These are research tools with limited applicability at most DNAPL sites, and in general, their use is not warranted.

- **Direct Push Technology and Cone Penetrometer Testing** – Direct push technology (DPT) is a cost-effective alternative to conventional drilling methods for rapid site characterization of unconsolidated formations. A significant logistical advantage of using DPT is that the generation of investigation-derived hazardous waste is minimized. DPT equipment is typically truck- or van- mounted and uses hydraulically advanced slides to push specialized tools that provide groundwater samples, soil samples, and other local soil/aquifer property measurements. Cone penetrometer testing (CPT) is a type of DPT that provides a screening level tool for identifying soil classifications (e.g., silty clay, sand, or gravelly sand, etc.). 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

Application of CPT:

- Resistivity measurements are collected as the probe is pushed downward through the subsurface.
- Resistivity measurements are correlated to soil type.
- Pore pressure measurements provide information on vertical groundwater gradients.

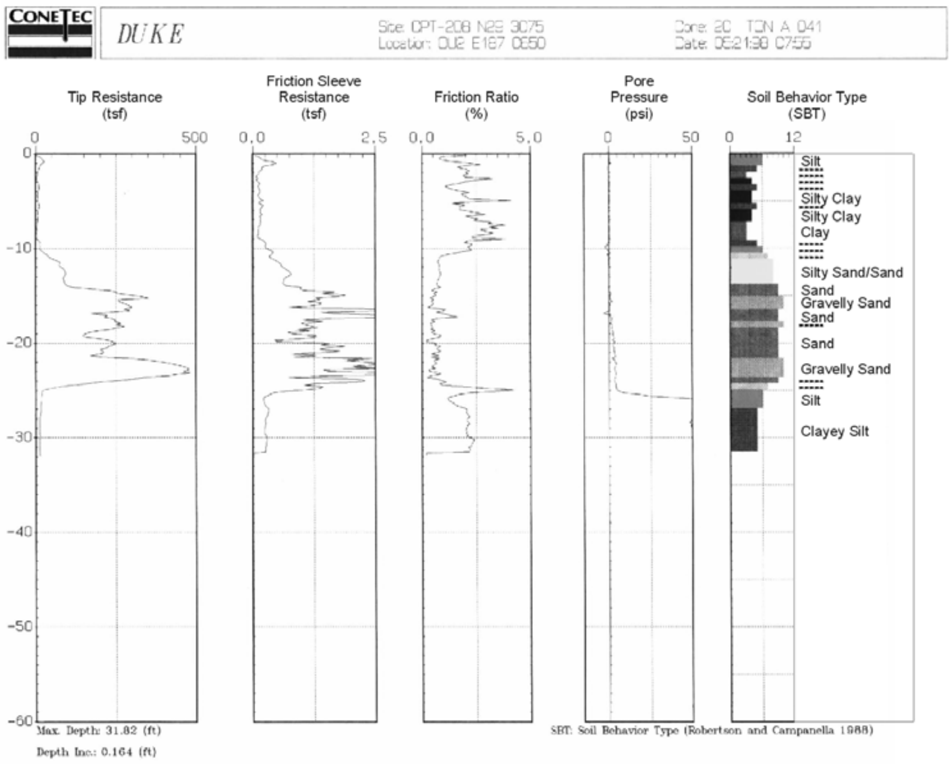


Figure 3-5. Sample CPT Log

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. A sample CPT log is shown in Figure 3-5. The major advantage of this tool is that it provides a quantitative, high-resolution record of the subsurface properties it encounters. 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 availability of heavier (35 ton) rigs has allowed this characterization method to be used recently to delineate the geologic structure of a DNAPL zone in very coarse-grained and gravelly alluvium (USAF, 1999). The use of DPT/CPT is strongly recommended to facilitate the collection of closely spaced quantitative and objective hydrostratigraphic data. High quality data can be obtained at depths up to 100 ft.

- ❑ **Soil Borings** - A drilling program should be developed if the use of DPT is infeasible at a given site. 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, to quantify contaminant mass, to determine geologic properties, and/or to conduct bench-scale testing, (3) Install a well or subsurface instrumentation (e.g., lysimeter for vadose zone DNAPL contamination), and (4) Ground truth/calibration for geophysical methods and CPT. 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. 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. See Appendix A for a more detailed discussion on how drilling methods can effect the success or failure of a site investigation program.

3.2.3 Soil Sample Collection for DNAPL Saturation Estimates and Analyses. With the appropriate sampling devices and sampling protocol, soil samples can be used to investigate DNAPL distribution in the source zone. If a statistically significant number of samples is collected in the proper zones, soil samples can also be used to by provide a baseline estimate of DNAPL mass. For distribution or mass information, contaminant concentration data is converted to saturation estimates. While integrating DNAPL saturation estimates obtained from individual soil samples can be used to obtain volumetric estimates of DNAPL mass in the subsurface, it should be noted that it is not usually cost-effective or advisable to use a soil-sampling program alone to attempt to obtain such estimates. Partitioning Interwell Tracer Tests (PITTs) can be used to provide DNAPL saturation and volume estimates within a relatively homogeneous subsurface volume (see Section 3.3.4). Issues that should be considered in developing a soil sampling program as part of a DNAPL site investigation program are included below. Additional data is provided in Appendix A.

- **Sampling Devices** - 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 maximize not only the recovery of sediment, but also retain as much of the fluid in the pore spaces as possible.

- **Sampling Protocols -** 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). 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 absolutely necessary to obtaining meaningful analytical results from a DNAPL zone.

- **Soil Sample Analyses and Measurements** – A common analytical method for quantification of chlorinated solvents in sediments is EPA Method SW846-8260 for volatile organics. Frequently chlorinated solvent spills involve spent degreasing fluid which will contain semi-volatile petroleum hydrocarbon compounds which can be detected using EPA Method SW846-8015B. In addition to the total concentration of chemical constituents, DNAPL saturation estimates will require soil samples be collected for determination of f_{oc} and bulk density. The fraction of organic carbon is an important parameter that affects contaminant and surfactant sorption in the subsurface. Samples for the fraction of organic carbon should be collected from areas with little to no contaminant concentration. The soil samples should be measured for total organic carbon (TOC). The TOC results are then converted to f_{oc} by dividing the measured TOC by the mass fraction of dry soil. Appendix B has additional data on performing DNAPL saturation calculations.

3.2.4 Other Soil Measurements and Soil Core Collection. It is also recommended that soil samples be collected to measure the grain size distribution for well filter pack design. If used to estimate the hydraulic properties of soils (Vukovic and Soro, 1992) primarily for the purposes of characterizing permeability heterogeneities, soil samples should be collected at a frequency sufficient to define the major hydrostratigraphic units of the DNAPL zone. For this purpose, CPT measurements may be more economical and advantageous, but pushes must be conducted in similar stratigraphy beyond the DNAPL zone.

The mineral content of the soils will also be relevant to the selection of an appropriate surfactant formulation and soil samples for X-ray diffraction analyses are recommended. If soil column studies are to be conducted for surfactant selection or optimization of the surfactant solution formulation, several intact soil cores should be collected from the contaminated zones or from uncontaminated zones of similar depths if the stratigraphy is laterally homogeneous throughout. (See Appendix A for sampling devices.) As discussed in the next section detailing surfactant selection studies, soil column testing with the surfactant solution can isolate issues such as an amendment to the surfactant formulation is necessary to prevent cation exchange and any undesired contaminant mobilization.

3.2.5 Characterization of Capillary Barriers. The presence and competency of a capillary barrier can substantially alter the design approach for a SEAR application. If a thick clay aquitard acts as a competent capillary barrier at the bottom of the DNAPL zone, then a mobilization type of surfactant flood with low interfacial tensions can be considered, since this is the most effective and rapid of the SEAR processes. However, if there is no capillary barrier, or if the aquitard is leaky, a solubilization or neutral buoyancy approach will be necessary. Therefore, accurately characterizing the extent, structure, and capillary entry pressures of an underlying aquitard can assist in designing a surfactant flood suited to the site conditions.

The site investigation program should minimally include determinations of the structural integrity of the aquitard on a macro-scale, such as whether there are inadequately sealed wells or borings, or other leakiness that can be detected from water level measurements obtained from depths above and below the aquitard. This may include surveys to determine the aquitard competency, e.g., thickness. Furthermore, detailed topographic data to detect elevation changes in the surface of the aquitard can assist in proper placement and screening of injection and extraction wells to prevent mobilized DNAPL from being deposited in an unrecoverable section of the aquitard. GPR can be used to obtain this data within the DNAPL contaminated zone, while CPT can be used away from the DNAPL contaminated zone once the DNAPL contamination has been fully delineated. If a mobilization flood is the objective, more detailed investigations may be warranted since DNAPL migration has been shown to occur through hairline fractures, as small as 10 microns in diameter (Cohen and Mercer, 1993).

The capacity of a capillary barrier to withstand and prevent DNAPL infiltration is influenced by the pore-size distribution of the medium, and the driving forces affecting DNAPL transport, which includes the interfacial tension of the DNAPL in contact with the mineral surfaces. Figure 3-6 shows the effect of pore radius (related to mean grain diameter) on the critical height of DNAPL required to penetrate an underlying finer-grained capillary barrier under the IFT conditions and contact angle stated. A very fine silt will require 100 times as much hydraulic head before DNAPL infiltration as a medium sand. The combined effect of these factors in preventing DNAPL infiltration into a capillary barrier can be evaluated with capillary pressure tests. Capillary pressure tests should be conducted with undisturbed aquifer samples to obtain an estimate for the entry pressure of underlying fine-grained units or aquitards. The aquitard can be sampled with any number of standard sampling devices designed to collect relatively undisturbed cores. Larger diameter samplers (2 inches or more) that collect cores at least 6 inches in length are recommended. These measurements are needed to ensure that the underlying geologic layers will act as an effective capillary barrier. There are a number of laboratory experimental methods, such as centrifuge and pressure cell tests, which are available to determine capillary entry pressure. More information about these tests is included in Appendix C.

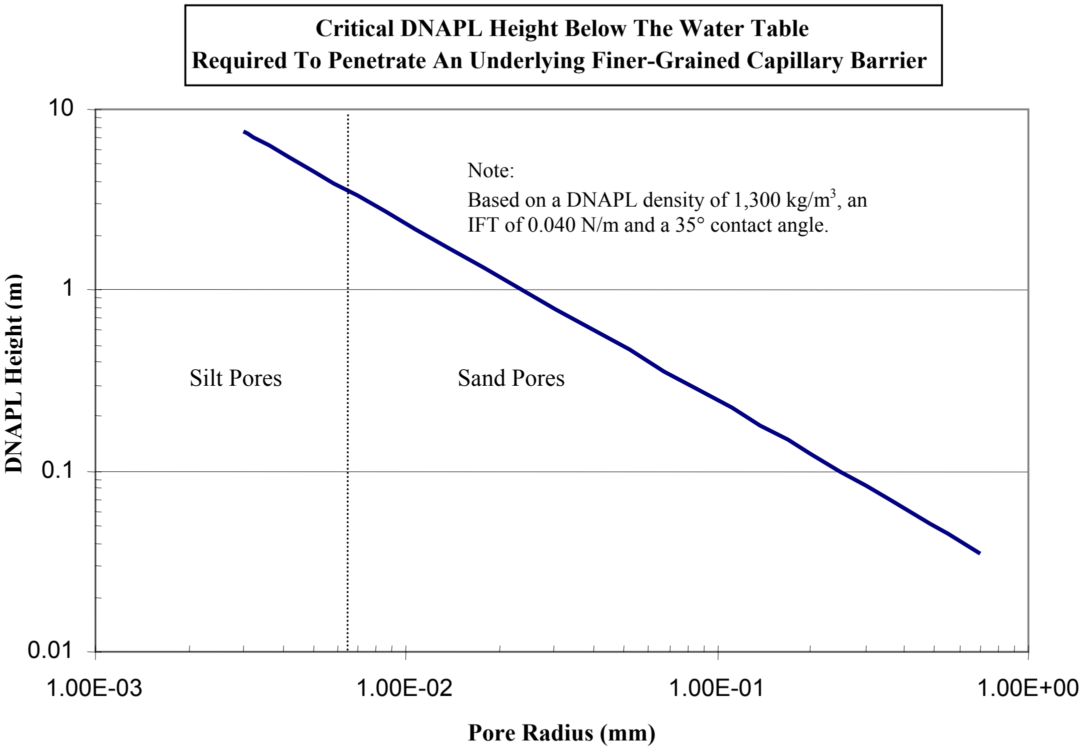


Figure 3-6. Effect of Pore Radius on DNAPL Infiltration

3.3 Aquifer Characterization Methods

This section will provide a description of the recommended methods and procedures used to characterize site hydrogeology as needed to predict and/or optimize SEAR performance. The hydrodynamics of the contaminated aquifer directly affect the design of the SEAR wellfield, as well as the SEAR flowrates, amounts of chemical reagents needed, and the duration of SEAR operations. While geophysical techniques can provide local permeability estimates, these, more often than not, do not reflect bulk aquifer hydraulic conductivity conditions. Aquifer characterization is usually done in conjunction with numerical modeling of the aquifer conditions (discussed further in Section 5.0).

The primary objectives of the aquifer characterization program include the following:

- ☐ Obtaining estimates of bulk hydraulic conductivity,
- ☐ Testing the sustainable injection and extraction rates for the aquifer and the wells.

The SEAR hydraulic testing program generally consists of installation and construction of groundwater injection/extraction wells, slug/bail tests, pumping tests, and conservative interwell tracer tests (CITTs). The design and implementation of a PITT can assist in predicting the quantity and distribution of DNAPL mass within the treatment volume (as opposed to local estimates).

3.3.1 Well Installation and Construction. Wells used for aquifer characterization should be constructed similarly to those used in SEAR operations in the event that free-phase DNAPL is contacted and DNAPL recovery from the well is necessary. Free-phase DNAPL should be collected prior to conducting aquifer tests that will involve water injection. DNAPL samples can be taken for further testing of physical parameters such as density, viscosity and interfacial tension.

The stratigraphy and DNAPL distribution within the DNAPL-contaminated zone should be understood prior to well installation. This is to properly screen wells to obtain accurate data on the hydraulic properties of the DNAPL-contaminated zone(s). SEAR well installation and construction methods are described below. More detailed information on well construction can be found in *Groundwater and Wells* edited by Driscoll (1986) and in the SEAR Implementation Manual.

As a general rule, the SEAR injection and extraction wells should be at least 4 inches in diameter and constructed using a stainless steel wire-wrapped screen (see Figure 3-7). Well screens and screen filter packs should be designed and selected on the basis of grain-size distribution analyses from the DNAPL zone (see Driscoll, 1986). Screen lengths should be as short as practical while extending across the entire interval to be treated to help ensure a more uniform delivery of surfactant to the treatment zone. The bottom slot of the screen should be installed below the interface between the aquifer and the underlying capillary barrier, if applicable to allow the capture of mobile DNAPL. Care should be taken during drilling to minimize the volume of the borehole below the well screen as it can act as a sump for mobile DNAPL. A solid screw-on sump no more than 5 inches long should be attached to the bottom of the screen. The well casing can be constructed of either stainless steel or PVC. Because PVC is less expensive, it can be advantageous to use this material above the depth of DNAPL contamination. However, if the casing will contact DNAPL through activities such as routine bailing of product, then stainless steel should be used for the entire well. Centralizers should be used during installation to ensure that the well is centered in the borehole as the filter pack is placed. The silica sand filter pack should be placed a minimum of 2 feet above the well screens, with the depth to the top of the filter packs being determined by measurements with a weighted calibrated tape. A thin layer of fine sand (approximately 6 inches) should then be placed on top of the coarser sand of the filter pack. A bentonite seal at least 2 ft thick can then be placed on top of each filter pack and hydrated. Once the bentonite seal has been allowed to hydrate, a concrete grout should be pumped (using a tremie pipe) into the annulus between the well and borehole from the bentonite seal to ground surface. This cement mixture can be formulated so that grout loss to the formation is minimized. With a surface completion finished to grade, the well should have a water-tight "gripper" cap to prevent the infiltration of surface or stormwater runoff. Wells completed above grade (as shown in Figure 3-7) can be vented (e.g. a vent hole drilled in the side of the casing just below the cap). The volumes and quantities of materials required to construct the well should be determined and recorded before the placement of the material. A careful inventory and record of each material used should be kept during construction to ensure that the well is properly installed.

The final step in constructing a high-efficiency pumping well is to develop it properly. Proper development involves the use of surge blocks or similar devices and methods to effectively move fine-grained sediments from the filter pack and even the aquifer itself into the well bore where they are evacuated with a pump or bailer. Surging should be conducted in stages across successively lower segments of the screen, while periodically removing the sediment-laden water in the well bore.

3.3.2 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 should be used to ensure that as large of an aquifer volume as possible is tested, and to minimize decontamination and investigation derived hazardous waste (IDHW). The slug-test analysis procedure developed by Peres et al. (1989) can be used to determine aquifer properties from the test data.

3.3.3 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 tests provide estimates of the hydraulic properties of the flow system at the scale of the entire target 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 the SEAR, including hydraulic conductivity and permeabilities for the hydrostratigraphic units incorporated into the conceptual geosystem model. The collection of depth-discrete hydraulic information using multilevel samplers (MLS) is recommended to identify vertical heterogeneities for improved SEAR remedial design. Additionally, pump tests can be used to determine parameters relating to specific wells in the wellfield 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 SEAR operations, a multiple well hydraulic test has been developed that provides wellfield scale transport properties in addition to the hydraulic parameters derived from pump tests. This test, known as a CITT, involves not only injection and extraction operations in the SEAR wellfield similar to the planned surfactant flood, but also the transport of a non-partitioning or conservative tracer across the target zone. CITTs are essential to the SEAR design process because they provide the swept pore volume (how much of the DNAPL zone is contacted by moving fluids that are represented by tracer movement), the residence time (how long it takes the advective front to traverse the contaminated zone), and tracer recoveries (a measure of how much of the injected fluids were captured at the extraction wells). Ultimately, CITTs provide an understanding of how forced-

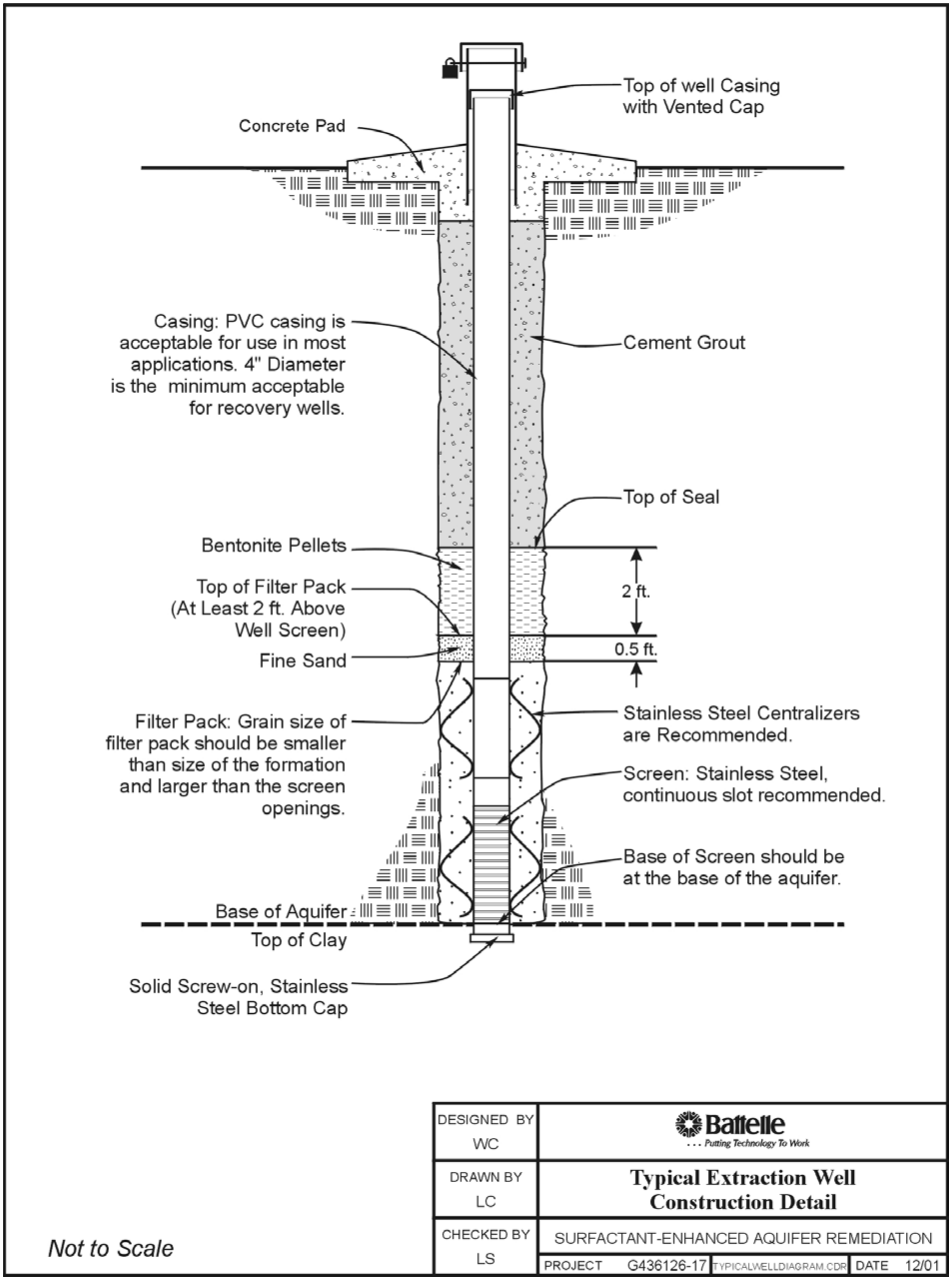


Figure 3-7. Typical Well Construction Detail for an Extraction Well

gradient flow systems behave in the aquifer volume affected by the wellfield array, and how well those fluids are controlled during injection/extraction operations. These issues have been critical to obtaining regulatory approval for SEAR applications. The main objectives of a CITT include the following:

- Obtaining data on the permeability heterogeneities of the aquifer based on tracer retardation between injection and extraction well pairs, and
- Demonstrating excellent tracer capture under pumping conditions.

As with pumping tests, depth discrete sample collection at the extraction point will be necessary to identify vertical heterogeneities. CITT results can be analyzed using several techniques including curve matching, trial and error, and the method of moments. Method of moments analysis can be used to obtain meaningful hydraulic parameter data such as the swept pore volume, the 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 Peclet number and the longitudinal dispersivity, both measures of heterogeneity in the geosystem (Jin, 1995).

3.3.4 Partitioning Interwell Tracer Tests (PITTs). A PITT is recommended as an additional remedial design tool to the CITT to determine the volume and spatial distribution of DNAPL within the subsurface. It provides data useful for predicting the quantity of SEAR chemicals required to achieve target cleanup levels and subsequently the anticipated duration and cost of SEAR implementation. Several studies have indicated 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). For heterogeneous aquifers, a large number of soil cores, each of a large volume, would be required to obtain a representative, average value for residual DNAPL saturation. A PITT can also be used as a performance assessment tool after SEAR application to measure system effectiveness by determining how much DNAPL remains in the subsurface. The PITT technology is patented by DE&S and the University of Texas (U.S. Patent Nos. 5,905,036 and 6,003,365), so proper licensing arrangements should be made before implementation of this technology.

A PITT involves the injection of a suite of chemical tracers into the saturated zone. The nonpartitioning (conservative) tracers pass unhindered through the DNAPL zone, while transport of the partitioning (nonconservative) tracers is retarded or slowed down by interaction with the DNAPL. The different recovery patterns of the tracers are evaluated and then used to estimate the swept pore volume and the total volume of DNAPL in the subsurface, from which the average DNAPL saturation can be computed. Multilevel sampling points (MLSs) should be used to ensure that all stratigraphic zones are being contacted with partitioning tracers. 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).

Table 3-4 includes preremediation PITT results from several recent field-scale projects. The first environmental application of a field-scale PITT took place in 1994 (Annable et al., 1998), and approximately 40 more pilot-scale PITTs have been conducted since then at several different sites. The first major sitewide application of PITT took place at Operable Unit 2 (OU-2), HAFB in Utah in 1998. Four large-scale PITTs were carried out within the containment slurry wall at this site (see Figure 3-8) and detected a total of approximately 1,100 gallons of DNAPL in an aquifer-swept volume of approximately 285,000 gallons. The average sitewide DNAPL saturation was estimated at 0.4%, while the saturation values ranged up to 10.7%.

Table 3-4. PITT Results from Selected Field Projects

Site	Primary Contaminant	Soil Material	DNAPL Volume (gal)	Swept Pore Volume (gal)
Camp Lejeune, NC	PCE	Sandy Silt	87	4,780
DOE Portsmouth, OH	TCE	Sand, Gravel	4-10	4,500
Hill AFB, UT	TCE	Sand, Gravel	1,100	285,000
PPG Chemicals, LA	1,2-DCA	Silty Sand	24	1,730
Sandia National Laboratory, NM	TCE	Sand, Gravel	40-180	30,000-100,000

The execution of a PITT requires the completion of a series of tasks as follows:

- **Tracer Selection -** Tracer selection is highly dependent on the characteristics of the DNAPL specific to the site, and can be accomplished using either laboratory batch tests or an empirical method based on the equivalent alkane carbon number of the DNAPL developed by Dwarakanath and Pope (1998). A suite of several tracers with a range of partition coefficients is selected to ensure that the PITT is robust enough to detect both low and high DNAPL saturations accurately.

- **PITT Design Simulations -** Design simulations are carried out to optimize PITT performance through selection of parameters such as tracer mass input, test duration, and target injection and extraction flowrates. The design simulations are based on the results of the CITT including the swept pore volume, the residence time, and tracer recoveries. These simulations can be performed using the University of Texas chemical flooding simulator (UTCHEM), which is discussed in detail in Section 5.2.

- **Tracer Test Operation -** The field application of 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. Under steady-state flow field conditions, the nonconservative tracers will continue to dissolve into the DNAPL in the pore spaces until equilibrium partitioning has been achieved. After the tracer slug is injected, tap water is injected to drive the tracers across the zone of interest. This flood of tracer-free water will cause a subsequent partitioning of the nonconservative tracers back into the groundwater. This transport to/from the DNAPL phase causes retardation of the nonconservative tracers relative to the conservative tracers which are unaffected by the presence of DNAPL.

- **Tracer Sampling and Analysis -** Samples of the extraction well effluent are taken periodically during the test and analyzed to define the tracer breakthrough curves. Enough samples should be taken to determine the tracer recovery of each tracer, including quickly eluting and slowly eluting tracers.

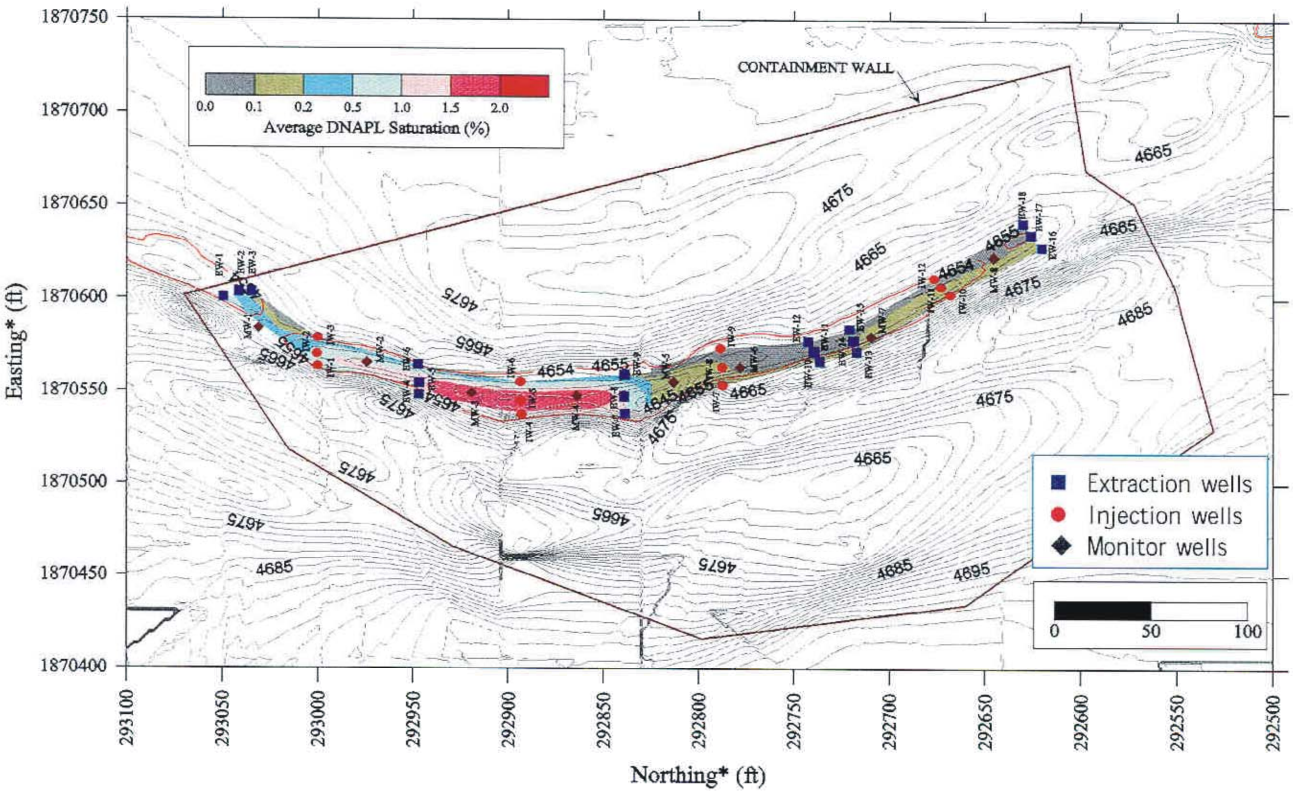


Figure 3-8. DNAPL Saturation Measurements with PITT

Examples of PITT tracer response or breakthrough curves are presented in Figure 3-9. Data collected from the PITT are analyzed using the method of moments to give the swept pore volume, the volume of DNAPL in the swept pore volume, and the average DNAPL saturation over the swept pore volume (as described in Jin et al., 1995). In Figure 3-9a, high residual saturations of DNAPL cause a large separation between the arrival times of the nonpartitioning and partitioning tracers. In Figure 3-9b, the nonpartitioning and partitioning tracers arrive at the same time, and separation of the curves occurs later in the test indicating lower residual saturations. As Figure 3-9b shows, low DNAPL saturations can be difficult to estimate due to scatter in the tracer recovery data.

Because the PITT is a relatively new, innovative technology, it is useful to be aware of its limitations and some of the consequences associated with improper test design and/or implementation. The following are some issues to be addressed prior to application of this technology:

- **Influence of Heterogeneity** - In a heterogeneous aquifer, PITT performance may be limited by permeability contrasts, which cause preferential flow of tracers through the more permeable zones.

- **Poor Tracer Recovery** - If hydraulic control is not properly maintained, poor recovery of the injected tracers will be experienced and the tracer test results may be inaccurate or difficult to interpret.

- **Matrix Interference** - PITT is sensitive to errors in the tracer partition coefficient. Because alluvial aquifer materials may contain small amounts of organic carbon material (typically, 0.1% to 0.01%), laboratory column tests of uncontaminated alluvium are performed before a PITT to determine if this natural carbon can cause interferences. If interference is detected, a correction factor is measured (see Jin et al., 1997). Usually, only fine-grained sediments contain sufficient natural organic carbon to interfere in this manner. Another consideration is the effect of the surfactant when a PITT is used to determine the DNAPL volume remaining following a surfactant flood. At the Marine Corps Base Camp Lejeune, the post-SEAR PITT results were unusable because an impurity in the surfactant solution sorbed to the aquifer soils which caused an unanticipated change in the partitioning behavior of the tracers.

- ☐ **Change in DNAPL composition** – Tracer partition coefficients may also be affected by changes in the DNAPL composition occurring from surfactant flood treatment. If both pre- and post- SEAR PITTs will be conducted, this needs to be accounted for during the PITT design process, and may affect the selection of tracers for the post-SEAR PITT.

- ☐ **High/Low DNAPL Saturations** - The volume of free-phase or mobile DNAPL may be underestimated due to mass transfer (surface area) limitations or partitioning between pooled DNAPL and the groundwater. These errors can be reduced by water flooding the DNAPL zone to residual-phase saturations prior to PITT implementation. Also, as shown in Figure 3-9b, the resolution of the tracer test may be limited at low DNAPL saturations. This will depend on the tracer detection limits relative to the DNAPL saturations being quantified.

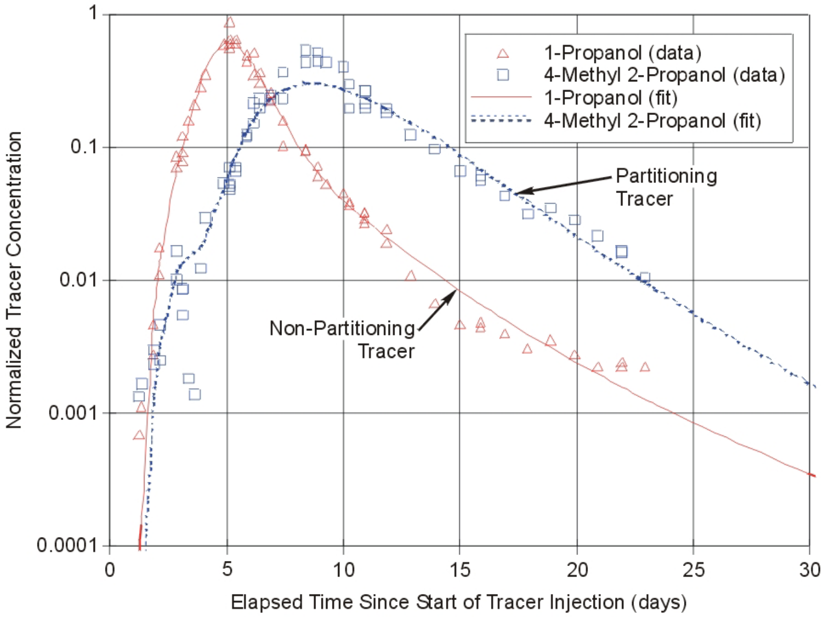
- ☐ **Other Issues** - Other common problems include the failure to use three or more tracers with sufficiently differing partition coefficients, the failure to accurately determine the partition coefficients, and the failure to observe the tails of the tracer response curves.

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 PITT systems should be available for rapid DNAPL site assessments in the near future.

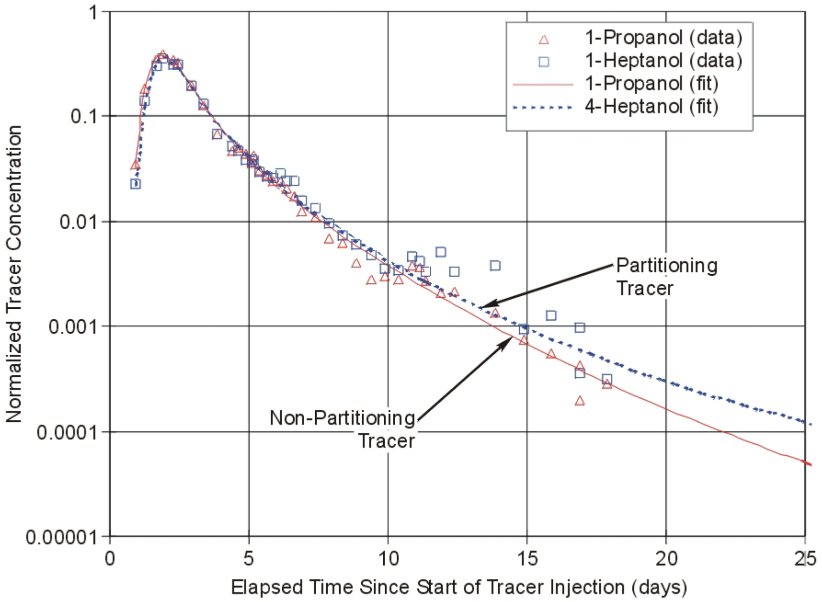
3.3.5 Characterizing Groundwater Chemical/Fluid Properties. Table 3-2 includes a summary of the required parameters for groundwater characterization, along with the appropriate analytical methods. During the hydraulic testing phase, groundwater samples are typically collected and analyzed for geochemical 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 these can significantly alter the behavior of the surfactant formulation. Carbonate and other sources of alkalinity should be quantified. 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. Samples from the source of water, i.e., tap water, to be used on site for mixing the surfactant solution, should also be collected and tested for geochemical parameters.

Application of PITT :

- A suite of chemical tracers is injected into the subsurface.
- Generally, the conservative (nonpartitioning) tracer peak will arrive first.
- The nonconservative (partitioning) tracer peak will arrive later, as the tracer is retarded by interaction with DNAPL.
- The difference in peak arrival time and tailing behavior can be correlated to DNAPL saturation.



(a) High Residual NAPL Saturation



(b) Low Residual NAPL Saturation

Figure 3-9. Example of PITT Breakthrough Curves

Section 4.0: SURFACTANT SELECTION

This section describes the surfactant properties needed for optimum performance and the laboratory procedures used to select appropriate surfactants. Selecting an efficient surfactant can make the difference between a moderately successful flood that removes only a fraction of the DNAPL present and a successful flood that removes >95% of the DNAPL in the swept pore volume. First, a brief introduction to surfactant chemistry is provided to familiarize the reader with some of the basic terminology used to characterize surfactant properties. Then, surfactant selection criteria are discussed, followed by a description of phase behavior experiments to optimize surfactant selection for the contaminant alone, and a discussion of soil column experiments to ensure surfactant compatibility with the aquifer soils.

4.1 Surfactant Chemistry

Surfactants, such as common household detergents, are chemical agents that enhance the effective solubility of organic compounds in the water or aqueous phase. Figure 4-1 provides examples of the two classes of surfactant compounds that are currently in use for SEAR applications. The term surfactant or surface active agent describes the tendency for this class of compounds to adsorb at the interface between two immiscible fluid phases. This behavior occurs because surfactant molecules consist of two components, a water-liking (i.e., hydrophilic) group and a water-disliking (i.e., hydrophobic) group. Surfactants are classified by the ionic charge of the hydrophilic group in aqueous solution. Anionic surfactants have been more frequently used for SEAR application in recent years because soil surfaces are generally negatively charged, and a negatively charged surfactant will be repelled, rather than attracted to the soil surface. For the same reason, cationic surfactants, e.g., hair-cleansing agents, have usually been avoided. Figure 4-1 provides a broad grouping of anionic and nonionic surfactants. An illustration of the chemical structure of an anionic surfactant is shown in Figure 4-2.

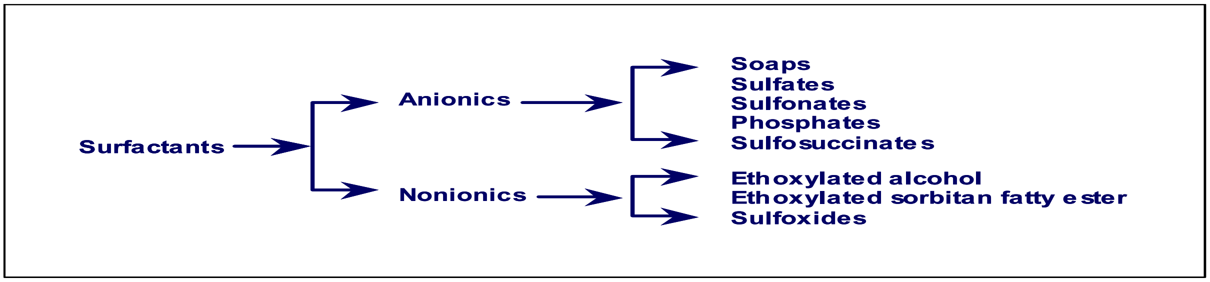


Figure 4-1. Examples of Anionic and Nonionic Surfactants

SEAR involves the injection of a surfactant solution consisting of surfactant, electrolyte (for an anionic surfactant), water and often cosolvent (i.e., alcohol). Commonly used anionic surfactants for SEAR include alcohol ether sulfates, alkane sulfonates and sulfosuccinates. The addition of electrolytes and cosolvents helps to improve contaminant mass recovery and to prevent the formation of gels in the subsurface. Sodium chloride and calcium chloride are examples of commonly used electrolytes (solutes that produce ions in solution). IPA is an example of a commonly used cosolvent.

Surfactants work to enhance contaminant mass recovery in the subsurface by reducing the interfacial tension of the fluid phases contacting the residual DNAPL. The extent of interfacial tension reduction will determine whether the primary mechanism of contaminant removal is via

1) Solubilization of the residual DNAPL into the surfactant solution, or
2) Mobilization of entrapped DNAPL as free product.

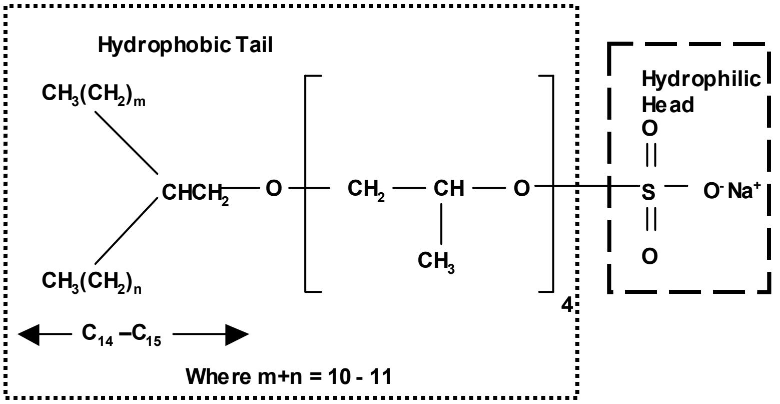


Figure 4-2. Molecular Structure of Alfoterra 145-4PO Sulfate™ Surfactant

Because surfactant properties will vary with the types of chemical constituents in their surroundings, a careful understanding of surfactant behavior in the presence of DNAPL, groundwater constituents, and other organic and inorganic chemicals is critical for the design of effective SEAR operations.

4.1.1 DNAPL Solubilization with SEAR. Low IFT reduction resulting in a single aqueous-phase solubilization system, also known as a Winsor Type I solubilization regime, is the preferred mode of SEAR application at locations where no capillary barrier exists or where it has been determined that the capillary barrier is fractured or otherwise not competent. Higher IFT reduction that increases the likelihood of an unsolubilized DNAPL moving front typically provides more rapid DNAPL removal, but may increase the potential for DNAPL migration, if no competent barrier to downward movement exists.

A surfactant solution designed to maximize solubilization significantly increases the total aqueous solubility of organic contaminants. The solubility increase allows residual DNAPL mass to be recovered much more rapidly than by pump and treat which relies upon the much less efficient process of dissolution into groundwater. The solubility enhancement under ideal laboratory conditions, where surfactant is completed saturated with DNAPL, is on the order of 100 to 1,000-fold. Under field conditions, the solubility enhancement will vary with the quantity of DNAPL contacted by surfactant.

Surfactants reduce interfacial tension (IFT) by accumulating at the interface between the DNAPL and water phases. At low concentrations, surfactants will exist as single molecules or monomers, at higher concentration they will begin to accumulate to form structures called micelles as shown in Figure 4-3. Micelles are generally spherical in shape and can consist of several hundred individual surfactant monomers. In water, surfactant molecules will form micelles such that the hydrophilic end of the molecule faces the water, and the hydrophobic end of the molecule faces away from the water. This aggregation of individual molecules begins when the critical micelle concentration (CMC) has been reached (Bourrel and Schechter, 1988). Above the CMC, a significant increase in the total aqueous solubility of the DNAPL constituents is observed, as the contaminant partitions from the DNAPL phase into the hydrophobic core of the surfactant micelles in solution. The term microemulsion is used to describe the thermodynamically stable, swollen micellar solution consisting of submicroscopic particles of DNAPL and surfactant suspended in solution.

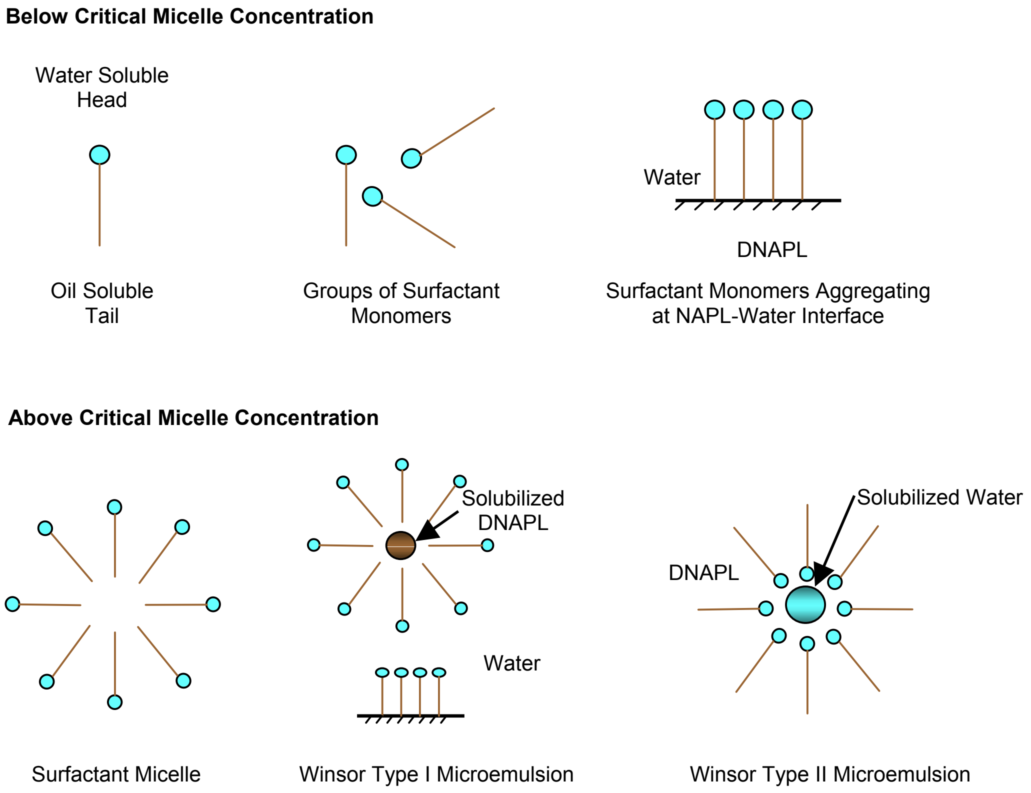


Figure 4-3. Micelle Formation Diagram

4.1.2 DNAPL Mobilization with SEAR. Mobilization should be used only at sites with minimal potential for further vertical migration of the DNAPL. A competent capillary barrier is needed to allow successful implementation of DNAPL mobilization with SEAR. Surfactants mobilize DNAPL by lowering the IFT sufficiently for the capillary forces holding the DNAPL in place to be overwhelmed by gravity and viscous forces. Table 4-1 shows the magnitude of IFT reduction that can be achieved with surfactant addition. The trapping number is a dimensionless quantity which considers the viscous and gravity forces that must be overcome to mobilize the DNAPL, and is dependent upon parameters such as the interfacial tension, DNAPL density and soil permeability. Capillary forces are inversely proportional to the soil permeability; the higher the soil permeability or the larger the pore size, the lower the capillary forces or pressure and the more easily mobilization will occur for a given IFT reduction. The lower the soil permeability, the greater the IFT reduction, or the lower the IFT value necessary to induce mobilization. Although an IFT of 0.001 dynes/cm will generally cause mobilization, the IFT value that induces mobilization must be computed on a site-by-site basis. While all surfactants have an effect on IFT, only certain surfactants can be used to achieve the ultralow IFTs needed to successfully mobilize residual DNAPL. However, ultralow IFT surfactant systems can also lead to the undesirable Winsor Type II solubilization systems where surfactants will begin to partition (i.e. be lost) into the DNAPL phase as shown above.

Table 4-1. Interfacial Tension Reduction by Selected Surfactants

Description of Fluids	Site	Contaminant	Surfactant Formulation	Interfacial Tension (dynes/cm)
DNAPL-Water	Hill AFB OU-2	DNAPL with TCE, O&G, and other solvents	Not applicable	9
DNAPL-Aerosol MA80I Solution	Hill AFB OU-2	DNAPL with TCE, O&G, and other solvents	4% MA, 4% IPA, 11,250 mg/L NaCl	0.01
DNAPL-Aerosol MA80I Solution	Laboratory	TCE	4% MA, 8% IPA, 9,350 mg/L NaCl	0.02
DNAPL-Alfoterra 145-4PO Sulfate™ Solution	Laboratory	PCE	4 wt% Alfoterra, 16 wt% IPA, 1800 mg/l CaCl2	0.002

4.1.3 Phase Behavior Description. As discussed previously**,** surfactants can either mobilize or solubilize DNAPL depending on the degree of IFT reduction involved. The degree of IFT reduction is related to the phase behavior of the surfactant or the stability and quality of the water, microemulsion, and DNAPL phases that form when a surfactant solution and DNAPL are mixed together. When anionic surfactants are used, the preferred type of flood (solubilization or mobilization) can be conducted by changing the salinity of the injected surfactant mixture. As salinity of the solution is increased, the interactions between the hydrophilic head group of the surfactant and the water molecules are reduced, which results in greater interactions between the hydrophobic tail group of the surfactant and the DNAPL. Therefore, the hydrophilic tendency of the surfactant molecule can shift, as the salinity of the aqueous fluid is changed. Salinity can be adjusted continuously in the field to optimize surfactant performance in the field. The ability to easily adjust surfactant properties such as IFT is a significant advantage of using anionic surfactants over nonionic surfactants.

A formal system has been developed to describe the complex interactions between DNAPL, water, and surfactants. Three types of phase behavior are expected when DNAPL and surfactant solutions are mixed together and are described as follows:

- Winsor Type I - The solubilization of DNAPL into the single aqueous-phase surfactant solution. An oil-in-water microemulsion exists which is characterized by inward-facing hydrophobic surfactant tails and solubilized DNAPL components in the center of the micelle (see Figure 4-3).

- Winsor Type II - The partitioning of the surfactant into the DNAPL phase, which means that DNAPL solubilization does not occur. A water-in-oil microemulsion or inverted microemulsion exists which consists of inward-facing hydrophilic surfactant heads and solubilized water in the center of the micelle (see Figure 4-3). Winsor Type II systems are highly undesirable for SEAR operations since the surfactant is essentially unrecoverable or lost in the DNAPL phase.

- Winsor Type III - This behavior is observed when three separate phases coexist in solution including the aqueous, microemulsion, and DNAPL phases. The separate middle phase has a density between that of water and DNAPL and consists of a surfactant microemulsion. Formation of this separate microemulsion phase is associated with ultralow interfacial tensions and high solubilization.

The transition between these phase behavior systems proceeds from Type I to Type III to Type II, and is affected by adding an electrolyte (for anionic surfactants), adding a heavy alcohol, increasing the surfactant tail length, or reducing the temperature. Surfactant-phase behavior experiments are used to develop a volume fraction diagram, which shows the transition in surfactant behavior from the Winsor Type I to Winsor Type III to Winsor Type II regimes, as shown in Figure 4-4. Figure 4-4 shows a volume fraction diagram produced by varying the electrolyte concentration between various samples and keeping all other parameters, such as surfactant concentration, constant. The volume fraction occupied by each phase (aqueous, microemulsion, and DNAPL) at equilibrium is measured and then plotted against the electrolyte concentration. The interpretation of volume fraction diagrams is discussed in more detail in Section 4.3. It should be noted that DNAPL mobilization is not strictly dependent upon surfactant phase behavior, but is a function of the trapping number as discussed previously (Jin, 1995; Pennell et al., 1996). If the IFT is lowered to the extent that the sum of the gravity and viscous forces exceeds the capillary forces, DNAPL will be mobilized. This can happen under both Winsor Type I and III regimes, but more commonly with the Winsor Type III regime.

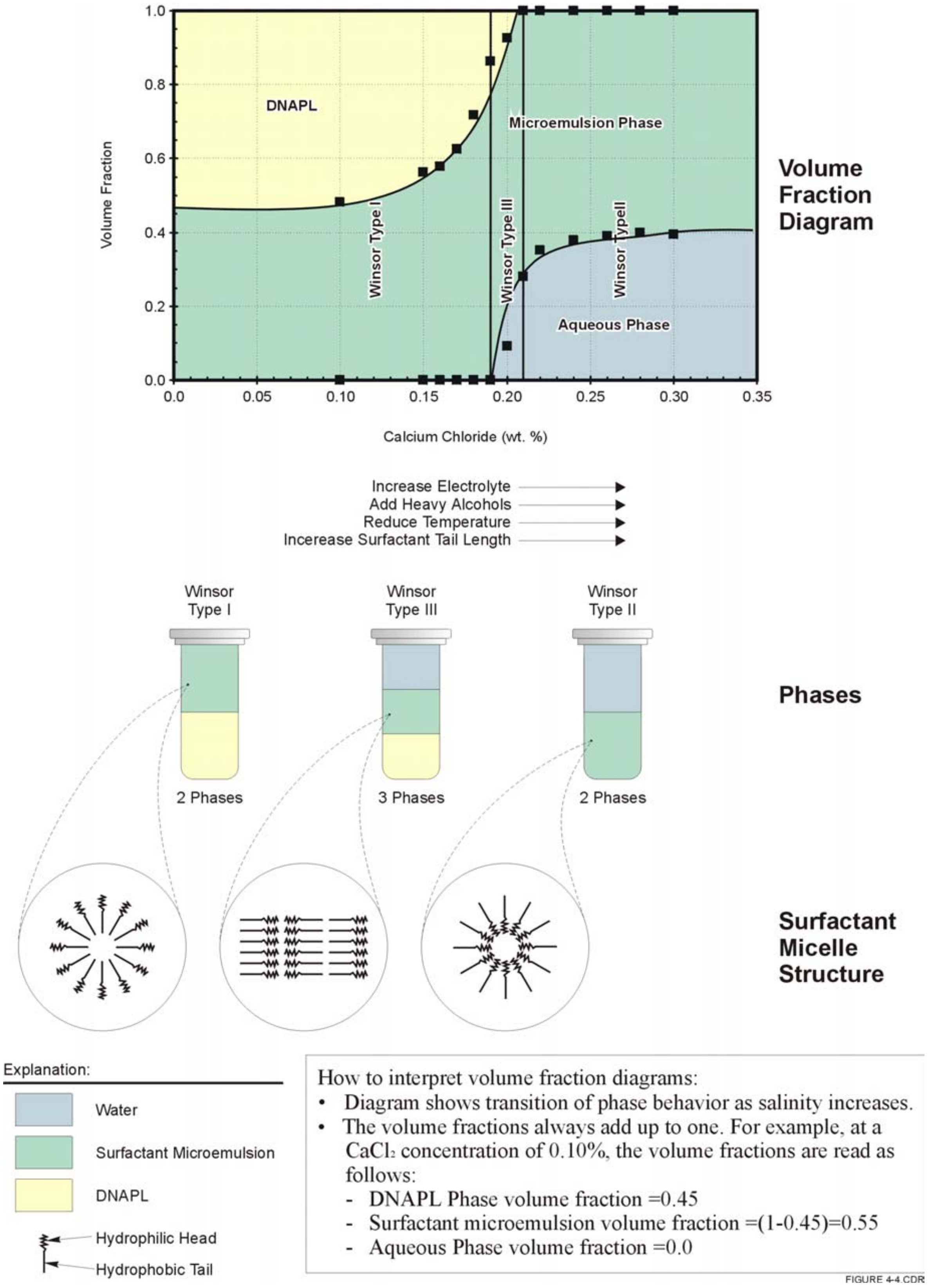
4.2 Surfactant Selection Criteria

Careful evaluation of the complex chemistry of surfactants is required to ensure selection of an optimal surfactant for the contaminant, groundwater, and soil characteristics at the SEAR remediation site. Surfactant selection criteria for SEAR are described in more detail in the literature (Pope and Wade, 1995; Shiau et al., 1995a; Dwarakanath et al., 1999; Dwarakanath and Pope, 1999). Desirable characteristics for surfactant formulations are as follows:

- ☐ Minimal propensity to form liquid crystals, gels, or macroemulsions,
- ☐ Rapid coalescence,
- ☐ High contaminant solubilization,
- ☐ Ability to promote DNAPL mobilization (if mobilization is desired),
- ☐ Environmental acceptability and biodegradability,
- ☐ Low adsorption on soil solids,
- ☐ Low critical micelle concentration, and
- ☐ Amenability to recycling.

4.2.1 Minimal Propensity to Form Liquid Crystals/Gels/Macroemulsions. Surfactants tend to precipitate out of solution to form liquid crystals, gels, and macroemulsions. A macroemulsion is an unstable, physical dispersion of one fluid within another. (Macroemulsions should not be confused with microemulsions; macroemulsions are viscous dispersions, whereas microemulsions have relatively low viscosities.) Liquid crystal, gel, and macroemulsion phases hinder transport through the aquifer, plug pores, and reduce aquifer permeability (Renshaw et al., 1997; Dwarakanath et al., 1999). The addition of a cosolvent or cosurfactant will minimize the formation of these undesirable phases. Their formation may be further limited by using a surfactant with a branched hydrophobic tail (Bourrel and Schechter, 1988).

4.2.2 Rapid Coalescence. When a surfactant solution and DNAPL mix, a macroemulsion forms with small DNAPL droplets suspended in surfactant micelles, which are dispersed in the aqueous phase. The excess DNAPL in the macroemulsion coalesces together to form larger DNAPL droplets, which eventually separate into a separate DNAPL phase and a microemulsion phase with dissolved DNAPL constituents. This phenomenon is termed coalescence. An important parameter for surfactant selection is rapid coalescence of surfactant-DNAPL mixtures into thermodynamically stable microemulsions. Surfactants with coalescence times of less than 24 hours are desirable. For example, sodium dihexyl sulfosuccinate, which was used at HAFB OU-2 to remediate a TCE-rich DNAPL, coalesced in less than 20 minutes (Mayer et al., 1999). Poor surfactants form stable macroemulsions, have high coalescence times (greater than 40 hours), and therefore have the potential to cause mass transfer limitations between DNAPL and surfactant micelles in the subsurface. This greatly impedes DNAPL removal efficiency and can account for mass transfer limitations (Pennell et al., 1993, Mason and Kueper, 1996).



How to interpret volume fraction diagrams:

- Diagram shows transition of phase behavior as salinity increases.
- The volume fractions always add up to one. For example, at a $CaCl_2$ concentration of 0.10%, the volume fractions are read as follows:
  - DNAPL Phase volume fraction =0.45
  - Surfactant microemulsion volume fraction =(1-0.45)=0.55
  - Aqueous Phase volume fraction =0.0

Figure 4-4. Explanation of a Sample Volume Fraction or Phase Behavior Diagram

4.2.3 High Contaminant Solubilization. The candidate surfactant should be capable of enhancing the effective solubility of the contaminant several orders of magnitude above the normal solubility of the contaminant in water alone while minimizing the possibility of contaminant mobilization. This will reduce the surfactant requirement.

4.2.4 Ability to Promote DNAPL Mobilization (Optional). As discussed in Section 3.2.3, if the site has a good capillary barrier, it is generally desirable to use a surfactant that will greatly reduce the IFT between the DNAPL and surrounding soil and water phases to mobilize the DNAPL contaminant. Surfactants that can form Winsor Type III systems are almost always mobilization systems. Not all surfactants can form stable Winsor Type III systems, so this may become an additional criterion for surfactant selection. It should also be noted that Winsor Type III systems will also achieve the highest possible contaminant solubilization. At Hill AFB in Utah, the equilibrium solubilization of TCE DNAPL containing oil and grease (O&G) by an optimized solution (i.e., at optimal salinity[1]) of sodium dihexyl sulfosuccinate (tradename Aerosol MA-80I) was 625,000 mg/L, which was 600 times the solubility of the DNAPL in water (Dwarakanath et al., 1999). Similarly, the equilibrium solubilization of PCE by an optimized solution of Alfoterra 145-4PO Sulfate™ was > 850,000 mg/L, which is >3500 times the solubility of PCE in water (DE&S, 2000).

4.2.5 Environmental Acceptability. The primary concern is the environmental effects of residual surfactants in the groundwater following SEAR treatment. Most surfactants approved for subsurface injection are food or cosmetic grade chemicals. Biodegradability and toxicity information should be used to assess the environmental safety of the surfactant prior to subsurface use.

4.2.6 Low Adsorption. Surfactant sorption by mineral surfaces can cause substantial loss of surfactant and reduce its performance. In addition to surfactant losses, sorption can also reduce the permeability of the aquifer material (Renshaw et al., 1997). Nonionic surfactants are more likely to be sorbed by mineral surfaces due to the presence of polar groups in the surfactant molecule that may attach to polar groups on mineral surfaces. Anionic surfactants are preferred since they typically exhibit low sorption in the presence of aquifer material (Pope and Baviere, 1991). This is because the negatively charged head of the surfactant is repelled by the net negative charge of aluminosilicates and other minerals that make up alluvium aquifers at typical values of groundwater pH. The commonly used anionic surfactants for SEAR include alcohol ether sulfates, alkane sulfonates and sulfosuccinates, all of which typically exhibit low adsorption. The tendency of surfactants to sorb to the aquifer solids is evaluated in soil column tests.

4.2.7 Low Critical Micelle Concentration. One of the objectives of SEAR is to maintain the surfactant concentration well above the CMC in the target aquifer zone in order to maximize DNAPL solubilization or mobilization. This means that a sufficient amount of surfactant needs to be injected to ensure that the in situ surfactant concentration remains above the CMC after dilution and dispersion in the aquifer. The use of a surfactant with a low CMC will lower the mass of surfactant required. Conversely, the use of a surfactant with a high CMC will necessitate injecting a larger mass of surfactant to affect the same level of remediation. Alfoterra I-12-3PO Sulfate™ has a relatively low CMC on the order 0.01 wt%. However, the surfactant used at Hill AFB, sodium dihexyl sulfosuccinate, had a higher CMC on the order of 0.2 wt% at optimal salinity. Due to this relatively high CMC, a higher surfactant concentration was required in the injectate surfactant formulation to overwhelm the effects of dilution and dispersion. However, the surfactant phase behavior and salinity can also be adjusted to accommodate CMC issues. A low CMC surfactant is more amenable to surfactant recycle, as discussed in the next section.

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[1] Optimal salinity is the electrolyte concentration at which equal volumes of NAPL and water are solubilized per unit volume of surfactant and is represents a Winsor Type III system. (Bourrel and Schechter, 1988)

SURFACTANT SELECTION CASE STUDY

Use of Alfoterra 145-4PO Sulfate™ Surfactant at Site 88, MCB Camp Lejeune, North Carolina

SITE BACKGROUND

A SEAR demonstration project was conducted in 1999 at the location of a dry-cleaning facility at MCB Camp Lejeune, North Carolina. The site was contaminated with tetrachloroethylene (PCE) and Varsol^{TM} present beneath the facility in a shallow aquifer at a depth of approximately 16 to 20 ft bgs. Much of the DNAPL was present in a low permeability silty layer at the base of the aquifer. The surfactant selection experiments were performed by the University of Texas (Austin).

SURFACTANT SELECTION

The surfactant formulation was designed specifically for the MCB demonstration project to meet two objectives: (1) to maximize DNAPL solubilization, and (2) to maximize surfactant recovery during the recycling process. Extensive laboratory testing was conducted to optimize to these dual objectives. The result was the selection of a custom surfactant, Alfoterra 145-4PO Sulfate™, that was manufactured by Condea Vista Company for the SEAR demonstration. The surfactant injectate formulation consisted of 4 wt% Alfoterra 145-4PO Sulfate™ surfactant, 16 wt% IPA, and 0.16-0.19 wt% calcium chloride ($CaCl_2$) mixed with source water (i.e., site potable water). These represent less than optimum salinity conditions because there was a concern that a Winsor Type III surfactant system would not be safe for the aquifer.

PHASE BEHAVIOR RESULTS

A total of 155 different surfactant formulations, i.e., combinations of surfactant(s), cosolvent and electrolyte, were screened for the selection of a surfactant with appropriate subsurface and aboveground treatability characteristics. A brief list of selected surfactants examined in this study and key results such as optimal salinity, solubilization parameter at optimal salinity, and contaminant solubilization are provided in Table 1. The initial focus of the phase behavior experiments was to identify surfactant formulation with quick equilibration times, low viscosities, and high solubilization.

SOIL COLUMN TEST RESULTS

The primary goal of the soil column experiments was to evaluate the ability of Alfoterra 145-4PO Sulfate™ to effectively remediate DNAPL-contaminated aquifer sediments from Site 88 while avoiding effects such as a reduction in the permeability due to sorption and plugging. From these experiments, the required concentration of calcium to mitigate ion exchange and prevent fines migration (and therefore loss of permeability in the clay-rich aquifer material near the bottom of the aquifer) was determined. Three surfactant flooding column tests were performed using the aquifer sediments from Site 88. The water used in the column tests was similar in ionic composition to the potable water available at Site 88 and the experiments were performed at a temperature of 25^{o}C, which is close to the average groundwater temperature at Site 88. Table 2 shows some key results from the soil column tests.

Table 2. Soil Column Study Results (Ooi, 1998)

Surfactant Solution (4 wt% Alfoterra 145-4PO Sulfate^{TM} and 16% IPA)	Viscosity (cp)	pH	PCE Solubilization (mg/L)	Pore Volumes of Surfactant Injected
0.4 wt% NaCl, 0.1 wt% $CaCl_2$ (Winsor Type I)	2.2	6.75	308,000	3.5
0.5 wt% NaCl, 0.1 wt% $CaCl_2$ (Winsor Type I)	2.4	8.45	490,000	4.0
0.2 wt% $CaCl_2$ (Winsor Type III)	2.4	8.3	490,000	3.6

SEAR PERFORMANCE

Using the selected surfactant, a total of 76 gallons of PCE was recovered from the high permeability zone of the aquifer during the demonstration compared to an estimated pre-SEAR DNAPL volume of 105 gallons in the entire test zone. The surfactant flood demonstration resulted in the recovery of PCE- DNAPL by enhanced solubilization and mobilization. The demonstration proved that surfactant injection can enhance the removal of DNAPL in comparison to conventional pump-and-treat technology, and that mobilized DNAPL can be effectively contained and removed for treatment above ground.

Table 1. Selected Phase Behavior Study Results (Weerasooriya et al., 2000)

Surfactant Solution	Optimal Salinity (wt%)	Solubilization Parameter (cc/cc)	PCE Solubilization (mg/L)	Viscosity at 10% DNAPL Added (cp)	Comment
4 wt% Glucopon 635FE/Aerosol MA-80 (90:10), 8 wt% IPA, 0.5 wt% $CaCl_2$	0.44 % $CaCl_2$	8.62	780,000	7.0	Good solubilization, but high viscosity
8 wt% Aerosol MA80/OT (65:35), 8 wt% IPA, 0.1% $CaCl_2$	1.22 % NaCl	3.31	790,000	2.6	Good solubilization, requires 8% IPA
4 wt% Alfoterra 145-4PO Sulfate^{TM}, 16 wt% IPA, 0.2 wt% $CaCl_2$	0.09 % NaCl	7.7	860,000	2.5	Good solubilization, low cmc, requires 16 wt% IPA

4.2.8 Amenability to Recycling. Recycling and reuse of surfactant can potentially lower chemical costs. The ability to recover surfactant from the effluent is a function of both the size of the individual surfactant molecules and the micelle formation behavior. A candidate surfactant molecule should be both large enough and form a sufficiently large micelle to allow for efficient filtration and recycling, i.e., high water removal with minimum surfactant loss through the filter membrane. Surfactant recycling is also promoted by a low CMC as it allows self-aggregation of surfactant molecules into micelles, which are larger and can be more easily filtered. Section 6.3.3 covers the issue of surfactant recycling in more detail.

4.3 Surfactant-Phase Behavior Studies

Phase behavior experiments quantify the behavior of DNAPL-surfactant solution mixtures and are essential for screening and selecting surfactants for SEAR. These experiments are described in detail in the literature (Baran et al., 1994a, b, c and 1996a, b, c; Dwarakanath et al., 1999). A detailed description of experimental procedures is beyond the scope of this section, but general guidelines are provided for interpreting the results of phase behavior experiments.

4.3.1 Surfactant Screening & Selection

Prior to conducting detailed phase behavior experiments on a particular surfactant, the following surfactant properties are generally evaluated:

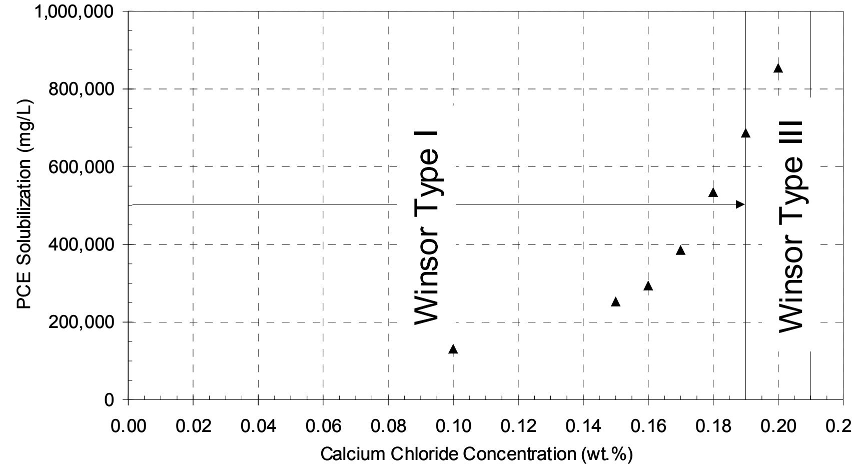
- ❑ Propensity to form liquid crystals, gels, or macroemulsions,
- ❑ Coalescence/equilibration time, and
- ❑ Equilibrium contaminant solubilization.

The general procedure for phase behavior experiments can still be followed. For ease of measurement, equal volumes of DNAPL and surfactant solution are mixed together. Anionic surfactant solutions may include electrolyte as a component, as contaminant solubilization is often sensitive to electrolyte concentration. The surfactant solution-DNAPL mixtures are visually observed to note the formation of liquid crystals, gels or macroemulsions. Surfactants that form viscous precipitates or are slow to equilibrate to microemulsions are rejected or amended by adding a cosolvent or cosurfactant to improve aqueous-phase stability. Crude estimates of equilibrium contaminant solubilization can be obtained by noting the total change in DNAPL volume so long as measures have been taken to prevent volatilization or other contaminant loss from the surfactant. Surfactants which show promise during screening batch studies (i.e., rapid coalescence, little to no gel formation, and relatively high solubilization) within an acceptable range of salinity and cosolvent/cosurfactant concentrations can be tested further for optimizing solubilization, IFT, and viscosity.

4.3.2 Surfactant Optimization

Optimizing the surfactant properties of anionic surfactants involves varying the electrolyte concentration while the surfactant and cosolvent or cosurfactant (if either are used) concentrations are held constant. This assists in selecting the preferred electrolyte range for formulating the surfactant solution. The relative volume fraction of the DNAPL, aqueous, and microemulsion phases are measured and plotted as a function of electrolyte concentration. The volume fraction or phase behavior diagram will show the transition in surfactant behavior from Winsor Type I to Winsor Type III to Winsor Type II behavior as additional electrolyte is added to the surfactant solution. A phase behavior diagram for Alfoterra 145-4PO Sulfate™ surfactant with 16 wt% IPA is shown in Figure 4-4. Under 0.19 wt% $CaCl_2$, the microemulsion and DNAPL phases coexist, implying Winsor Type I behavior. Above 0.21 wt% $CaCl_2$, water precipitates out of the surfactant solution and an oily-phase microemulsion exists, representing Winsor Type II behavior. At these higher electrolyte concentrations, an inversion of surfactant properties occurs, resulting in surfactant loss into DNAPL. Between 0.19 wt% and 0.21 wt% $CaCl_2$, DNAPL, aqueous and microemulsion phases coexist, implying Winsor Type III behavior. The desirable operating range are the electrolyte concentrations that correspond to either Winsor Type I or Winsor Type III behavior, depending on the integrity of the capillary barrier underlying the DNAPL contamination and the hydraulic gradients available for recovering the DNAPL-laden surfactant solution.

Simultaneous with volume fraction measurements, the equilibrated microemulsion can be analyzed using a gas chromatograph (GC) to obtain a precise measurement of the concentrations of solubilized contaminant and cosolvent. In Figure 4-5, which is comparable to the volume fraction phase behavior diagram, contaminant solubilization data is plotted against the salinity. The solubilization of PCE is observed to increase from approximately 130,000 mg/L at 0.10 wt% $CaCl_2$ to approximately 530,000 mg/L at 0.18 wt% $CaCl_2$. The IFT between the DNAPL and the microemulsion is sometimes measured to determine the extent of IFT reduction. Usually it is estimated using correlations such as the Chun-Huh (1979) relationship. Conversely, the allowable IFT for the site conditions can be specified to determine the appropriate contamination solubilization and hence the required electrolyte concentration.



Note: PCE Solubilization by 4% by Weight Alfoterra 145-4PO Sulfate™, 16% by Weight IPA, PCE, and Calcium Chloride at 25° C

Figure 4-5. Effect of Salinity on Contaminant Solubilization

The final step is viscosity optimization. Viscous surfactant solutions are difficult to move through shallow aquifers, as doing so requires high-induced gradients and will result in unacceptably slow flowrates and long remediation times. As a rule of thumb, an aqueous surfactant viscosity of less than 10 centipoise (cp) is required for good phase behavior and ease of transport of a surfactant in the subsurface. Therefore, measuring the microemulsion viscosity and estimating the aqueous surfactant viscosity (which are not equivalent for Winsor Type III conditions) is critical during the surfactant selection process. Both are a function of the contaminant viscosity and therefore the quantity of contaminant solubilized. Viscosity is also a temperature-dependent parameter, and at low groundwater temperatures a higher viscosity is expected and should be factored into the overall surfactant selection process.

Adding a cosolvent, such as IPA, can significantly reduce the viscosity of the surfactant microemulsion. For example, in one study, a surfactant microemulsion showed a 56% reduction in viscosity with an increase in the IPA concentration from 4.5% to 8% by weight. The concentration of cosolvent should be optimized such that both the quantity of cosolvent and the viscosity of the microemulsion are minimized. The addition of cosolvent will affect the phase behavior of the surfactant, e.g., parameters such as the extent of contaminant solubilization and the optimum salinity. If cosolvent is to be used in the surfactant formulation, the phase behavior experiments conducted must include cosolvent.

4.4 Soil Column Studies

After surfactants have been optimized for the site DNAPL, soil column studies are initiated to further refine the surfactant formulation with contaminated site soils. Surfactant performance in situ is strongly influenced by soil permeability and mineral content, so successful design of a surfactant flood relies upon column tests, which are carried out under conditions as similar as possible to those encountered in the field. These conditions include using site DNAPL, soil, and groundwater, and performing the tests at a temperature and pH that are representative of subsurface conditions. The primary purpose of soil column experiments is to determine whether injecting the surfactant formulation will cause any pore plugging due to adverse interactions between the surfactant, DNAPL, and the aquifer soils, such as clay mobilization, surfactant adsorption, or the formation of liquid crystal, gel, or macroemulsion phases. Soil column experiments are also useful for determining whether any DNAPL is mobilized by the surfactant solution. Details on soil column experimental procedures and methods are provided in Appendix D and are discussed further in Dwarakanath et al. (1999). The following sections include a discussion of how to interpret the results of surfactant column measurements.

4.4.1 Solubilization and Mobilization Performance. Figure 4-6 shows effluent sampling results from both a mobilization and a solubilization surfactant flood in a laboratory soil column. The soil column test results provide the following information:

- ❑ Surfactant requirement,
- ❑ DNAPL mass recovered,
- ❑ Mass transfer characteristics between surfactant micelles and residual DNAPL, and
- ❑ Final contaminant concentration as a result of surfactant flooding.

As shown in Figure 4-6, for the mobilization experiment, high contaminant concentrations on the order of 700,000 mg/L are observed during the first pore volume of the surfactant flood followed by a rapid decline to less than 100 mg/L after 2 pore volumes. On the other hand, the solubilization experiment exhibits a steady plateau of the effluent contaminant concentration for 7 pore volumes followed by a decline to low concentrations. A decline in the contaminant concentration below 100 mg/L is observed after 10 pore volumes. Only 1 pore volume of surfactant was used for the mobilization experiment, while 11.9 pore volumes were used for the solubilization experiment. In general, mobilization will require much fewer pore volumes of surfactant solution compared to solubilization methods. During mobilization, more than 80% of the contaminant is can be recovered as free phase DNAPL followed by a rapid decline to low concentrations of contaminant in the effluent. It should be noted, however, that the experiment results shown in Figure 4-6 were accomplished using soils with18-20% DNAPL saturation whereas at typical field sites, the average DNAPL saturation is less than 3%. At lower, more typical saturations, the difference in surfactant requirement to achieve target DNAPL removals by mobilization compared to solubilization is usually not so pronounced. Finally, much greater hydraulic gradients are achievable in the laboratory than in the field, and it should be remembered that mobilization of a bank of DNAPL is limited by sustainable field hydraulic gradients being sufficient to recover remediation fluids.

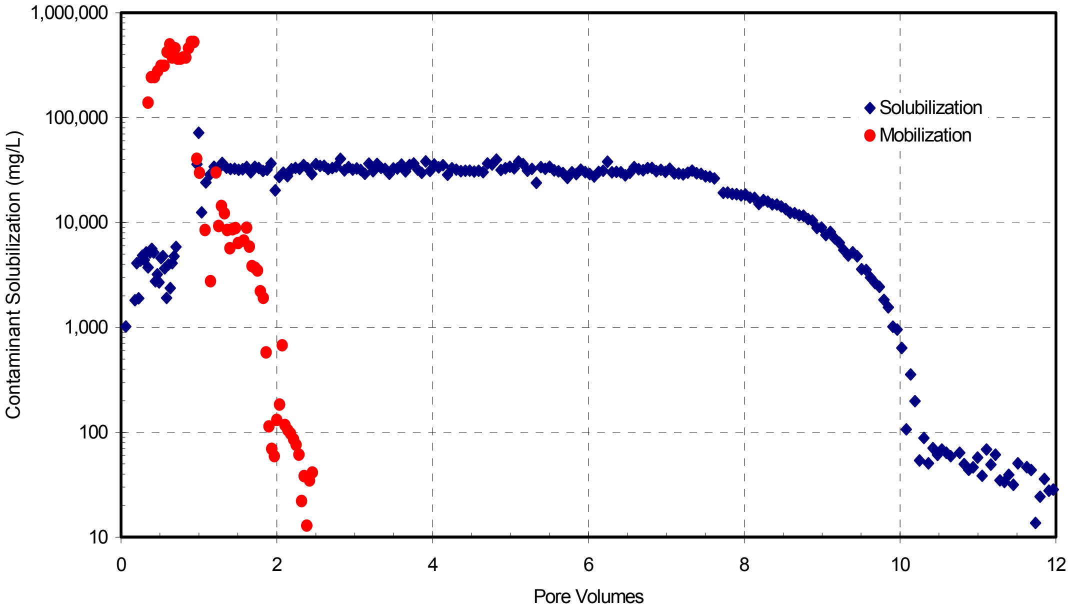


Figure 4-6. Soil Column Comparison of Solubilization and Mobilization Remediation Approaches

4.4.2 Cation Exchange and Mobilization of Fines. Measuring cation exchange is essential as anionic surfactants are strongly affected by the release of calcium ions from clay minerals as a result of ion exchange with the electrolyte in the surfactant formulation. If a sodium-ion-rich surfactant is injected into a clay-rich aquifer, the monovalent sodium ions replace the divalent calcium ions in the clays. This replacement causes mobilization of soil fines and pore plugging, reducing aquifer permeability. Furthermore, salinity conditions may be altered by this cation exchange process such that the surfactant exhibits Winsor Type II phase behavior, which is unfavorable for DNAPL recovery. This effect can be mitigated by using calcium ions instead of sodium ions for the electrolyte, which minimizes ion exchange and other effects associated with the release of calcium from the aquifer clays. For example, preliminary soil column experiments with aquifer material from MCB Camp Lejeune (DE&S, 2000) indicated that a significant increase in the production of fines and a concomitant decrease in the soil permeability (Ooi, 1998; DE&S, 2000) would occur when the soil was flooded with fresh water containing less than 150 mg/L of both sodium and calcium. Furthermore, the soil column experiments also indicated that NaCl could not be used in the surfactant formulation to enhance PCE solubility. Therefore the surfactant composition was altered to use $CaCl_2$ as the sole electrolyte. All solutions used to flood the soil column required at least 1,000 mg/L $CaCl_2$ to control the production of fines. The same quantities of $CaCl_2$ were used in the field demonstration for all source water injection.

4.4.3 Sorption. Sorption of the surfactant to the soil matrix can reduce the amount of surfactant delivered to the target treatment area. Anionic surfactants such as the sulfates, sulfonates and sulfosuccinates are preferred since they typically have lower adsorption than nonionic surfactants. Batch surfactant sorption tests with site soils can be used as a preliminary step in determining the amount of surfactant that will be lost to the soil matrix. These may be followed by soil column experiments to examine surfactant losses under dynamic conditions. The magnitude of sorption can be measured during the soil column experiment by calculating a retardation factor for the transport of the surfactant with respect to a conservative tracer. The surfactant effluent concentration data, along with the tracer test data, can be used to calculate a distribution coefficient (K_d). Surfactants with low values of sorption (e.g., K_d <0.3 mg/kg) are preferred for SEAR. More information on sorption studies is included in Appendix D.

Section 5.0: NUMERICAL MODELING FOR SEAR SYSTEM DESIGN AND OPTIMIZATION

The remedial action objective for a SEAR system should be to maximize DNAPL recovery, at minimal cost, while maintaining control over the movement of injected chemicals and DNAPL. With accurate site characterization, a SEAR system can be designed that ensures an efficient sweep of the contaminated subsurface zones, hydraulic control of the injected chemicals and contaminant in the target zone, and optimized pumping rates to minimize the project duration. In order to develop an optimal design that meets the above objective, the SEAR design process often involves design simulations to understand the dynamics of the surfactant flooding process under the anticipated hydrogeologic conditions at the site. The purpose of this section is to present the basic design parameters for SEAR, and to discuss the use of design simulations for SEAR system design and optimization.

5.1 Design Parameters

The successful implementation of SEAR requires that several key design parameters be fulfilled. These include the following elements of the SEAR system design which are typically optimized using numerical models:

- ☐ Target injection and extraction flowrates to achieve adequate hydraulic control,
- ☐ Effect of heterogeneities on recovery of the DNAPL and surfactant solution,
- ☐ Mass of surfactant required to solubilize and/or mobilize the DNAPL, and
- ☐ Duration of the surfactant and postsurfactant water flood.

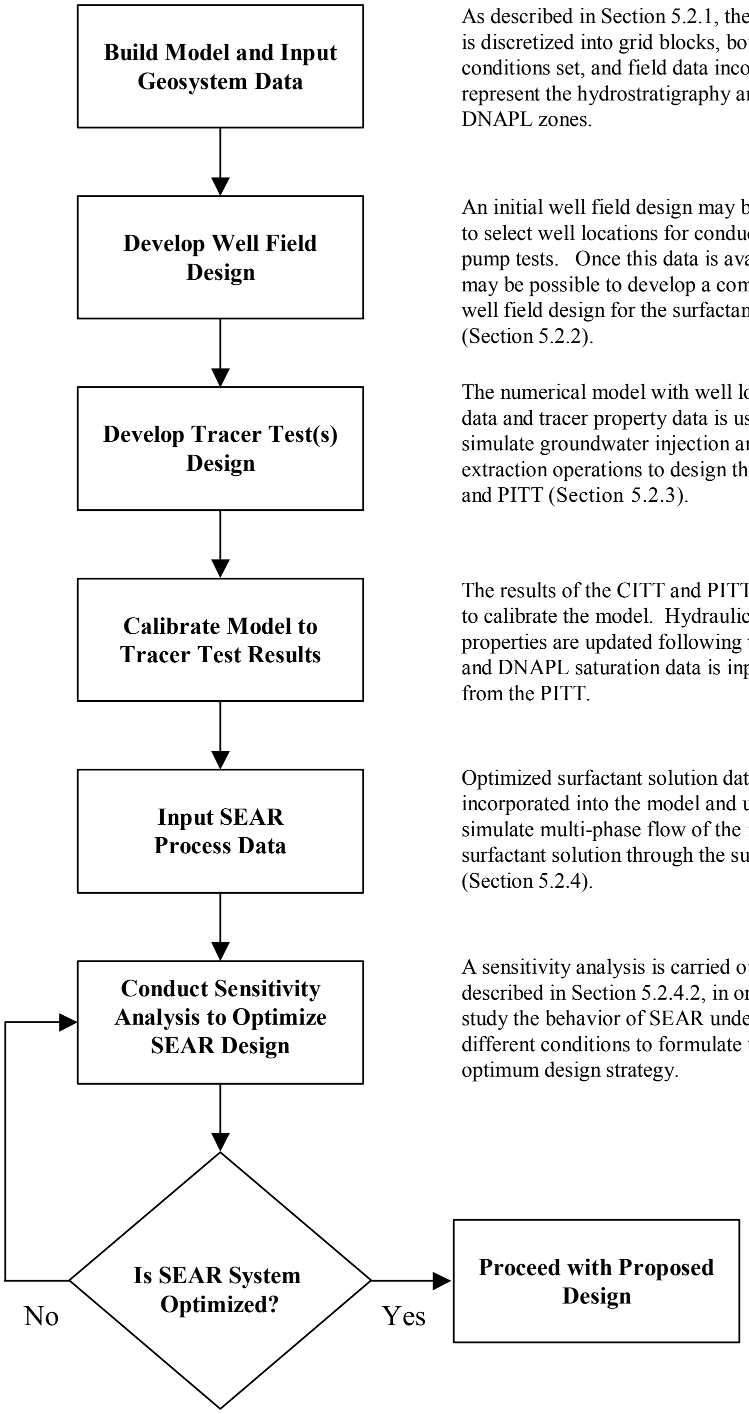
The phases of SEAR design and associated key design criteria are summarized in Table 5-1. As can be seen, it incorporates many of the design concepts introduced in earlier chapters. The first phase of SEAR design is source zone characterization. Data collected on the site geology/ hydrogeology and groundwater, soil, and DNAPL characteristics during source zone characterization is used to determine the applicability of SEAR for DNAPL removal at a given site and to make design decisions such as the preferred type of SEAR implementation (i.e., DNAPL mobilization or solubilization and whether mobility control is necessary). This will influence the selection of an appropriate surfactant formulation, which is the objective of the next phase of SEAR design. Surfactant testing is performed in the laboratory using site soils and DNAPL (if available). The surfactants selected should meet the criteria outlined in Section 4.0. Finally, site investigation data and surfactant property data are used to construct a numerical model to simulate surfactant injection and extraction in the contaminated subsurface.

5.2 Modeling Design Approach

Optimum design of the SEAR system typically involves iterative use of a numerical model containing geosystem data. The numerical model is used to design the wellfield, to design tracer tests that amplify and refine the geosystem data, and finally to select the key design parameters for surfactant remediation. Numerical models provide a tool for understanding how variations in subsurface properties can affect a SEAR design on the field scale. Modeling results can be used to make the design more robust with respect to potential performance variations caused by uncertainties in site characterization. A general flowchart illustrating the SEAR system design approach is shown in Figure 5-1. The steps involved are described in the subsections that follow.

Table 5-1. Key Design Criteria for SEAR

Design Phase	Key Design Questions	Section
I. DNAPL Source Zone Characterization	- Is there DNAPL at the site?	3.2.1
	- Where is the DNAPL located, and what is its approximate volume and extent?	3.2.2, 3.2.3, 3.3.4
	- Is the hydraulic conductivity (K) of the aquifer sufficient for the depth of the aquifer and saturated thickness?	2.2.1, 2.2.2, 3.3.2, 3.3.3
	- Is the aquifer a layered system with a high-permeability contrast between various layers?	3.2.2
	- Is there a good capillary barrier to downward DNAPL migration at the site?	3.2.5
II. Surfactant Selection	At groundwater temperature and pH:	
	- Does the surfactant have acceptable characteristics to inject into the aquifer?	4.2
	- Are the surfactant characteristics acceptable for performing enhanced solubilization (Winsor Type I) or mobilization (Winsor Type III), depending on remedial objectives?	4.1
	- Does the surfactant-electrolyte-DNAPL system reach equilibrium rapidly (with a stable surfactant phase forming within several hours to 24 hours depending on the anticipated residence time in the aquifer)?	4.3
	- Is the required surfactant, cosolvent concentration economically acceptable?	2.4
	- If surfactant regeneration is desired, does the surfactant have the necessary characteristics for filtration?	4.2.8
	- Do soil column test results confirm that surfactants are as effective in removing DNAPL from site soils as predicted from phase behavior testing?	4.4
	- Is there any pressure increase observed during soil column testing (i.e., surfactant sorption and/or pore plugging)?	4.4
	- Is the salinity of the system acceptable to the aquifer?	4.3.2, 4.4.2
III. Numerical Simulations	- Is hydraulic control/containment being accomplished?	5.2.2.3, 5.2.3.1
	- Have subsurface heterogeneities (i.e., variations in aquifer conductivity and DNAPL distribution) been taken into account?	5.2.3
	- How many pore volumes of surfactant solution are required to remove the desired quantity of DNAPL?	5.2.4
	- Is the duration of water flooding sufficient to accomplish acceptable recovery of injected surfactants and cosolvent (as determined by regulatory requirements)?	5.2.4



As described in Section 5.2.1, the study area is discretized into grid blocks, boundary conditions set, and field data incorporated to represent the hydrostratigraphy and the DNAPL zones.

An initial well field design may be conducted to select well locations for conducting slug or pump tests. Once this data is available, it may be possible to develop a comprehensive well field design for the surfactant flood (Section 5.2.2).

The numerical model with well location data and tracer property data is used to simulate groundwater injection and extraction operations to design the CITT and PITT (Section 5.2.3).

The results of the CITT and PITT are used to calibrate the model. Hydraulic properties are updated following the CITT and DNAPL saturation data is inputted from the PITT.

Optimized surfactant solution data is incorporated into the model and used to simulate multi-phase flow of the injected surfactant solution through the subsurface (Section 5.2.4).

A sensitivity analysis is carried out, as described in Section 5.2.4.2, in order to study the behavior of SEAR under different conditions to formulate the optimum design strategy.

Figure 5-1. General SEAR Design Optimization Process

5.2.1 Numerical Model Development. An appropriate flow and transport model must be selected in order to characterize the physical system, build the geosystem model based upon field data, and eventually to simulate multiphase flow of surfactants in the subsurface. Numerical models are powerful tools to optimize the preliminary well field design, to compensate for site conditions and uncertainties in site characterization, and to explore the effect of variations in subsurface properties on SEAR performance. Heterogeneities in permeability and DNAPL distribution, which cannot always be precisely characterized, can reduce the effectiveness of a SEAR design. Furthermore, surfactant performance is sensitive to the chemical composition of the subsurface. Thus, the primary objective of SEAR multiphase flow modeling is to optimize the SEAR design by assessing the performance of the proposed preliminary design and by exploring alternative scenarios and approaches to improve implementation at the field scale. The modeling results are used to establish the operating parameters for the SEAR test, demonstrate to regulators that hydraulic capture can be accomplished, and predict the concentrations of contaminant and injected chemicals in the extracted groundwater.

The numerical model must simulate the advection, dispersion, and transformation of the different species (contaminant, surfactant, water, electrolytes, and cosolvent) in the aquifer under various pumping and injection strategies. A sophisticated flow and transport model such as the University of Texas chemical flooding simulator (UTCHEM) is required to model the multiphase flow problems presented when surfactants are a component of the groundwater. However, a basic groundwater flow model, such as MODFLOW, can be used in a limited capacity to represent the geosystem to assist in preliminary well field design that includes the selection of the well pattern, well spacing and flowrates. The required hydraulic gradients to capture the DNAPL fluids, also known as hydraulic control, must be satisfied. MODFLOW is an efficient and user-friendly pseudo three-dimensional groundwater flow model, and has the advantage of simplicity and short simulation run times when used to simulate system hydraulics. It may be used to design a conservative tracer test; however, a non-conservative or partitioning tracer test requires a three-dimensional (3-D) transport model. Model parameters, such as gridblock construction and geosystem data with scaling to less than 1 foot for zones with transitional properties, will eventually need to be transferred to more sophisticated simulators with the capability of modeling processes important to SEAR. Therefore, if a pre and post SEAR PITT are planned, it may be easier to use UTCHEM to design the first PITT.

UTCHEM is a multiphase, multicomponent three-dimensional modeling program capable of simulating DNAPL migration and groundwater flow and transport in aquifers. Use of this simulator allows the study of phenomena critical to the design of SEAR systems as follows:

- Solubilization,
- Free-phase mobilization,
- Organic and surfactant adsorption,
- IFT reduction,
- Capillary desaturation,
- Dispersion/diffusion, and
- Phase behavior of groundwater, surfactant solution, and DNAPL mixtures.

Detailed explanations on the full range of UTCHEM capabilities can be found in *Three Dimensional NAPL Fate and Transport Model* (U.S. EPA, 1999a). The EPA recognizes UTCHEM as an approved numerical simulator to model DNAPL problems. Several 1-D and 2-D numerical models have been developed for modeling surfactant solubilization (Rathfelder et al., 1998; Adeel et al., 1995; Grimberg et al., 1996; and Ji and Brusseau, 1998); however, because these are not 3-D models, they are generally more applicable to bench-scale testing rather than to the implementation of SEAR in the field. UTCHEM is discussed further in Section 5.2.4.

5.2.2 Well Field Design.

The initial design of the well field will be based on the conceptual geosystem model that identifies the depths of the contaminated zone(s) and predicts the extent of DNAPL contamination. This may be modified as additional site data becomes available to identify the actual boundaries of source zone contamination and to quantify the permeabilities of the contaminated depths. A comprehensive well field design will select the number of injection, extraction, and hydraulic control wells, the well spacing and geometry, and screen depth(s) and interval(s). The well placement within the DNAPL source zone will also be selected to account for the desired sweep efficiency, hydraulic control requirements of the system, and objectives of the SEAR remediation. For most SEAR applications, a field of drilled vertical wells will be needed to inject and extract fluids. The SEAR well field design is critical because once the wells are installed, the use of SEAR is hydraulically constrained to the volume of aquifer that can be swept using those wells. A favorable well configuration must be designed to ensure efficient and cost-effective remediation of the DNAPL source zone. The numerical simulations will allow a determination of the minimum number of injection/extraction wells required and the best possible well pattern and spacing. Limiting the number of injection/extraction wells installed to the minimum number required eliminates unnecessary well installation, equipment, and monitoring costs. The well field design also should be consistent with constraints such as safety, time, cost, regulations, and other site factors.

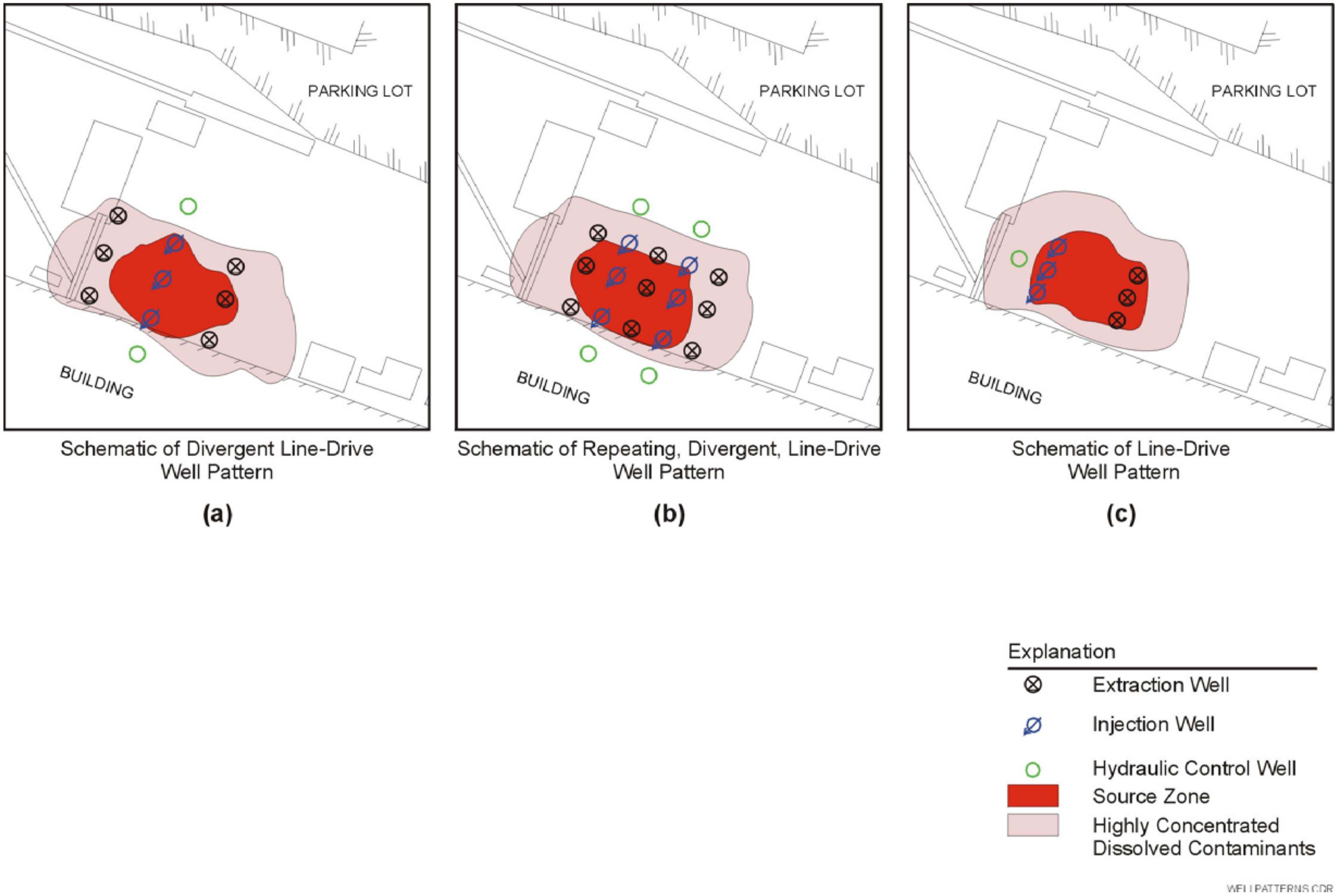
5.2.2.1 Well Spacing and Geometry. The selection of well spacing and geometry (i.e., the pattern of injection, extraction and hydraulic control wells) is an important step in SEAR design. The adverse effect of factors such as the natural hydraulic gradient and aquifer heterogeneity typically can be offset by the selection of a robust well pattern. The primary consideration in the selection of well spacing configurations is to ensure that injected fluids and DNAPL are captured at one or more extraction wells. One well pattern that has been very effective for SEAR is a divergent line-drive well pattern as shown in Figure 5-2(a). With this configuration, the aquifer pore volume within the well pattern can be adjusted by changing the distance between the rows of the wells and the distance between the wells. The swept volume can also be adjusted by the number of wells used in a row and number of rows as shown in Figure 5-2(b). This well pattern can be used as a repeating pattern to treat a larger source zone. The main advantages of the divergent line-drive well pattern are as follows:

- ☐ It maximizes the hydraulic containment of both the injected fluids and the solubilized or mobilized contaminants,
- ☐ It reduces the time required to sweep the same amount of aquifer pore space and therefore increases the efficiency and effectiveness of the flood,
- ☐ It minimizes the dilution of the injectate inside the well pattern, and
- ☐ It minimizes any potential stagnant flow zone between the wells.

Other well patterns such as the three-well line drive as shown in Figure 5-2(c) have also been successful in the past for SEAR demonstrations.

5.2.2.2 Sweep Efficiency. The term sweep efficiency refers to the extent to which the surfactant flood contacts all zones in a pore space. The sweep efficiency of the preliminary well field design will be evaluated and optimized during multiphase flow numerical simulations. While it is desirable to attain 100% sweep efficiency, this is not usually achieved under field situations due to aquifer heterogeneity.

The primary factors controlling sweep efficiency are the location of the injection and extraction wells and the permeability variation or heterogeneity of the aquifer hydrostratigraphic units. For sites with significant heterogeneity, the sweep efficiency can be enhanced by the addition of a viscous polymer



Schematic of Divergent Line-Drive Well Pattern

(a)

Schematic of Repeating, Divergent, Line-Drive Well Pattern

(b)

Schematic of Line-Drive Well Pattern

(c)

Figure 5-2. Well Field Configuration Patterns such as xantham gum. In addition to poor sweep efficiency caused by preferential flow through the more permeable zones, small-scale channeling may be induced by fluid instabilities (Lake, 1989). These phenomena are usually induced when fluids of higher viscosity are displaced by less viscous fluids (for example, a water flood to displace a viscous coal tar). The addition of a viscous polymer can be employed to overcome this channeling issue.

5.2.2.3 Hydraulic Control. Hydraulic control must be achieved to minimize the risk of surfactant or DNAPL escaping the capture zone, as well as to deliver surfactant fluids to the appropriate DNAPL contaminated zones. Insufficient hydraulic control can cause unintended migration of the contaminant and increase the amount of chemicals required to achieve adequate cleanup levels. The SEAR well design should evaluate the number and placement of hydraulic control wells and the ratio of extraction to injection rates needed to provide adequate hydraulic control at the site. Slight overextraction is generally required to control the movement of the higher viscosity surfactant fluids. Numerical simulations will determine the minimum number of hydraulic control wells required, the optimal locations, and the target flowrates for all wells.

Hydraulic control wells are essentially water injection wells. A dual injection system (i.e., injection wells installed with two or more screened intervals at different depths) can be used at sites where hydraulic control is needed in the vertical direction. The use of hydraulic control to contain injected fluids without any other physical control has been successfully demonstrated in numerous PITTs and surfactant floods (INTERA, 1997b, 1998, 2000; DE&S et al., 1998). Incorporating a physical groundwater barrier such as a slurry wall or sheet pile to assist lateral containment of SEAR fluids has been used on some small-scale field SEAR demonstrations (ACS, 1999) in the place of hydraulic control wells. However, installing physical barriers in large-scale SEAR applications may prove to be unrealistic.

5.2.2.4 Monitoring Network Construction and Installation. The monitoring network for a SEAR system consists of groundwater monitoring wells and multilevel samplers (MLS). Groundwater monitoring wells are traditional wells with a relatively large screened interval (approximately 5 ft) in the contaminated zone of the aquifer. Multilevel sampling points are designed to collect groundwater samples from discrete intervals within the test zone. The porous devices used to collect the groundwater samples are typically a few inches in size. Wells used for sampling or monitoring do not need to be as highly efficient as the injection/extraction wells, although screen placement is still crucial to obtaining representative data for SEAR performance assessment. For wells or multilevel samplers installed within the treatment zone, numerical simulations can be used to anticipate contaminant concentrations at these locations if continual low-flow sampling devices are used.

- ☐ **Groundwater Monitoring Wells** - Existing groundwater monitoring wells should be incorporated into the monitoring network design, as appropriate. The number of monitoring wells upgradient, downgradient, within and below the treatment area will be specified by the project context and site conditions.

- ☐ **Multilevel Sampling Points** - MLS are used for collecting groundwater samples at discrete intervals and are the preferred type of installation. Sampler placement must be determined on a site-specific basis by site characterization (sampling and lithology) and aquifer permeability test data. A minimum of two samplers will be placed over the depth interval of the extraction well. The objective of the location is to be representative of the target treatment area and aquifer depths conducting contamination and to facilitate tracking of the performance of the system in situ. MLS are usually distributed within the target treatment area to collect undiluted groundwater samples for measuring the progress of the surfactant solution or tracer solution from injection to extraction point. The actual number installed is site-specific and is driven primarily by the cost of installing and monitoring additional points, the scope of the project, and regulatory requirements. Additional information is provided in the Implementation Manual.

5.2.3 Numerical Model Calibration by Tracer Testing Data.

Following development of a well field design that selects well locations and screen intervals, simulations may be conducted to design interwell tracer tests. Tracer test data is then used to calibrate the numerical model for permeability and DNAPL volume and distribution. As discussed previously, a CITT provides data on the maximum sustainable flowrates and the aquifer heterogeneities and the PITT provides data on DNAPL volume and distribution. MLS data obtained from the CITT and PITT will greatly improve understanding of vertical heterogeneities within the DNAPL-contaminated zone. The results of the CITT and PITT tests are an integral part of SEAR system design and numerical modeling plays an important role in the design and analysis of CITT and PITT data as discussed below.

5.2.3.1 Conservative Interwell Tracer Test. The sensitivity studies conducted for CITT design include varying the injection and extraction rates, permeability field characteristics, etc. The results from these sensitivity studies are then used to determine the duration of the CITT, the mass of each tracer needed, the injection and extraction rates to be used, the extraction well effluent tracer concentrations, and the amount of tracer recovered by the end of the tracer test. An optimum operational design for the CITT is arrived at iteratively by comparing the results of these sensitivity studies. A successfully designed and conducted CITT will demonstrate efficient capture of injected tracers (as predicted during the design studies) that will set the stage for regulatory approval of SEAR operations.

5.2.3.2 Partitioning Interwell Tracer Test. Once the CITT is conducted and interpreted, it may be desirable to proceed with a PITT to gain more detailed information on the DNAPL volume and distribution. Under these circumstances, the recalibrated model is used to design the PITT. Again, a number of numerical simulations will be conducted to study the behavior of different partitioning tracers and to formulate an optimum design strategy for the PITT. The results of these sensitivity studies will then be used to:

- ☐ Finalize the selection of the partitioning tracers,
- ☐ Determine the duration of the tracer test,
- ☐ Determine the mass of each tracer needed,
- ☐ Finalize the injection and extraction rates,
- ☐ Predict the swept volume,
- ☐ Predict the extraction well effluent tracer concentrations, and
- ☐ Predict the amount of tracer recovered by the end of the tracer test.

Detailed data on the vertical distribution of DNAPL obtained from a well-designed PITT implemented with MLS can be very useful for SEAR design optimization. The duration of surfactant flood operations and the mass of surfactant and other chemicals required is sensitive to variations in the DNAPL distribution and volume throughout the test zone.

5.2.4 Multiphase Flow Modeling and Dynamics with Surfactant Property Data.

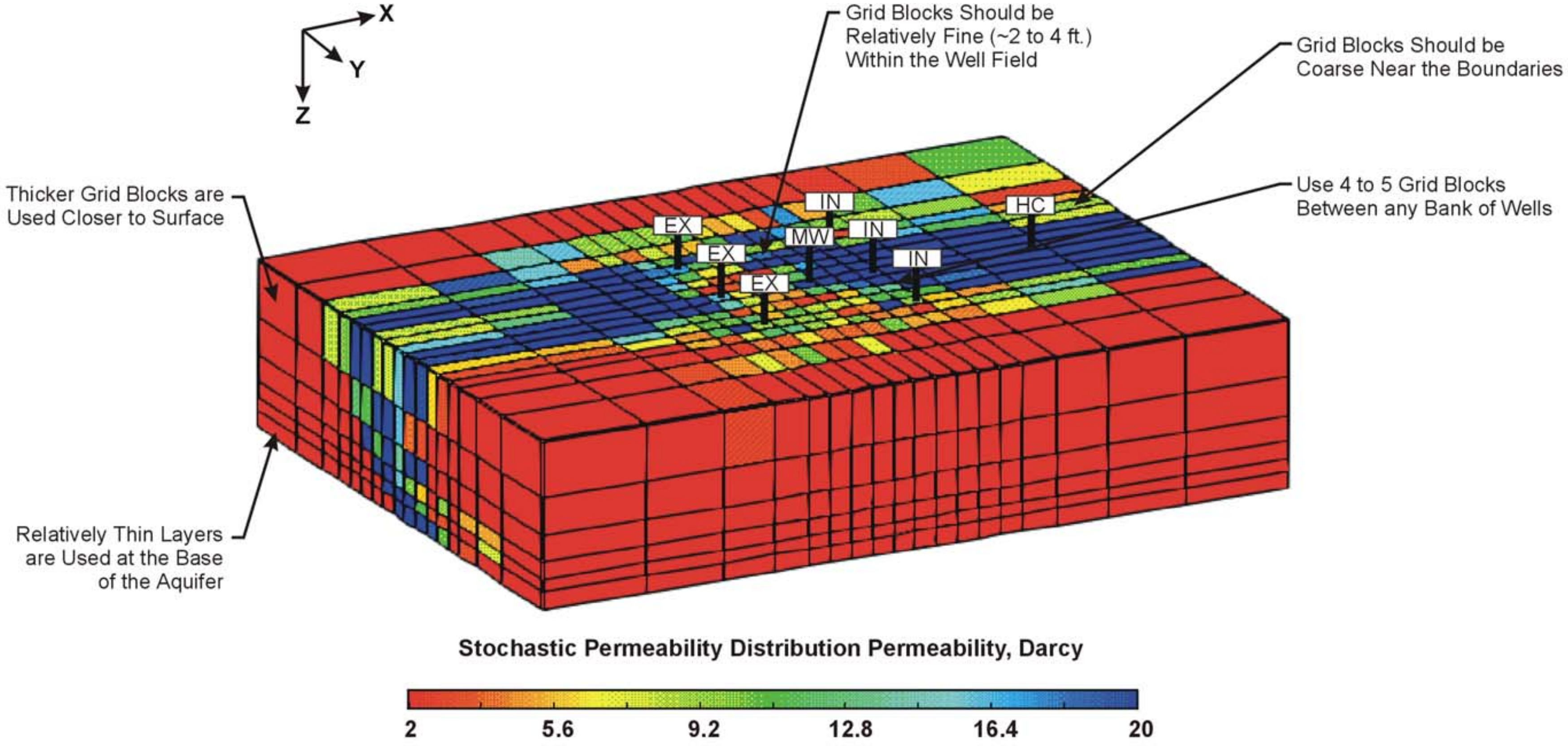
The final step of SEAR design optimization requires incorporating surfactant property data collected during surfactant selection studies into the numerical model. At this point, if UTCHEM has not been the model of choice, model parameters need to be transferred to UTCHEM. The addition of surfactant property data to UTCHEM then allows multiphase flow simulations to be conducted to study the dynamics of flooding the DNAPL-contaminated zone with a surfactant solution. Over the course of varying sensitive parameters, potential DNAPL migration issues may be detected in advance. The following sections describe the use of UTCHEM for multiphase flow modeling in more detail.

Table 5-2. Summary of UTCHEM Geosystem Input Parameters

Input Parameter	Description
Simulation grid	Includes model area and thickness, number and size of grid blocks.
Aquifer properties	Includes permeability, porosity, initial DNAPL saturation and distribution, clay aquitard elevations and properties.
Resident fluid properties	Includes density, viscosity, and composition of water and DNAPL, DNAPL/Water IFT, and effective contaminant solubility in water. Also, the initial DNAPL volume and saturation distribution.
Well field data	Includes well locations, well pumping rates, well conditions, well screening length and depth, injection compositions and times.
Boundary conditions	Includes direction and gradient for the natural groundwater flow.

5.2.4.1 UTCHEM Modeling Input. The UTCHEM model includes the following parameters for representing the geosystem: the permeability, porosity, morphology of capillary barriers, and aquifer fluid properties. Table 5-2 summarizes the geosystem model input data. These are incorporated into a grid-based numerical model, which represents the physical aquifer. The next step is integrating the surfactant properties for an understanding of the multiphase flow. The SEAR model input data fall into two major categories: geosystem model data and SEAR process data.

- ☐ **Geosystem Model Data -** The first step in UTCHEM modeling is to decide on the number of gridblocks needed to represent the geometry of the aquifer in the test area, and simultaneously, to determine which simplifications are justified. Nonuniform grid spacing is recommended to permit greater definition in some parts of the aquifer relative to other parts, and to minimize the number of gridblocks and consequently the computational time required (as shown in Figure 5-3). Figure 5-3 is an example of a 3-D grid used for the design of the surfactant test at the Hill AFB SEAR (INTERA, 1998). The gridblock takes into account external geometry including the aquifer limits and the top and bottom boundaries of the aquifer, and hydraulic gradients. The internal geometry is comprised of the horizontal and vertical extent of the individual permeability (stratigraphic) units, initial DNAPL saturation distribution, well position and screen intervals, etc. Water and DNAPL properties (i.e., density, viscosity, and water/DNAPL IFT) and their composition need to be measured during the initial fieldwork and incorporated into the model. Information should also be included on permeability and capillary properties of any underlying aquitard that might act as a capillary barrier to downward migration of DNAPL. The structure and properties of the aquitard are critical for the DNAPL problem since vertical containment below is essential for all remediation approaches. These data can be directly set up in UTCHEM or can be transferred from the 3D flow and transport models calibrated against the field data as discussed earlier.



Explanation

IN	Injection Well
EX	Extraction Well
HC	Hydraulic Control Well
MW	Monitoring Well

Note: In general finer grid spacing is used in regions where better numerical accuracy is needed.

FIGURE 5-4.CDR

Figure 5-3. Example of Gridblock and Permeability Distribution Used in a SEAR Design

- **SEAR Process Data** - Table 5-3 summarizes the SEAR process input data. The physics and chemistry of the SEAR process can be quite complicated, and simulating such processes demands that the user specify more data than are normally required for simulating groundwater flow for applications such as pump and treat. For example, the presence of surfactant and DNAPL causes multiple phases of liquid to be present, and each has its own flow properties. The viscosity and density of a given phase (properties that affect the fluid flow behavior) are functions of the composition of that phase, the temperature and occasionally the pH. Additionally, the surfactant solution has the potential to alter the permeability of the porous media not only due to contaminant solubilization, but also due to changes in the water/DNAPL IFT. To model all of these phenomena, the phase behavior, IFT, viscosity, and density must be known at conditions similar to those encountered in the field.

5.2.4.2 UTCHEM Sensitivity Analysis. The best way to understand the interaction and relative importance of various processes during SEAR is to carry out a sensitivity analysis using the UTCHEM model. This involves varying key input parameters one at a time within a realistic range and assessing the response of the model to those changes. A systematic sensitivity analysis study can aid in obtaining an optimum operational design and provide essential guidelines for SEAR field operations.

Once the SEAR simulation model is set up with the appropriate input parameters, sensitivity study simulations can begin. There are a number of variables that have a major influence on the SEAR design but their exact values are uncertain. These include uncharacterized heterogeneities in permeability and DNAPL distribution. The chief concern is that all mobilized contaminants can be retrieved at the extraction points. Results of these sensitivity studies are then used to select the surfactant injection scheme, to determine the chemical requirement, as well as to establish the injection and extraction rates for different phases of SEAR operations. A brief listing of common sensitivity variables is provided below.

- Permeability variations (Figure 5-3 depicts the use of a stochastic permeability field that accounts for horizontal and vertical heterogeneities),
- Initial DNAPL volume and saturation distribution,
- Number of pore volumes of surfactant needed and the optimum composition of the surfactant/cosolvent mixture, taking into account mixing and dilution effects,
- Concentration and pore volumes of polymer (if used) during and after surfactant injection for mobility control.

Table 5-3 Summary of UTCHEM SEAR Process Data Input Parameters

Input Parameter	Description
Phase Behavior	Phase behavior is influenced by temperature and concentrations of all the species in the system. In UTCHEM, Hand's rule (Hand, 1939) is used to estimate the solubility of the organic contaminant in the microemulsion phase as a function of surfactant, cosolvent, and electrolyte concentrations.
Cation Exchange	The ion exchange model in UTCHEM allows for calculations of ions that may be free in solution, adsorbed on the soil, and associated with surfactant. Any increased calcium concentration picked up by surfactant due to ion exchange is accounted for in the calculation of electrolyte concentration.
Interfacial Tension	IFT measurements are relatively difficult to perform; therefore, phase behavior data and a few IFT measurements are used to estimate the IFT reduction for a specific surfactant formulation using the Chun Huh relationship.
Density	Accurate modeling of microemulsion density is critical due to the risk of vertical migration of contaminant solubilized in the denser-than-water microemulsion phase in aquifers with insufficient capillary barriers such as clay or shale. UTCHEM continually calculates the microemulsion density as a function of the concentration of each component as the flood progresses.
Viscosity	The viscosity of each phase is modeled in terms of the pure water and contaminant viscosities and the phase concentration of the water, surfactant, and contaminant in each phase. The measured microemulsion viscosity is generally used to calibrate the microemulsion-phase viscosity correlation in UTCHEM.
Adsorption	Adsorption of contaminant on soil can be modeled as linear or nonlinear isotherms in UTCHEM based on the measured data from soil column testing. The level of surfactant adsorption (and polymer if used) can be inferred from the soil column experiments using the soil from the site.
Relative Permeability Curves	The relative permeabilities must be known over a range of saturations for the water, DNAPL, and microemulsion phases. The basic trends of these relative permeability data for a particular aquifer material are usually defined by laboratory tests on representative soil samples.
Capillary Pressure Curves	For a heterogeneous aquifer, a set of capillary pressure curves is required. These curves are calculated in UTCHEM based on the semiempirical, J-Leverett function, which estimates capillary pressure at a given saturation based on medium and fluid properties such as porosity, permeability, and IFT.
Trapping and Mobilization Data	The trapping parameters for water and microemulsion phases are based on the fit of the model to published data of Delshad (1990) for mixtures of petroleum sulfonate, decane, and brine in Berea sandstone. The relative permeability curves are then adjusted based on residual saturations computed from the capillary desaturation curves.
Physical Dispersion	Heterogeneity and dispersion both cause mixing in a reservoir. Both molecular diffusion and dispersivity are modeled in UTCHEM. The longitudinal dispersivities can be estimated by calibrating simulation results against the CITT field data. When a stochastic heterogeneity field is used with a fine grid, dispersion is not very important because heterogeneity dominates. When homogeneous layers and a coarse grid are used, large effective dispersivities are appropriate.

5.3 UTCHEM Modeling Results

The UTCHEM simulator provides comprehensive output information, and the computed data for many parameters can be written to the output files for every grid block and at different times during the simulation. The output data routinely examined in the SEAR simulation design study are:

- Quantity of DNAPL within the model displaced from the aquifer in the dissolved phase and as free product (i.e., free-phase DNAPL),
- Recoveries of contaminant, surfactant, and cosolvent (if used) in the dissolved phase for each extraction well,
- Recovery of contaminant as a free product for each extraction well,
- The pressure/water level at the injection and extraction wells,
- The saturated volume of the DNAPL in the target treatment area both at the beginning and end of the demonstration for performance assessment,
- 2-D images of total concentrations of contaminant and surfactant, saturation of DNAPL and microemulsion phases, and pressure at selected times during the simulation,
- Total effluent concentrations of contaminant, surfactant, cosolvent (if any), and calcium as a function of time for each extraction well.

There are two Graphical User Interfaces (GUI) available to postprocess the UTCHEM output. The utility called UTHIST converts the well history output files to a column format to be processed and viewed in Microsoft Excel. The utility called UTSURF generates 2-D maps of pressure, saturation, and species concentrations along with the simulation grid and well locations using Golden Software Surfer. These utilities are written in Visual Basic and they can only be run on Windows (NT, 95 or higher).

The graphical displays of pressure, concentration, and saturation contours at different depths give valuable insights into the simulation results of the SEAR design. For example, the extent of the injectate concentration at selected times gives a qualitative measure of the sweep efficiency and hydraulic control with depth. Effluent concentration curves can be valuable in determining the residence time of injected fluids, as well as time to peak breakthrough of injected chemicals and contaminants. The latter can be predictive value for effluent treatment operations. A case study of the SEAR numerical simulation modeling follows.

NUMERICAL SIMULATIONS FOR SEAR DESIGN CASE STUDY

Use of UTCHEM at Site 88, MCB Camp Lejeune, North Carolina

SITE BACKGROUND

A SEAR demonstration project was conducted in 1999 at the location of a dry-cleaning facility at MCB Camp Lejeune in North Carolina (see Figure 1). The site was contaminated with immiscible-phase PCE and Varsol^{TM} present beneath the facility in a shallow aquifer at a depth of approximately 16 to 20 ft bgs. Varsol, an LNAPL, was not targeted for remediation, but was present as a minor of component of the PCE DNAPL and was removed incidentally with the PCE DNAPL. Much of the DNAPL was present in a low permeability silty layer at the base of the aquifer. The University of Texas Austin used UTCHEM to conduct numerical simulations to optimize the SEAR system design and operational parameters.

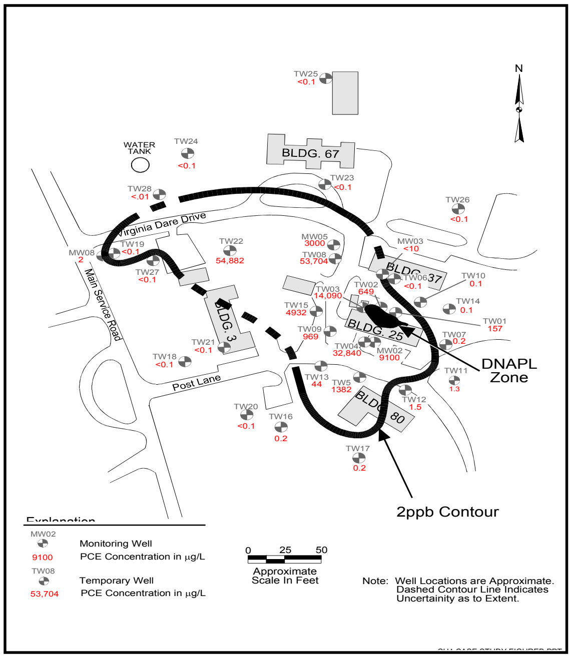


Figure 1. MCB Camp LeJeune Site Map

MODEL DEVELOPMENT

Figure 2 shows a plan view of the 3-D grid used in UTCHEM to design the Site 88 surfactant flood. Table 1 presents the grid and aquifer properties used in the UTCHEM design simulation. The horizontal extent of the model was 141 ft long by 99 ft wide with a 13-ft saturated thickness. A two-layer system for the stratigraphy of the contaminated zone was initially modeled based on soil boring data. (It was ultimately determined that a third, lower permeability layer existed that had not been adequately characterized.) The final design simulation (# ISA26m) assumed a low permeability in only the bottom two layers of the aquifer. Most of the physical properties used in the model were based on typical values for soils with similar permeability. However, these input parameters were calibrated against the field data obtained from the results of the CITT and PITT. The aquitard gridblocks were treated as a no-flow boundary and were assigned a low porosity of 0.01 and a low permeability of 10^{-5} md. No DNAPL saturation was assigned to the aquitard cells. A ratio of horizontal to vertical permeability of 0.1 was used throughout the model.

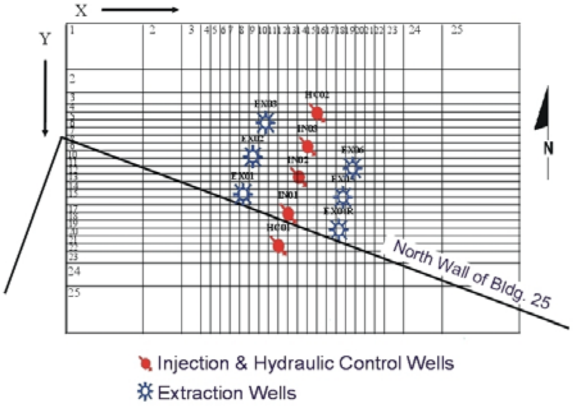


Figure 2. Aerial View of Stimulation Grid

This value gave a satisfactory match to the CITT and PITT field results. The top boundary was closed and a no-flow condition was assigned. The two outer west-east boundaries were open with a constant assigned head. The constant assigned head to each side reflected groundwater flow from east to the west with a hydraulic gradient of 0.0123 m/m, which is representative of observed field static water level conditions in the demonstration area.

Table 1. Summary of Simulation Grid and Aquifer Properties for MCB Camp LeJeune Site 88

Parameter	Simulation # ISA26m
Dimension	141 ft × 99 ft × 13 ft
Porosity	0.28
Pore Volume	33,095 ft^3 (247,567 gals)
Range of Grid Block Sizes	3 ft × 2 ft × 0.5 ft to 24 ft × 12 ft × 2 ft
Permeability Distribution	Stochastic
Permeability, md	Average of 1–14: 400 Average of 15–16: 100

WELL FIELD DESIGN

Before installing the SEAR well field, several well patterns with different numbers of wells were simulated and the most efficient well pattern was a line of three injection wells flanked on both sides by lines of three extraction wells (Figure 2). To maintain hydraulic control and to ensure adequate sweep efficiency in the well field, the model results suggested that each injection and extraction well should be spaced 10 ft apart and the distance between any pair of injection and extraction wells should be 15 ft. Two hydraulic control wells were included on each end of the line of injection wells to contain injected fluids, as shown in Figure 2. The injection wells were installed with two screened intervals, one at the bottom and one spanning the water table. The dual injection system was recommended based on the results of the field CITT results. It allowed the flowpaths of injected tracer or surfactant to be focused along the bottom portion of the aquifer where the DNAPL exists and also to minimize upward flow into uncontaminated regions of the aquifer. In addition, several scenarios were evaluated to identify the optimal number and location of hydraulic control wells.

UTCHEM SIMULATION RESULTS

The input and output from the surfactant flood simulation with UTCHEM are shown in Tables 2 and 3. Figure 3 provides a contaminant contour map of the estimated reduction in DNAPL saturations from pre- to post-SEAR conditions.

Table 2. Sample Model Input

Process	Rate (gpm)	Surfactant/IPA (wt %)	$CaCl_2$ (wt%)	Inj. Time (days)	Cum. Time (days)
Preflush	Injection (L): 0.1334 Injection (U): 0.0800 Extraction: 0.1667 Hydraulic control: 0.2000	0	0.22	6	6
Surfactant flush	Injection (L): 0.1334 Injection (U): 0.08 Extraction: 0.1667 Hydraulic control: 0.2000	4/16	0.22	48	54
Water	Injection (L): 0.20 Injection (U): 0.08 Extraction: 0.25 Hydraulic control: 0.30	0	0.1	16	70
Final PITT	Injection (L): 0.20 Injection (U): 0.08 Extraction: 0.25 Hydraulic control: 0.30	0	0.1	42	112

L = lower screen; U = upper screen

Table 3. Sample Model Output

Extraction Well	Run ISA27	Run ISA27	Run ISA27	Run ISA27
	Cum. DNAPL (gal)	Cum. Free product (gal)	Cum. IPA (lbs)	Cum. surf. (lbs)
EX01	35.06	0.0	3,363	982
EX02	35.08	0.0	6,831	2,013
EX03	5.574	0.0	3,391	995.2
EX04	35.41	0.07	6,564	1,940
EX05	39.39	0.0	6,703	1,984
EX06	13.66	0.3022	3,635	1,071
TOTAL	164.174	0.3722	30,487	8,985.2

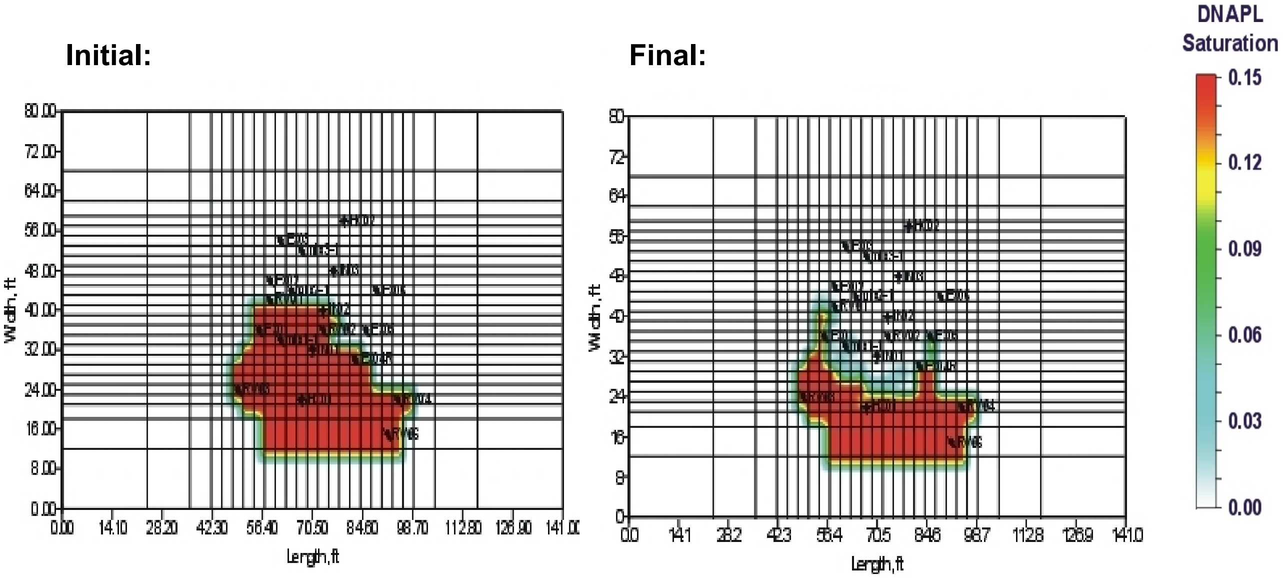


Figure 3. Model DNAPL Saturation Predictions

Section 6.0: WASTEWATER TREATMENT PROCESS SELECTION

This section provides a general discussion of effluent treatment design concepts as well as a description of the processes used to treat SEAR effluent once extracted from the subsurface. It includes a discussion of the various options available for contaminant removal, cosolvent removal, and surfactant removal or recycle and integration of these unit operations within a treatment train.

6.1 Treatment Objectives

SEAR requires the capture of injected surfactant solution fluids along with solubilized and/or mobilized DNAPL. Capture of the injected fluids and DNAPL contaminants at the extraction wells controls movement of contaminants out of the treatment zone and minimizes the amount of residue left in the subsurface. High recoveries (> 90%) of the injected chemicals is desirable.

The extracted groundwater can contain up to several weight percent surfactant and cosolvent (if used). Contaminant concentrations will vary depending on the quantity of DNAPL contamination in the treatment zone and upon the performance of the surfactant and SEAR design in the field. The presence of listed hazardous wastes (e.g., F001 and F002 halogenated solvents) or elevated concentrations of hazardous constituents can cause the extracted groundwater to be classified as RCRA hazardous waste. Off-site management of a large quantity of hazardous waste would significantly increase SEAR operating cost. Therefore, treating the extracted groundwater on site to allow discharge to a POTW or to a sewer drain typically will reduce costs. Treatment also provides the potential to recover and recycle the injected chemicals, which can further reduce costs for some sites.

The overall objectives to consider when treating groundwater extracted during a SEAR application are as follows:

- ☐ Protect human health and the environment from further contamination
- ☐ Minimize the generation of hazardous waste
- ☐ Produce a waste stream which can be readily discharged
- ☐ Provide an effective approach for recovering and recycling injected chemicals
- ☐ Be consistent with site-specific space, utility, and aesthetic constraints.

The design of the SEAR wastewater treatment system requires consideration of site-specific requirements and conditions. Federal, state, and local regulations will govern the discharge standards of the treatment system. The process flowrate will be governed by the hydraulic conductivity of the treatment zone and SEAR design. The concentrations of SEAR chemicals and contaminants in the extracted groundwater can be estimated using numerical modeling done during the SEAR design.

A SEAR wastewater treatment system designed to recycle surfactant must be able to reduce the contaminant concentrations sufficiently to allow regulatory approval for reinjecting the extracted water while retaining as much surfactant and cosolvent as possible. Regulatory requirements for contaminant removal prior to surfactant reinjection will vary from state to state. The injected constituents of the extracted groundwater will be diluted by water from the aquifer and water that was injected to maintain hydraulic control. Therefore a wastewater treatment system that includes surfactant recycle must include a process to remove the dilution water.

The constraints on disposal of wastewater from a SEAR application are as follows:

- ☐ Adequate reduction of concentrations of hazardous and toxic constituents

❑ Reduction of biological and chemical oxygen demand (BOD/COD)
❑ Prevention of formation of nuisance foam.

Discharge of the effluent from the SEAR wastewater treatment system to a POTW typically is the most cost-effective approach if the POTW has sufficient capacity to accept the volume and there is a sewer pipe near the site. Discharges to the POTW must meet the permit requirements for the POTW, which typically include limits on contaminants such as specific metals and organic compounds, total organics and total toxic organics (TTO), and BOD/COD. The chemicals summed to measure TTO are priority pollutants defined by 40 CFR 433.11 and include numerous chlorinated compounds that are common DNAPLs. Presence of the alcohols frequently used as cosolvents increases the BOD/COD so that treatment often is needed to reduce the oxygen demand of the wastewater. Surfactants in the wastewater can cause the formation of foam with air contact, which may interfere with the SEAR wastewater treatment process as well as with downstream treatment at the POTW. Therefore, SEAR wastewater treatment must provide sufficient cleanup and/or the use of antifoam agents to avoid excessive foam formation in the facility that will receive the treated discharge.

If the discharge to a POTW is not feasible, discharge to a storm drain may be a possible alternative if surfactant, cosolvent and contaminant concentrations are reduced to acceptable levels. Such a discharge would require obtaining an NPDES permit. The discharge limits needed for an NPDES permit are usually much more stringent than the permit limits for discharge to a POTW.

6.2 Removal Principles

The primary approaches for removing chemicals from the extracted water involve application of one of the three broad separation principles as follows:

❑ Physical separation
❑ Phase partitioning
❑ Degradation.

Gravitational settling and size exclusion are the main physical principles governing groundwater treatment by physical separation. Examples of applications involving gravity-based separation include decanting and flocculation and sedimentation used to separate a precipitate from the water phase. A typical application involving size exclusion-based separation is membrane filtration.

Phase partitioning removes the species of interest from the extracted groundwater by transfer into a different phase. This separate phase can be a solid, a liquid, or a gas. The transfer mechanism may consist of differing chemical and physical principles, but volatility and solubility are the leading chemical principles governing groundwater treatment phase separations. Typical applications using volatility-based separations are air stripping and steam stripping. The tendency of a contaminant to partition from the water phase into air is measured by the Henry's law constant (see Table 6-1) (with a high number indicating a strong tendency to volatilize from the dissolved phase). The presence of surfactants tends to hold contaminants in solution, which reduces the Henry's law constant as illustrated in Figure 6-1. Typical applications involving solubility-based separations are carbon adsorption and solvent extraction. The octanol-water partitioning coefficient, K_{ow} (see Table 6-1), is a common measure of the solubility in organics versus water (with a high number indicating a nonpolar material that tends to partition to the organic phase).

Table 6-1. Properties of Selected DNAPL Contaminants and Cosolvents

Compound	Formula	Henry's Law Constant (atm/mol/m^3)	Octanol/Water Partitioning Coefficient ($\log_{10} K_{ow}$)
DNAPL Contaminants			
Methylene chloride	CH_2Cl_2	2.46 E –3	1.25
Perchloroethylene	C_2Cl_4	2.69 E –2	3.40
Trichloroethylene	C_2HCl_3	1.16 E –2	2.42
1,1-Dichloroethylene	$C_2H_2Cl_2$	2.28 E –3	2.13
cis-1,2-Dichloroethylene	$C_2H_2Cl_2$	7.36 E –3	1.86
trans-1,2-Dichloroethylene	$C_2H_2Cl_2$	6.70 E –3	2.09
Vinyl chloride	C_2H_3Cl	2.24 E –2	1.62
1,1,1-Trichloroethane	$C_2H_3Cl_3$	2.17 E –2	2.49
Cosolvents			
Methanol	CH_4O	5.19 E –6	-0.77
Ethanol	C_2H_6O	8.11 E –6	-0.31
Isopropyl alcohol	C_3H_8O	1.24 E –5	0.05

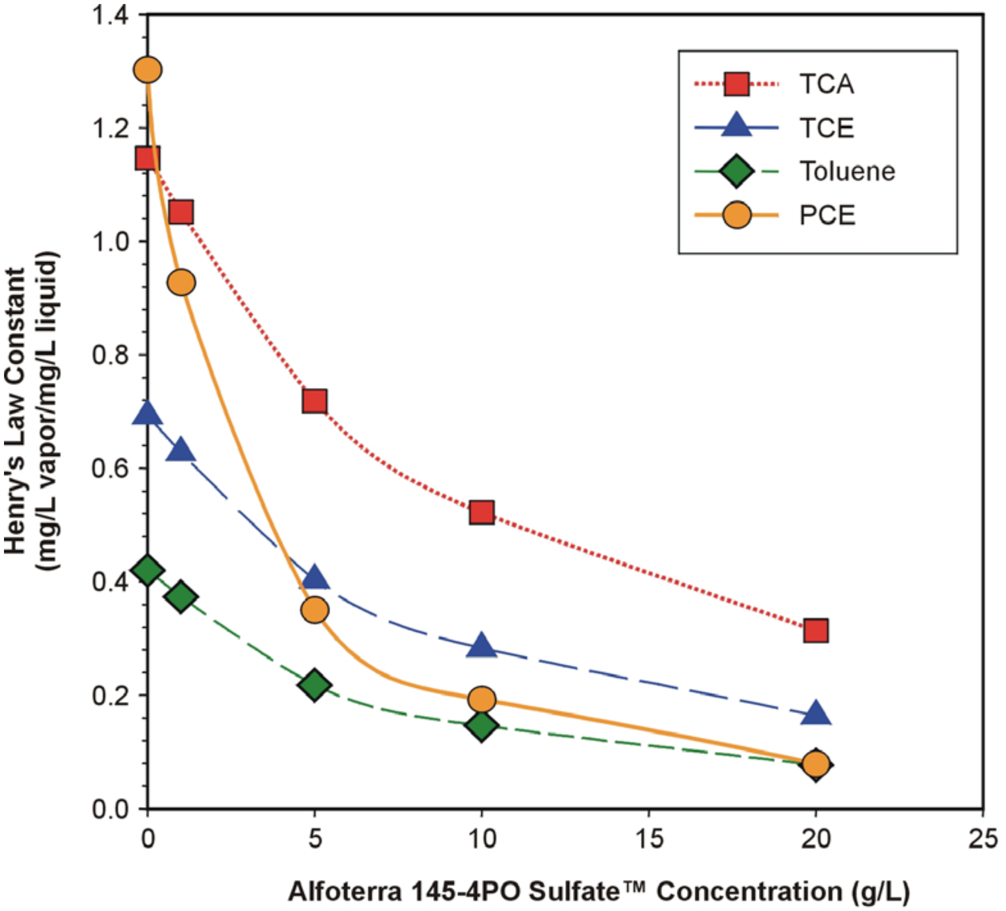
Source: Yaws, 1998.

Degradation is an attenuation process that relies on chemical, photochemical, biological, or thermal processes to destroy dissolved chemicals of concern. Due to the percent concentrations of organic chemicals present in the extracted groundwater, degradation processes are either infeasible or uneconomical unless high concentrations of contaminants are first reduced to tens of ppm levels by physical separation or phase partitioning processes. Biological degradation usually is the most cost-effective treatment method for a SEAR wastestream containing readily biodegradable surfactants. Biological degradation applications use biological organisms to consume organic chemicals as an energy and/or carbon source. Mineralization, the complete degradation of the contaminants to carbon dioxide and water, is the ideal endpoint for biodegradation processes. However, biodegradation of organic contaminants can generate by-products, which are simpler structures than the parent compound but may be more or less toxic. By-products may require further treatment or disposal considerations (e.g., vinyl chloride production from chlorinated solvent degradation or sludge disposal from biological operations).

Although chemical oxidation and chemical reduction reactions can be effective for treating dissolved-phase PCE and TCE in groundwater (Hirvonen et al., 1996; Glaze and Kang 1988; Yan and Schwartz, 1999), SEAR wastewater can be several orders of higher in organic compound concentrations. Oxidizing agents are not selective and will react with any organic matter including surfactant solution chemicals. Thus, oxidation of PCE and TCE competes with oxidation of other organics present in the wastewater, and large quantities of chemicals can be consumed to reduce the COD loading. Photochemical degradation processes are more selective but are considerably more expensive. Additionally, ultraviolet lamps are susceptible to fouling by the precipitation of divalent cations. Thermal processes are impractical for degrading organic compounds within large volumes of wastewater.

6.3 SEAR Wastewater Treatment

Contaminants, cosolvents, and surfactants have dramatically different chemical properties and behavior. Therefore, different processes often are needed to achieve treatment goals. Unit operations appropriate for treating each of these chemical classes are discussed in more detail in the following sections. These unit operations must be combined based on site-specific conditions and requirements to assemble a cost-effective integrated treatment train (see Section 6.4).



Source: Vane, 2000(a)

SURFACTANT01.CDR

Figure 6-1. Reduction of Contaminant Henry's Law Constant Due to Surfactants

6.3.1 Contaminant Removal Unit Operations. Selection of the appropriate unit operation for contaminant removal requires consideration of the contaminants present at the site and the site groundwater composition (see Table 6-2). Subsurface remediation of DNAPL-contaminated sites is most often associated with releases of volatile solvents such as chlorinated ethylenes. However, these solvents often are associated with other chemicals, such as nonvolatile greases and oils that have different properties. Inclusion of DNAPL inside stable microemulsions can increase the difficulty of removing these contaminants from the water. The extracted groundwater also contains nonaggregated surfactant and cosolvents that can hinder the separation efficiencies of processes such as activated carbon adsorption and steam stripping respectively.

6.3.1.1 Decanting. Decanting involves physical (gravity-based) separation of two immiscible liquid phases based on density differences. During the process, fine droplets of DNAPL dispersed in the continuous water phase are allowed to coalesce and separate as a second continuous phase. The decanting system is designed to enhance the rate of coalescence and provide a clean separation between the DNAPL and water phases. Decanting is an essential first step in processing groundwater that contains free-phase DNAPL.

Table 6-2. Summary of Contaminant Removal Unit Operations

Treatment System	Treatment Applications	Advantages	Limitations
Decanting	Removal of free-phase DNAPL	Mature, commercially available technology	Does not reduce dissolved contaminant concentrations
Air stripping	Removal of contaminants with high Henry's law constants and controllable foaming tendency	Mature, commercially available technology	Inefficient for contaminants with moderate to low Henry's law constant Contaminant removal hindered by surfactant in micelle formation Typically requires use of antifoaming compound and oversized stripper to help control foam formation Produces a large volume of off-gas that requires treatment due to high contaminant concentrations
Macroporous polymer extraction	Removal of hydrophobic contaminants by an organic solvent immobilized in a macroporous polymer	Applicable to a wide range of contaminants Limited foaming tendency	Innovative technology High capital cost Surfactant may partition to extractant and vice versa Polymer must be regenerated when the capacity of extracting liquid is saturated
Membrane air stripping	Removal of contaminants with high Henry's law constants and high foaming tendency	Air and water do not come into direct contact, so foaming is reduced and stripping can be more efficient (i.e., a higher air to water ratio is possible compared to air stripping) More compact compared to air or steam stripping	Innovative technology High capital cost Membrane prone to fouling Inefficient for contaminants with moderate to low Henry's law constant Contaminant removal hindered by surfactant in micelle formation Stripping air must be maintained at higher pressure than the water to avoid weeping of wastewater through the membrane
Pervaporation	Removal of contaminants with high vapor pressure and high foaming tendency	Air and water do not come into direct contact, so foaming is reduced Contaminants collected in condensed form as a separate phase Membrane fouling possible, but more resistant to fouling than permeable membranes	Innovative technology for this application High capital cost Inefficient for contaminants with moderate to low volatility Contaminant removal hindered by surfactant in micelle formation May not be amenable to the use of polymer

Table 6-2. Summary of Contaminant Removal Unit Operations (Continued)

Treatment System	Treatment Applications	Advantages	Limitations
Steam stripping	Removal of contaminants with low Henry's law constants and controllable foaming tendency	Mature, commercially available technology Contaminants collected in condensed form as a separate phase	High capital cost Energy intensive, high operating cost Typically requires use of antifoaming compound and oversized stripper to help control foam formation Contaminant removal hindered by micelle formation due to surfactant
Activated carbon adsorption	Removal of low (ppm level) concentrations of contaminants with moderate to high affinity to adsorb on carbon when most surfactant has been removed	Mature, commercially available technology Limited foaming tendency	High surfactant concentrations will plug carbon bed Unaggregated surfactants will sorb to carbon and reduce contaminant removal efficiency

Adapted from: Lowe et al., 1999b; Strbak, 2000; Vane et al., 2000.

6.3.1.2 Air Stripping. Treatment with air stripping involves transfer of volatile contaminants from the wastewater into an air stream. Contaminant-free air is contacted with the wastewater in a countercurrent flow configuration such that contaminants vaporize out of the liquid phase and enter the gas phase. The vapor liquid contacting is done in a column filled with packing or trays that increase the area of the air-to-water interface. Due to the high concentration of DNAPL in wastewater that is characteristic of SEAR applications, treatment of the contaminant-loaded air exiting the stripper typically is required.

The presence of surfactants in aqueous streams contaminated with volatile organic solvents alters the vapor-liquid equilibrium of the system. The presence of surfactants in groundwater treated by air stripping or steam stripping will decrease the mass transfer of contaminant from the liquid phase to the vapor phase by reducing the mass transfer driving force. Therefore, the efficiency for treating PCE- and TCE-contaminated groundwater by air stripping and steam stripping will be reduced in the presence of surfactants.

High air flowrates are desirable because gas-phase resistance typically limits the overall mass transfer rate. However, maximum air flowrates usually should be kept between 30:1 and 40:1 to minimize foaming problems (Lowe et al., 1999b). Designing a stripper with a larger diameter than that used for nonsurfactant applications reduces the liquid and gas velocities and can broaden the range of operating conditions, which may help minimize foaming. Foaming generally increases with increasing surfactant concentration, and the addition of antifoaming agents may be necessary even if other design measures are taken for the air stripper; the tendency of the surfactant to foam will influence decisions to use antifoam agents and the concentrations needed.

6.3.1.3 Macroporous Polymer Extraction. Treatment with macroporous polymer extraction (MPPE) involves transfer of hydrophobic compounds from the water phase into an organic extraction solvent. The organic extraction solvent is immobilized in a polypropylene polymer matrix that forms a solid media and allows contact between the water and organic extraction solvent without allowing the organic and water phases to mix. During treatment operations wastewater passes over the solid MPPE media contained as a bed in one or more vessels.

The MPPE system requires regeneration as the system approaches saturation and breakthrough becomes imminent. Regeneration is accomplished with low-pressure steam and can potentially produce a two-phase waste stream, one aqueous and one organic. The organic phase can be separated and recovered in a liquid-liquid phase separator for disposal/reuse, the aqueous phase can be recycled through the column for further treatment or captured for disposal.

With proper solvent selection, removal of contaminants from the water can be more efficient compared to air stripping because the separation is controlled by solubility in the solvent rather than the Henry's law constant. Thus separation efficiency depends on the hydrophobicity of the contaminant, so the MPPE system can efficiently remove contaminants with high K_{ow}. MPPE is not suggested for use in removing common alcohols because of their high aqueous solubility and consequently low partition coefficients for MPPE.

6.3.1.4 Membrane Air Stripping. Membrane air stripping separates volatile contaminants from wastewater using the same operating principles as air stripping in column (see Section 6.3.1.2) but with a different type of equipment. In the membrane air stripping system, hollow fiber membranes form a large surface interface between the air and water streams. These porous membranes keep the air and water separate, but allow volatile gases to pass from the water into the air. Because the air and water phases do not mix, formation of foam is minimized. The membrane systems allow higher air to water flow ratios and more surface area per unit volume compared to the packing or trays in conventional air stripping columns, so that a membrane unit typically is smaller than a conventional unit of comparable capacity. The membrane units are more expensive than conventional air strippers and can be more prone to fouling. The surfactant in the wastewater will wet either hydrophobic or hydrophilic membranes, so water will tend to leak through into the air stream unless the air stream is maintained at an elevated pressure.

6.3.1.5 Pervaporation. Pervaporation is a liquid/vapor separation process in which volatile contaminants in the water vaporize through a nonporous, selective membrane to form a concentrated vapor stream. The term pervaporation is derived from the two major steps in the operation: permeation and evaporation. Hydrophobic pervaporation membranes have a high affinity for organic compounds and a low affinity for water. Organic compounds partition into the membrane and diffuse through the membrane under the influence of a pressure gradient. The pressure gradient induced by heating the feed and applying a vacuum to the vapor side of the membrane enhances the evaporation of the compounds from the membrane. The contaminant vapor is recovered by cooling in a condenser.

The operating efficiency of a pervaporation system is controlled by the contaminant volatility as well as solubility in the membrane material, with contaminants having a high vapor pressure and high K_{ow} tending to dissolve into the membrane (U.S. EPA, 1994, EPA/540/R-94/512). Thus the selection of membrane material is important. Silicone rubber membranes are often used for organic contaminant separation from groundwater. Chlorinated solvents typically are amenable to treatment using pervaporation, but higher molecular weight hydrocarbons may not be sufficiently volatile for treatment in a pervaporation unit (Lowe et al., 1999b).

Pervaporation can be used to treat SEAR wastewater streams containing high concentrations of organic compounds, such as chlorinated solvents. Unlike stripping processes, the water being treated does not directly contact a turbulent air stream, so foaming is minimized. However, pervaporation operations, like all membrane operations, can be subject to fouling and chemical incompatibilities. A prefilter may be used to address particulates, but any oils and greases present (e.g. in spent degreasing solvents) will tend to coat the membrane and significantly reduce mass transfer of volatile components across the membrane. The type of membrane module selected can help to reduce fouling by particulates and oily substances.(Vane et al., 2000) Finally, pervaporation for surfactant-VOC separations is an innovative technology and these membranes and systems are currently selling at a premium and may not be readily available.

6.3.1.6 Steam Stripping. Steam stripping is similar to air stripping with steam generated by boiling the treated water used as the vapor phase in place of air. Stripping occurs in a tray or packed column, but at a higher temperature, so removal of semivolatile compounds is improved. The vapor exiting the top of the column is condensed by cooling such that the water and organic contaminants form two phases which can be separated by decanting. Some or all of the water condensed from the stripper overhead stream is returned to the column and the organic is collected for disposal or reuse.

Steam stripping typically is used for treating effluents containing nonvolatile or semivolatile components. Although the removal of hydrophobic, volatile compounds (e.g., light petroleum hydrocarbons, TCE, or PCE) is achievable by air stripping, the process is generally reserved for effluents containing low concentrations of these compounds because the mass transfer is limited by the Henry's law coefficient of a given compound or mixture of compounds. In contrast, steam stripping is governed by the laws of vapor-liquid equilibrium and can efficiently remove high concentrations of organic contaminants from wastewater. However, because of the considerably higher unit treatment costs compared to air stripping, stream stripping is less cost effective for wastewater streams consisting of volatile hydrophobic compounds only. If semi- or non- volatile hydrophobic components (e.g. oils and greases) are present in high enough concentration to require removal, stream stripping may be the ideal choice. Additionally, volatile hydrophilic compounds (e.g. low molecular weight alcohols used as surfactant cosolvents) vaporize in a steam stripper and are concentrated in the water phase of the overhead product of the column. Thus, these compounds can be incidentally removed with the aqueous stripping fluids (see Section 6.3.2.2).

6.3.1.7 Activated Carbon Adsorption. Treatment with activated carbon involves transfer of contaminants from the wastewater to a solid-phase adsorbing media. The wastewater passes through one or more vessels containing a packed bed of granular activated carbon (GAC) where contaminants dissolved in the water sorb onto available sites on the carbon. When the GAC capacity is exhausted (i.e., all available sites filled) the material can be discarded or regenerated. Carbon adsorption can be effective for polishing treatment system effluent containing low surfactant concentrations to discharge standards, but it is not a good stand-alone system for treating groundwater extracted during a SEAR application. Surfactants will tend to foul the carbon bed and thereupon reduce the carbon capacity for contaminants.

6.3.2 Cosolvent Removal/Recovery Unit Operations. Common cosolvents in SEAR applications include low molecular weight alcohols such as methanol, ethanol, and IPA. IPA commonly is used because it promotes good subsurface-phase behavior. Injected alcohol concentrations can be similar to or higher than injected surfactant concentrations. Therefore, cosolvent concentrations in the extracted groundwater must be addressed in the wastewater treatment system design. Unit operations for removing cosolvents from SEAR wastewater are summarized in Table 6-3. Biological degradation is perhaps the most cost-effective option, but has not been implemented as a separate wastewater treatment process for the degradation of alcohols derived from a SEAR waste stream.

Table 6-3. Summary of Cosolvent Removal/Concentration Unit Operations

Treatment System	Treatment Applications	Advantages	Limitations
Biological degradation	Degradation of aerobically degradable compounds and removal of BOD/COD	Mature, commercially available technology Can convert cosolvents to mineral constituents (i.e., H_2O and CO_2) Also degrades some contaminants and surfactants	Operation requires maintenance of a large volume of biomass Produces sludge that requires disposal
Distillation	Removal of cosolvents with higher vapor pressure than water	Mature, commercially available technology Produces concentrated cosolvent stream Also removes contaminants	High capital cost Energy intensive, high operating cost Cosolvent may contain contaminants that vaporize in the distillation column that require further treatment for removal Typically requires use of antifoaming compound and oversized column to help control foam formation
Pervaporation	Removal of cosolvents with higher membrane solubility and higher vapor pressure than water	Air and water do not come into direct contact, so foaming is reduced Contaminant-free cosolvent collected in condensed form as a separate phase	Emerging technology for this application High capital cost Membrane prone to fouling Contaminant will not be removed to any significant extent when alcohol removal is the primary goal

Adapted from: Lowe et al., 1999b; Strbak, 2000; Vane et al., 2000.

6.3.2.1 Biological Degradation. Biological degradation involves aerating wastewater, possibly adding any nutrients required, and allowing contact time with a biomass of degrading organisms. This treatment method can effectively treat cosolvents used in SEAR applications but, due to the high cosolvent concentration, a large biomass population must be sustained to achieve the desired reduction in BOD/COD. Large biomass populations are easily sustained in a wastewater treatment plant, but on a remote field site with a limited footprint, this application may not be feasible.

Biological treatment in an off-site POTW (after the DNAPL contaminants are removed on site) may be an option. A conventional wastewater treatment plant typically can treat the cosolvents to desired discharge limits, but may not be able to handle the large input of cosolvents, DNAPL, and surfactants (BOD/COD loading) from the SEAR system. A typical wastewater treatment plant, domestic or industrial, is designed to handle a certain influent feed composition and flowrate. Thus, water treatment facilities using biological processes are not infinitely flexible. The plant's treatment capacity is limited and the limiting factor may be oxygen or nutrient supply, solids retention time, sludge production and removal, hydraulic loading, or some other treatment aspect. This limit is often characterized by the Theoretical Oxygen Demand (ThOD) and is different for every operating facility.

The BOD/COD loading to the treatment plant cannot exceed the ThOD for extended periods of time or the plant will likely violate discharge allowances as some waste material passes through the plant untreated. Therefore, some onsite removal of cosolvent may be required prior to offsite disposal.

6.3.2.2 Distillation. Distillation is very similar to steam stripping except for the handling of the overhead product. The low molecular weight alcohols used as cosolvent are highly soluble in water and do not form a separate phase when condensed. As a result, the product from the condenser is a concentrated alcohol. By increasing the number of theoretical stages in the distillation column and the fraction of overhead product recycled, the product produced by distillation can approach nearly pure alcohol.

When the wastewater stream contains both DNAPL contaminants and a cosolvent, a distillation unit will remove both. Removal efficiencies for cosolvent alcohols (e.g., IPA) will be lower than stripping efficiencies for chlorinated solvents. Therefore, a distillation column processing PCE/TCE and IPA should be designed to give the required IPA residual concentration in the treated wastewater. PCE/TCE removal requirements will most likely be met if the system is designed to remove significant quantities of IPA (60-95%).

The overhead product from a distillation unit/steam stripper treating water containing both DNAPL contaminants and cosolvent may form two phases when condensed: a DNAPL organic phase and a concentrated alcohol/water phase. Some of the DNAPL contaminant will partition into the alcohol/water phase. If the alcohol is to be recycled and reused, contaminant removal from the concentrated alcohol/water product stream typically is required. The MPPE system or air stripping followed by carbon adsorption are suitable for cleaning up the cosolvent that has been concentrated in a distillation system. The auxiliary removal of contaminant from the alcohol/water stream not only allows for the reuse of the alcohol, it also reduces the amount of hazardous waste generated by reducing the hazard associated with the entire product stream. If the cosolvent concentration in the discharge stream from the bottom of the distillation column is not a concern (e.g., the residual BOD/COD is acceptable to the POTW that will receive the wastewater), then the column should be designed for optimal contaminant removal in the presence of IPA.

6.3.2.3 Pervaporation. Pervaporation (see Section 6.3.1.5) has been tested to remove cosolvents from an aqueous surfactant stream. However, a different membrane material is required for efficient alcohol removal from water, as alcohol will not partition to any significant extent into the hydrophobic membranes that are used to remove organic contaminants. IPA removal by a hydrophobic pervaporation membrane may be increased if thinner membranes are selected (Vane et al., 2000). Currently there are no industrial units designed to remove IPA from groundwater.

6.3.3 Surfactant Removal/Concentration Unit Operations.

Additional processing to increase the surfactant concentration is needed after the contaminants are removed to allow for recovery of the surfactant for reuse. If surfactant is not to be recycled, it may be necessary to reduce the surfactant concentrations in wastewater to meet discharge limits. Four surfactant removal/concentration unit operations considered for treatment of SEAR wastewater are summarized in Table 6-4. Biological degradation is another option that was already discussed in Section 6.3.2.1 for cosolvent removal. This option may be feasible if treated wastewater is discharged to a POTW with an activated sludge process. It is not included in Table 6-4 as generally it will not be feasible to quickly degrade surfactant to the required discharge levels for short-term SEAR projects.

Table 6-4. Summary of Surfactant Removal/Concentration Unit Operations

Treatment System	Treatment Applications	Advantages	Limitations
MEUF	Concentrates surfactant micelles	Mature, commercially available technology Efficiently recovers surfactant micelles	Not effective if surfactant CMC is high or influent surfactant concentration is low Membrane prone to fouling Significant quantities of surfactant monomers may pass through the membrane with the water permeate Micelle recovery may concentrate contaminants and cations Micelle recovery is adversely affected by the presence of cosolvents
Nanofiltration	Concentration of surfactant monomers and micelles	Mature, commercially available technology Can recover monomers and micelles	Lower membrane flux and higher operating pressure compared to MEUF Higher membrane area required compared to MEUF Membrane prone to fouling Micelle recovery may concentrate contaminants and cations High capital and operating costs
Foam fractionation	Concentrates surfactants near the CMC	Mature, commercially available technology Efficiently recovers surfactant monomers Low cost	Will not be cost-effective to remove surfactant micelles Residual volatile contaminants may be volatilized during the foaming process Multiple fractionation stages are needed if the surfactant concentration is high
Chemical precipitation	Removes surfactant monomers and micelles	Mature, commercially available technology	Significantly increases the total dissolved solids (TDS) content and reduces the pH of the treated water The precipitation reaction is slow, requiring a large reaction vessel Surfactant sludge will remain with DNAPL

Source: Adapted from Lowe et al., 1999b; Strbak, 2000; Vane et al., 2000.

6.3.3.1 Micellar Enhanced Ultrafiltration. MEUF involves the use of ultrafiltration membranes designed with a high molecular weight cutoff (MWCO) to retain surfactant micelles while allowing water, surfactant monomers, cosolvents, and dissolved salts to permeate through the ultrafiltration (UF) membrane. Typical surfactant molecules have a molecular weight ranging from 300 to 2,000 g/mole when they aggregate into micelles with 50 to several hundred surfactant monomers. Therefore, the UF membrane can be designed for an MWCO in the range of 10,000 to 50,000 (i.e., large pore size compared to conventional UF membranes). These membranes retain micelles, whether they are surfactant-contaminant microemulsions or self-aggregating surfactant micelles (depleted of contaminant), because their size is larger than the pore size of the membrane. The membranes can give a high permeate flux at low pressure drop due to their large pore size. UV sterilization of the surfactant stream can avoid biofouling of the membrane.

Laboratory experiments (DE&S, 2000, Appendix I) show that surfactants at concentrations below the CMC typically permeate through the membrane; thus, at a concentration of 1 CMC in the feed, surfactant recovery by MEUF is negligible. Consequently, MEUF is most effective if the surfactant concentration in the treated water is considerably above the CMC of the surfactant. This likelihood is maximized if the surfactant used in SEAR has a low CMC.

MEUF is used to recover surfactant after the contaminants have been removed. Diluted surfactants are concentrated to just above their reinjection concentration, which should not exceed an order of magnitude concentration factor (e.g. from 0.5 wt% to 5 wt%). Using MEUF to obtain a highly concentrated surfactant stream is not cost-effective. Any components that tend to partition to surfactant micelles will be concentrated with surfactant micelles. This includes hydrophobic components and ions such as calcium and sodium that remain preferentially with the surfactant. These are undesirable effects and must be considered in the design of the surfactant recycle processes. For example, higher contaminant removals will be required of upstream contaminant removal processes. The concentration of ions during MEUF is a more challenging issue as there are no immediate processing solutions and the design of the surfactant formulation is likely to be impacted. MEUF should not be used to reduce the volume of SEAR effluent, unless further treatment of the DNAPL waste will occur. Contaminants remaining with the surfactant micelles typically cause the retentate to require management as a RCRA hazardous waste.

Tucker (1999) indicates that the presence of the IPA cosolvent reduces the effectiveness of the MEUF process for concentrating surfactant for recovery and reuse. IPA in the solution reduces the size of surfactant/DNAPL microemulsions. The smaller micelles are more likely to permeate through an ultrafiltration membrane with a pore size designed to capture large aggregates. IPA also reduces the fluid viscosity, further enhancing micelle permeation through the ultrafiltration membrane.

6.3.3.2 Nanofiltration. Nanofiltration is similar to MEUF but involves the use of ultrafiltration membranes designed with a lower MWCO. These membranes have smaller pores and can retain surfactant monomers as well as micelles. However, the smaller pore size results in a lower flux and higher pressure drop compared to a MEUF unit. Therefore a higher membrane surface area and/or more passes will be necessary compared to MEUF. Biofouling will be of greater concern due to higher membrane and surfactant retention of microorganisms; this is possibly prevented by the addition of a UV sterilization unit prior to nanofiltration treatment. Nanofiltration membranes and systems are more expensive because of the necessity of withstanding higher pressures.

6.3.3.3 Foam Fractionation. Surfactant in water near the CMC has a strong tendency to form foams. This property can be used to concentrate the surfactant by sparging air bubbles into water such that foam collects on the surface of the water. This foam can be collected to allow recovery of the surfactant. The inlet stream to the foam fractionation unit should be relatively free of volatile contaminants as the air sparging process will strip them from solution.

Formation of the foam depends strongly on the surfactant concentration with maximum foaming tendency occurring at the CMC. As a result, recovery is less efficient at higher or lower surfactant concentrations. Surfactant can be recovered from concentrated solution but more theoretical stages are needed to perform the separation, which increases capital and operating cost. At concentrations below about 1 to 5 mg/L, the foam becomes unstable so that foam fractionation is not possible (Lowe et al., 1999b).

6.3.3.4 Chemical Precipitation. Surfactant removal by chemical precipitation involves adding a multivalent positive ion in solution (e.g., aluminum from alum addition) that reacts with the surfactant to form a precipitate. This precipitate tends to settle slowly, so separation typically requires use of a centrifuge. To prepare the surfactant precipitate slurry from the centrifuge for reuse, the multivalent ions are exchanged away from the precipitate by contacting it with an excess of monovalent positive ions in solution (e.g., sodium from sodium chloride). This surfactant slurry is then washed and redissolved.

Separating the alum-surfactant precipitate from the treated water requires a continuous throughput centrifuge or large clarifier. A separate DNAPL phase may form when the surfactant precipitates so the separation system may also need to be able to handle a DNAPL phase in addition to separating the precipitate from the water. Either of these pieces of equipment is expensive and a large clarifier will be difficult to accommodate at many sites due to constraints on available space. It was also determined that IPA hinders the flocculation process. Flocculation only occurred in process waters with an IPA concentration below 10%, pushing the limit of some SEAR-NB applications.

Although chemical precipitation with alum is an effective and inexpensive method for breaking microemulsions and aggregating the surfactant for precipitation, this method has its disadvantages. The pH of the treated wastewater drops to about 3.5 due to the alum addition. Surfactant precipitation only occurs at this pH and over a limited temperature range. Adjustment of the pH to return the water to near neutral conditions, and possibly ion exchange to reduce the dissolved solids concentration, will be required to adjust treated wastewater chemistry before discharge to a POTW. The presence of ionic species in the treatment chemicals, as well as recovered injectate species will saturate ionic exchange columns quickly, so operating costs for these columns may be high.

6.4 An Integrated Treatment Train

Currently, no one unit operation is capable of treating all of the constituents (contaminants, cosolvents, and surfactants) in the groundwater extracted during a SEAR application so unit operations must be integrated into a treatment train that meets site-specific requirements. The anticipated onsite project duration will influence treatment options, particularly the choice of a biological treatment pond to degrade cosolvents and/or surfactants.

6.4.1 System Requirements. The SEAR wastewater treatment design must comply with environmental requirements and provide cost-effective processing. For example, site-specific volatile organic compound (VOC) discharge limits may require special treatment of the vapor phase from an air stripper used to process extracted groundwater. Treatment ponds, if used to biodegrade surfactant and/or cosolvent, should be designed to avoid attracting birds and other wildlife. Issues such as these should be addressed from the outset.

The SEAR wastewater treatment system must be designed to meet the receiving facilities requirements and not adversely affect the existing operations. Discharge standards will vary depending on site-specific conditions. Discharge with minimal wastewater treatment may be possible if an on-site industrial wastewater treatment facility has available capacity and adequate permitting limits to accept the SEAR wastewater. Somewhat more wastewater treatment typically will be needed, if the discharge will be made to a POTW. Good communication and coordination with the receiving facility throughout the design process is essential to maximize design efficiency. In instances of discharge to a surface water body under an NPDES permit, stringent discharge standards usually are imposed.

Space limitations are also a concern in the final treatment design. Process equipment with a small footprint should be considered when on-site space is limited. Skid-mounted units are preferred over permanently erected units because the event duration is usually short and will not require permanently erected confinement structures.

6.4.2 **Pretreatment.**

The SEAR flushing may mobilize some free phase DNAPL in addition to DNAPL solubilized in micelles. Free-phase DNAPL is most efficiently removed by decanting performed separately from other processing steps. Therefore, if free-phase DNAPL is expected in the extracted groundwater, a decanting (see Section 6.3.1.3) step should be included as the first unit operation.

Prefiltering and pH adjustment can reduce particulate and iron oxide fouling in processing equipment. Because the particulates suspended in groundwater can vary from location to location, the selection of the filter material and size is not trivial. The proper filter will be chemically compatible with the effluent stream and remove the desired fraction of suspended particulates. A balance between screening size and pressure drop losses will be met in an optimal design. Filter pore sizes below 1 μm will likely cause high pressure drops and are not an ideal choice for pretreatment particulate filtration.

Iron oxides are likely to form if there is a high iron content in the groundwater. Iron oxide precipitates can foul small pores in the process equipment (i.e., stripping or distillation column internals or membrane pores), reducing performance and increasing the pressure drop in the treatment unit. Iron oxides are more soluble at low pHs; therefore, low pH operations (pH 3-5) are recommended to prevent iron oxide fouling. It is important to consider that all process equipment coming in contact with the effluent stream must be rated to handle low pH solutions, otherwise pH adjustment to control fouling may not be beneficial.

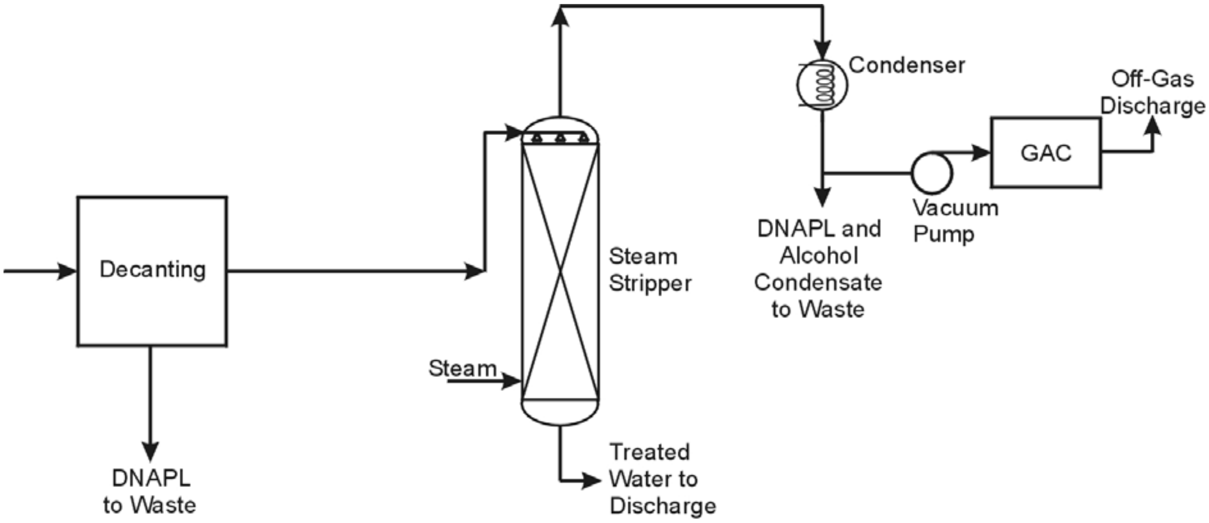
It is desirable to provide surge storage for process water at various points in the treatment train as compatible with space available at the site. Storage vessels provide emergency storage capacity should a unit in the treatment train fail. Storage basins also allow concentration averaging to reduce peak concentrations and provide a steady, consistent effluent stream that can be processed by the treatment system with few parameter adjustments.

6.4.3 **Treatment Train Options.**

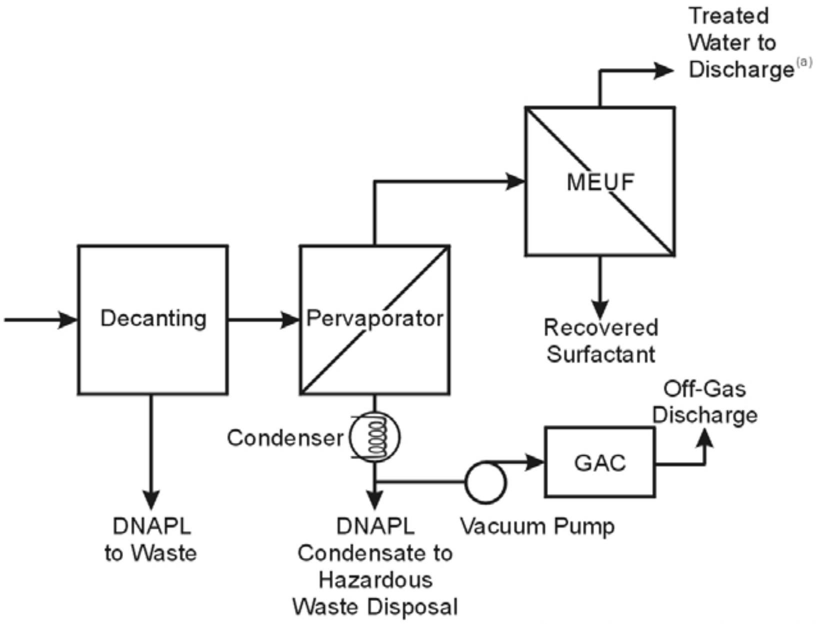
Unit operations for contaminant, cosolvent, and surfactant treatment can be combined in a wide variety of ways to meet the site-specific processing requirements. Two hypothetical treatment trains, one for a discharge option and one for a surfactant recovery option, are shown in Figure 6-2. Figure 6-2 provides an illustration of some of the concepts involved in assembling a treatment train to process groundwater extracted during a SEAR application. However, the treatment train that is optimal for a particular site frequently will differ significantly from these examples depending on site-specific factors. Some of the main factors to consider during the development of a system concept are summarized in Figure 6-3.

In the discharge option, the aqueous stream is sent to a steam stripper to remove 95% or more of the remaining DNAPL and cosolvent from the surfactant solution. The surfactant solution, stripped to low levels of contaminants and low levels of cosolvent, is discharged. Once exposed to heat, surfactants should degrade readily.

In the surfactant recovery option, the DNAPL contaminant is removed in a pervaporation unit with a membrane optimized for DNAPL removal. DNAPL permeates through the membrane and is condensed and collected for disposal as a hazardous waste. The surfactant solution, stripped to low levels of contaminants (i.e., ppm range residual), is sent to a MEUF to recover surfactant micelles. The permeate, containing residual surfactant, is discharged, as long as all chemical concentrations are below appropriate limits.



a) Discharge Option



Note: (a) If a cosolvent is used, treated water from the MEUF unit may need further processing for alcohol removal prior to discharge.

b) Surfactant Recovery Option

Figure 6-2. Examples of Possible Treatment Trains for SEAR Wastewater

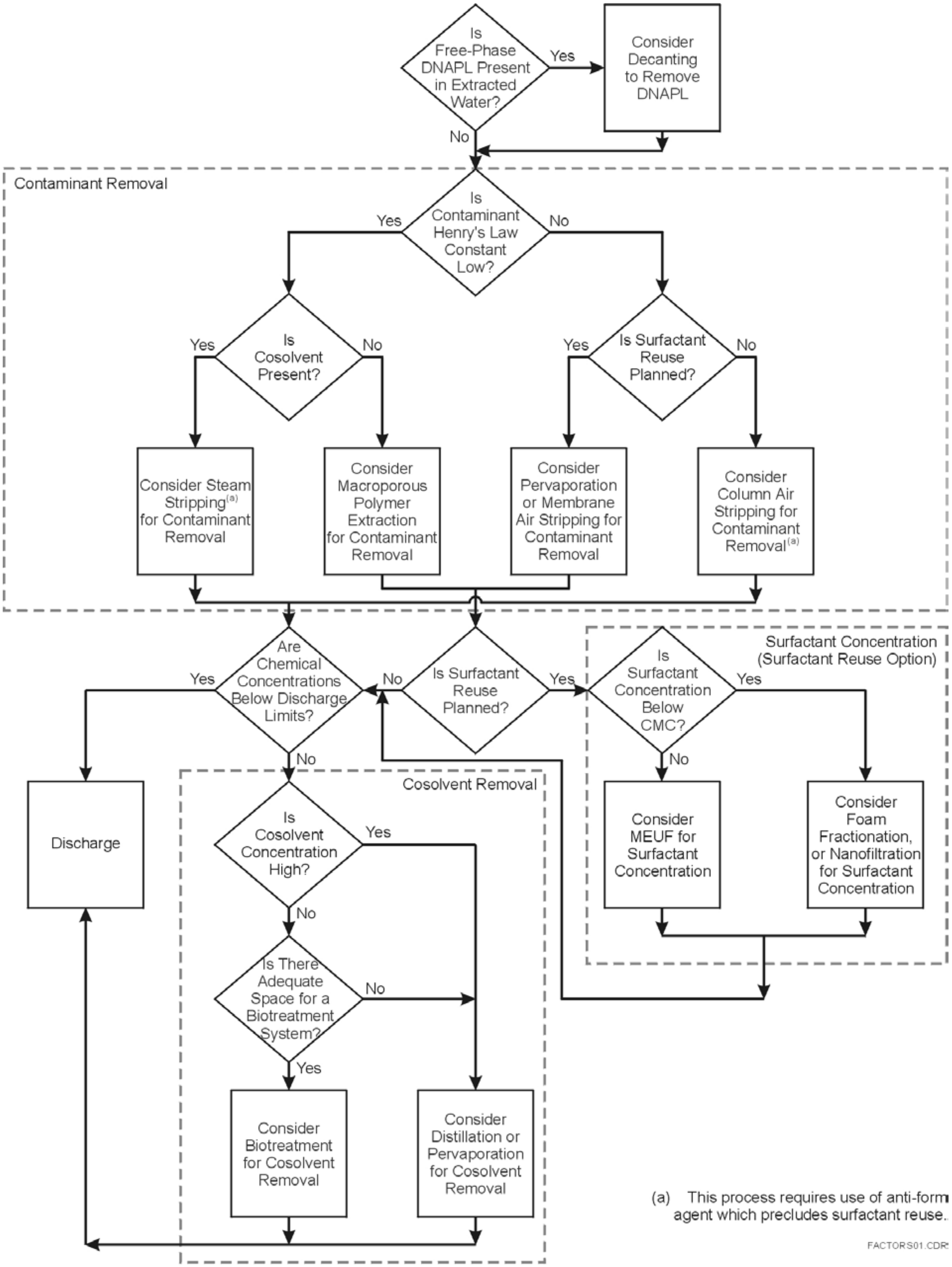


Figure 6-3. Major Factors Influencing Selection of Options for SEAR Wastewater Treatment

6.4.4 Cost Considerations. A significant portion of the operating costs of a SEAR application is the cost of the effluent treatment, which is controlled by the availability of existing facilities, the processes selected, the flowrates selected, the concentrations of chemicals in the extracted water, the desired removal efficiency and the duration of the remediation effort. For a small-scale (~3000 sq ft) surfactant flood targeting DNAPL removal over a 5 ft saturated thickness, the wastewater treatment costs can be as high as 38% of the total remediation costs (ESTCP, 2001).

The potential for cost saving by treating groundwater extracted during a SEAR application is bounded by the cost of off-site disposal of the untreated groundwater. Typical estimates for off-site disposal of RCRA hazardous waste are $1.00 to $3.00 per gallon, whereas discharge to a POTW (if available) typically ranges from $0.15 to $1.00 per 1,000 gallons (Means, 2000). To be cost-effective, an on-site SEAR wastewater treatment system must treat the groundwater and meet the differential between the off-site disposal cost and the POTW discharge fee. If a POTW is not available, the cleanup criteria for the wastewater typically will be much more demanding, which will significantly increase the cost of on-site treatment.

Treatment system design must carefully balance economics, availability, and performance. In general, higher flowrate applications require larger capacity process units that have higher capital costs. Economic evaluations should compare the costs of leasing or purchasing equipment. Fabrication time and mobilization costs must be factored into the comparison. Cost comparisons must also be made to compare different technologies and incorporate performance evaluations. Operation and maintenance costs, as well as the associated downtime on the SEAR, must always be considered.

Many variables impact the system costs and net project savings associated with the implementation of a surfactant recovery system for SEAR processes. All other factors being equal, net project savings will be greater for:

- Higher-cost surfactants
- Contaminants easily separated from surfactant
- Systems where surfactant recovery is high (i.e., high UF recovery, high subsurface capture with minimal losses to soil and groundwater)
- Surfactants to which air stripping can be applied for contaminant removal without the need for anti-foam agents that reduce the likelihood of acceptable surfactant injection
- Less stringent contaminant removal requirements
- High surfactant concentrations, i.e., low dilution of surfactant in the subsurface (as long as contaminant removal efficiency is not impacted significantly).

Because the economics of surfactant recycle is a function of many site-specific variables, as well as the SEAR design, the potential benefits of surfactant recovery processes for future SEAR projects should be evaluated on a site-by-site basis. Table 2-3 shows sample costs and cost savings for recovery and reuse of the Alfoterra 145-4PO Sulfate™ surfactant. Additional details may be found in the Final Cost & Performance Report for Surfactant-Enhanced DNAPL Removal at Site 88, Marine Corps Base Camp Lejeune, North Carolina (ESTCP, 2001).

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APPENDIX A

SOIL SAMPLING METHODS AND PROCEDURES FOR DNAPL SOURCE ZONE CHARACTERIZATION

APPENDIX A

SOIL SAMPLING METHODS AND PROCEDURES FOR DNAPL SOURCE ZONE CHARACTERIZATION

A.1 Soil Sampling Collection Methods

The use of direct push technology (DPT) for soil sampling is recommended because it is a lower-cost alternative to drilling and can substantially increase the quality of the data obtained from the soil sampling program. DPT is most applicable at sites with unconsolidated sediments and at depths less than 100 ft. However, if a DPT platform cannot be used, then drilling with a hollow stem auger (HSA) method is recommended. Typically, drilling activities should be proceeded by geophysical investigations as discussed in Section 3.2.2, so that the location and depth of the resulting borehole can be optimized for the objective of the drilling operation. Continuous soil sampling is recommended to verify stratigraphic information. 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. A variety of efficient sampling systems (e.g., wireline) and sampling tools are available for use with HSA. Samplers for use during drilling in DNAPL zones are discussed in the next section. Wells and the associated filter packs can be installed quickly and efficiently through the HSA, provided that the inside diameter of the auger has been properly chosen. Some limitations to the HSA drilling method should be noted as follows:

- ❑ **Depth Limitations** - The depth to which one can drill is limited by the size (outside diameter) of the auger and the torque that the drill rig is capable of developing. Experienced drilling contractors can help define the depth limitations for specific sites.

- ❑ **Hydrostatic Pressure Limitations** - Sand heave or "run in" into the lead auger flight due to hydrostatic pressure can create substantial problems when attempting to sample in loose sediments below the water table. This problem can be mitigated by pumping at a well very close to the borehole to relieve the pressure, or by using drilling muds (polymers) recently developed for environmental applications to counteract hydrostatic pressure and prevent sand from flowing into the augers at the bottom of the drill string.

- ❑ **Soil Matrix Issues** - Drilling through or into clay may cause clay cuttings to be carried up the borehole by the rotating auger flights. These clay cuttings can damage the permeability of the borehole wall by smearing and creating a "skin" effect. Avoiding this situation requires that the clay units be previously identified so that the auger can be tripped out of the hole and the flights cleaned after drilling a short distance (approximately 2 ft) in the clay. This technique was used very successfully for a thin gravelly aquifer within a thick weathered marl unit at USAF Plant 4 in Fort Worth, Texas (DE&S, 1998).

A major factor that determines the efficiency and success of a drilling program for DNAPL zone characterization is the competence and experience of the drilling contractor. Drilling of this type is often tedious and slow work because of the need for accuracy in drilling measurements, and the requirements of the sampling effort. For example, installing a remediation well with the screen positioned correctly at the contact between the contaminated aquifer and the underlying aquitard requires the driller to keep precise track (±0.5 ft or better) of where the bit of the lead auger is during drilling and sampling.

This is accomplished by knowing the length of the lead auger/bit assembly, the length of all of the attached auger flights, and accurately measuring the amount of auger exposed above the ground surface for each sampling interval. These types of expectations, along with the drilling objective(s), should be communicated clearly to the driller before starting drilling operations, included in the scope of work, and written into the drilling subcontract, if possible. The contract vehicle should not provide the incentive for the drilling contractor to focus on drilling as fast as possible, and should be fair and equitable to the driller. For example, additional standby time should be budgeted to allow for the more complex, and therefore, lengthier sampling process. Common (and costly) problems created by recalcitrant drilling crews that can be avoided through careful selection and communication include:

- Losing track of the number of auger flights in the ground,
- Sloppiness in measuring and attaining target depths,
- Drilling beyond target zones or the next sampling interval(s),
- Sampling faster than the hydrogeologist can process the samples, thereby allowing VOCs to volatilize away as samples sit waiting on the logging table,
- Accidentally dropping equipment down the hole,
- Using augers with too small of an inside diameter,
- Using improper or damaged equipment, and
- Not decontaminating equipment properly.

Finally, once the drilling is finished, the resulting borehole must be properly abandoned if it will not be completed into a well. The commonly used method for abandonment is to fill the boring with bentonite or bentonite grout and then to seal the surface with a cement and bentonite mixture. However, this practice can irreparably damage the formation by drastically reducing the permeability in the immediate vicinity of the former borehole. This is especially true if the DNAPL zone encompasses permeable sand and gravel units into which grout can be lost. To preserve the ability to transmit SEAR fluids through the DNAPL zone, the boring should be abandoned by filling the permeable portions of the borehole with the same type of sand that is being used for the well filter packs at the site. The top portion of the borehole above the water table can then be grouted and sealed to prevent a connection with the surface. Undesirable communication between multiple permeable zones intercepted by the boring can be avoided by filling the appropriate intervals with bentonite to create seals adjacent to low permeability units. If a previously installed well must be abandoned in place, sand should be placed in the screened interval and the casing filled with bentonite. The use of this abandonment method may require special permission from the regulatory agency that has jurisdiction over the drilling of wells at the DNAPL site.

A.2 Soil Sampling Device Selection

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 maximize not only the recovery of soil, but also retain as much of the fluid in the pore spaces as possible. Other important considerations for sampler selection include the following:

- The sampler diameter should be large enough to provide a substantial volume of soil. In addition, when sampling soil in which gravel and larger components are present, the sampler diameter should be large enough to incorporate these into the sample instead of obstructing the core barrel and preventing soil from filling the sampler.

- ❑ The length of the coring interval should be relatively short, so that the friction between the soil and the sampler does not become excessive enough to compress the soil significantly, or even to prevent soil from the bottom of the sampling interval from entering the sampler. The length of the core is highly dependent on site conditions, but a standard rule of thumb is that 2 to 3 feet is generally the practical length limit.

- ❑ The sampler should be constructed in such a manner that it can be rapidly opened so that the soil can be accessed quickly.

A cohesionless soil or “saturated sand” sampler should be used which uses a piston inside a dedicated sleeve to develop a suction that retains sediment and pore fluids. This allows for continuous samples to be obtained in dedicated liners or sleeves that can be capped and sent for analysis. This type of sampler works best in finer-grained sediments, but larger diameter barrels (up to 5 inches diameter) are available for coarser-grained units containing gravel and cobbles. Cryogenic samplers that use nitrogen or carbon dioxide to freeze samples in the core barrel before they are retrieved from the sampled interval have also been used to successfully recover pore fluids and to minimize the amount of mass lost during sample handling (Murphy and Herkelrath, 1996). Unfortunately, this type of environmental sampler is not yet available commercially, and has therefore only rarely been used in the shallow subsurface.

A.3 Soil Sampling Protocol

The procedures discussed below for in-field sample preservation (EPA Method 5035) should be used for logging and soil sampling. A two-person crew will be needed to complete the following steps:

- ❑ **Sample Jar Preparation -** The jar and the solvent added must be weighed on an accurate balance so that the VOC concentrations in the solvent (methanol) can be converted to concentrations per unit mass of soil. It is best to prepare and weigh the sample jars indoors out of the wind and other elements. The containers must be uniquely and permanently marked in a manner that allows them to be identified even if the methanol dissolves away the ink and the glue holding the label on the jar (e.g., a number engraved on the lid). Given that methanol and glass jars are relatively inexpensive, we suggest preparing more soil jars than will actually be sent for analysis. This allows the sampling team to take soil samples very rapidly and then choose a subset of those for actual analysis based on screening conducted after the samples have been preserved. In addition to the sample jars needed for each boring, prepare sample jars for the required quality control/quality assurance samples, and prepare a methanol blank for each lot of solvent used as preservative.

- ❑ **Soil Core Preparation -** The soil core, once retrieved from the boring should be brought (unopened) rapidly to the logging table. If the sample contains or is suspected to contain free-phase DNAPL (e.g., on top of a clay layer acting as a capillary barrier), it should not be placed completely horizontally since this can redistribute the DNAPL along the length of the core and result in unrepresentative samples. Once the core is on the table and the prepared sample jars are in position, the core barrel should be quickly opened for access to the soil. In the case of a split barrel, a soil knife can be used to split the sample into two equal lengthwise halves.

- **Sample Interval Selection** - Next, a rapid assessment of the grain size distribution present in one of the core halves is conducted to select those intervals to be subsampled and preserved. An inspection of the core halves for visual or odor indications of DNAPL can be used to determine the contaminated zones. A PID is an additional tool that is frequently used on a newly opened core to screen the core for contaminated zones. One half of the core should be set aside for observation of the soil types after samples have been collected. Samples should be obtained from each contaminated unit represented in the core, and from the boundaries or transitions between units as well.

- **Soil Sample Preservation** - To maximize the detection of volatile DNAPLs, samples should be immediately transferred to a jar or vial containing a methanol preservative. This step takes the place of dissolving the volatile soil contaminant into a solvent in the laboratory prior to GC/MS analysis. Field sample preservation can increase the recovery of DNAPL contaminant for an accurate depiction of the DNAPL distribution, but it also raises the analytical detection limit. Uncapping the sample jar, placing the sample into the methanol without splashing, cleaning the threads of the jar, and then recapping the jar tightly is an operation for four hands and some practice is necessary to perfect the coordination needed to perform these tasks rapidly without error. In fine-grained soil, a large syringe with the end of the barrel removed makes an inexpensive and handy subcoring device. In coarser-grained material, stainless steel laboratory spatulas have been used successfully. Large pieces of gravel should be excluded from the sample, as they bias the sample weight. Instead, the matrix material between the gravel piece should be collected as these represent the flowpaths through the aquifer. Once the solvent-preserved soil samples have been collected and properly stored, a portion of the soil from each sampled interval should be placed in a foil-covered glass container for headspace analyses using a photoionization detector (PID). Screening each subsampled location with the PID in this manner will provide data that can be used to help determine which samples will be sent to the laboratory for analysis and which will be retained on hold. The other half of the soil sampler is then used to describe the sampled interval on the boring log.

- **Soil Core Documentation** - Finally, the core should be photographed along with a photo scale and a label identifying the boring number, the core run number, and the depth interval sampled. A laminated piece of cardstock with a photo scale and blank lines for the information listed above, and erasable pen (an overhead pen) works well to identify each photo.

- **Soil Sample Shipping** - Because methanol is a Class 3 flammable liquid, care must be taken to ship the preserved soil samples correctly. The person shipping the samples must have the appropriate U.S. Department of Transportation training, and must follow the proper shipping regulations and packing instructions. It is recommended that the samples be shipped by ground transport, not only to avoid shipping complications, but also so that they are minimally disturbed during transport. The prescribed holding time for methanol-preserved samples given by different guidance documents varies, but for all practical purposes, the actual holding time over which there is almost no detectable contaminant loss is well over a year if the samples are refrigerated to minimize methanol loss.

- **Soil Sampling Waste Disposal** - Disposing of the solvent and soil in the sample jars can be a hazardous investigation-derived waste issue that needs to be addressed in the planning stages of the sampling activity. However, this issue should not deter one from using methanol preservation during a drilling and sampling operation. The data quality of unpreserved soil samples is so poor that it is not justifiable to incur the expense of a drilling and sampling program, if solvent preservation is not used in the field.

APPENDIX B

ESTIMATING DNAPL SATURATION FROM SOIL SAMPLES

APPENDIX B

ESTIMATING DNAPL SATURATION FROM SOIL SAMPLES

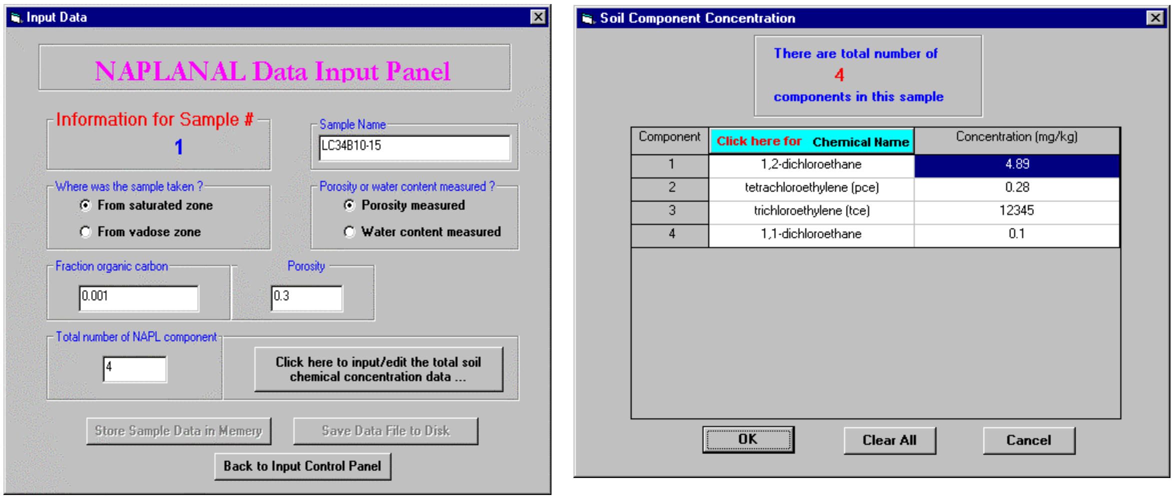
The mass reported by the laboratory in the soil sample represents only a fraction of what is actually present in the subsurface because the contaminant will be distributed (or partitioned) between the soil, groundwater, free phase, and/or air phase. Because SEAR applications focus almost exclusively on the saturated zone, the air phase is assumed to be negligible. The partitioning of contaminant mass between soil, groundwater, and DNAPL depends on parameters such as the fraction of organic content (f_{oc}) and porosity of the saturated zone soils and well-established partition coefficients and solubility constraints. The partitioning of contaminant mass between soil, groundwater, and DNAPL depends on well-established partition coefficients and solubility constraints. Using these relationships and published values of solubility data, analytical relationships can be developed to determine if sample results are indicative of DNAPL presence. NAPLANAL is a program developed by DE&S to automate this process and convert the laboratory soil sample results to estimated DNAPL saturations (Mariner et al., 1997). NAPLANAL distributes the measured total VOC concentrations in a sample among the various fluid and solid phases present. If the calculations indicate that aqueous VOC concentrations would exceed solubility constraints, the NAPLANAL algorithm determines that DNAPL is present in the sample and automatically includes DNAPL as one of the partitioning phases. A free copy of the NAPLANAL software package can be downloaded from www.napl.net/publications.html.

B.1 NAPLANAL Input

To enter the VOC data acquired from the laboratory into NAPLANAL, the VOC concentration in the solvent extract must be converted to a concentration per soil mass (mg/kg). This is accomplished using the jar, methanol, and soil weights recorded in the field, and using the density of the soil and the solvent. A value for the fraction organic carbon (f_{oc}), soil bulk density, and the porosity of the soil must also be entered. Other input parameters are obtained from a database of physical and chemical constants, which is incorporated in NAPLANAL. Table B-1 includes a summary of NAPLANAL input parameters and Figure B-1 shows sample input screens.

Table B-1. NAPLANAL Input Parameters

Field Parameters (User Input)	Database Parameters
Sample identification number	Organic partition coefficient, K_{oc} for each component
Depth of sample	Henry's law constant, K_H for each component
Total concentrations for each component, mg/kg	Molecular weight of each component
Volumetric water content ($\phi_w = 1$ in saturated zone)	Density of soil, water, air, DNAPL
Soil porosity	
Fraction of organic carbon, f_{oc}	



Information for Sample # 1

Sample Name: LC34B10-15

Where was the sample taken ?
● From saturated zone
○ From vadose zone

Porosity or water content measured ?
● Porosity measured
○ Water content measured

Fraction organic carbon: 0.001

Porosity: 0.3

Total number of NAPL component: 4

There are total number of
4
components in this sample

Component	Click here for Chemical Name	Concentration (mg/kg)
1	1,2-dichloroethane	4.89
2	tetrachloroethylene (pce)	0.28
3	trichloroethylene (tce)	12345
4	1,1-dichloroethane	0.1

Figure B-1. NAPLANAL Input Panels

B.2 NAPLANAL Output

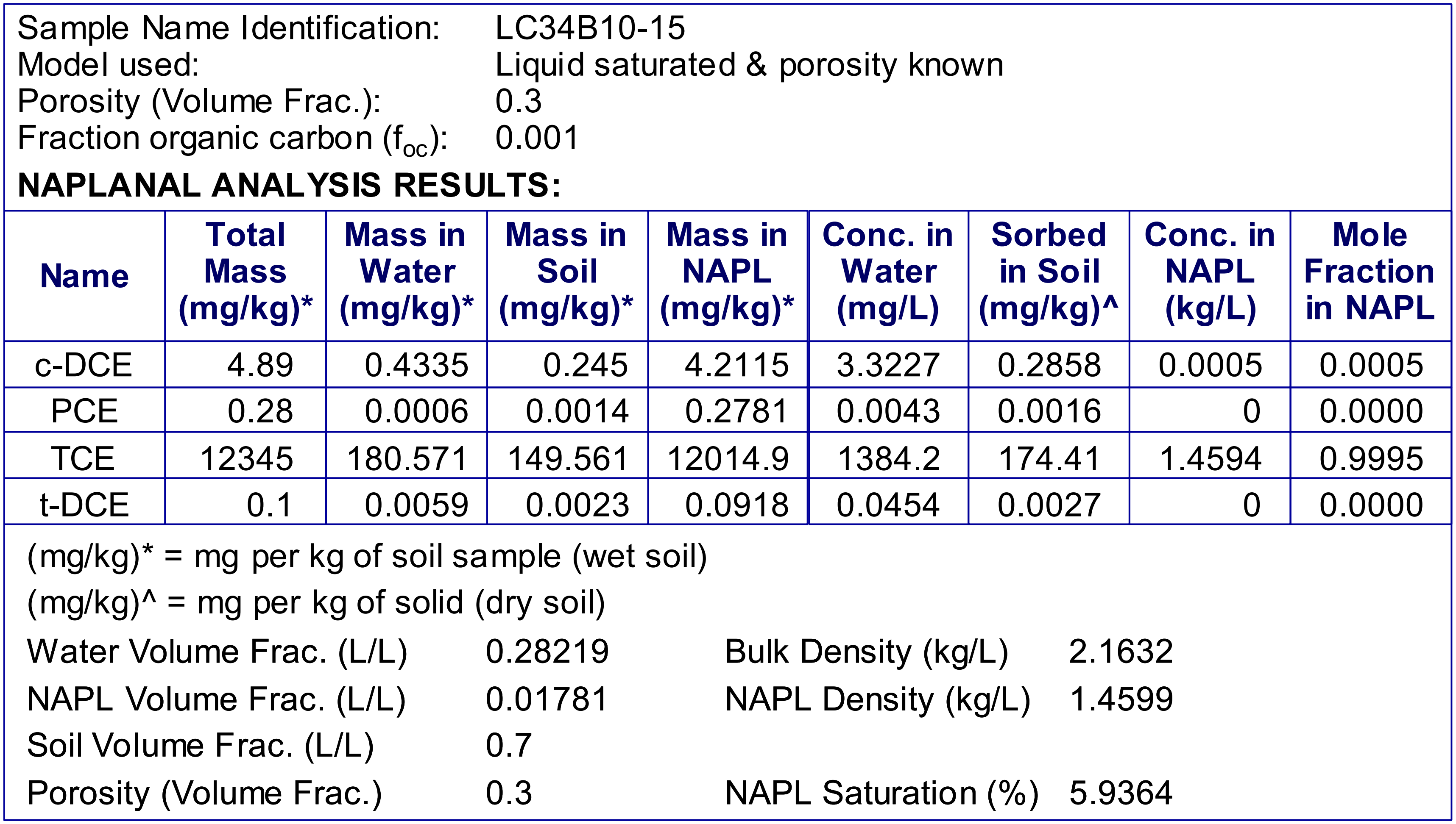
The NAPLANAL output includes calculations of the concentrations of VOCs in each phase and the sample DNAPL saturation (volume of DNAPL per volume of pore space). If no DNAPL is present, a dilution factor (as defined in Jackson and Mariner, 1995) is calculated to provide a measure of how much more concentrated the VOCs must be before a DNAPL would be predicted to exist in the sample. NAPLANAL is a powerful tool for understanding the distribution of VOC mass between the different phases at the site and should be used to guide the development of the geosystem model and the characterization activities. Figure B-2 shows the sample output from the program.

B.3 Interpretation of Modeling Results

The NAPLANAL program can be used to estimate the threshold concentration that must be exceeded in a soil sample for DNAPL to be considered present in the free phase based on equilibrium partitioning considerations. For example, in a soil sample from HAFB OU-2 (having a typical porosity of 28% and a f_{oc} of 0.001, typical of the arid southwest), free-phase DNAPL can be considered present, if the contaminant concentration exceeds the following levels:

- 345 mg/kg TCE
- 62 mg/kg TCA
- 23 mg/kg PCE

DNAPL saturation profiles can also be developed from NAPLANAL results. Measuring DNAPL saturation distributions vertically in the hydrostratigraphic cross section of the source allows the SEAR designers to determine if mobility control (adjusting the surfactant flood design to compensate for heterogeneity) is necessary, and if so, what type to use. The results of NAPLANAL modeling can also be used to investigate spatial variability in the composition of the free-phase DNAPL. NAPLANAL results provide the mole fraction of the VOC components in the DNAPL, allowing both soil and water chemical data to indicate the nature of the chemical composition of the DNAPL present in the source zone. This information can be used to build an analog of the DNAPL for bench-scale SEAR design tests if samples of the DNAPL are not obtainable from a site.



Sample Name Identification: LC34B10-15
Model used: Liquid saturated & porosity known
Porosity (Volume Frac.): 0.3
Fraction organic carbon (f_{oc}): 0.001

NAPLANAL ANALYSIS RESULTS:

Name	Total Mass (mg/kg)*	Mass in Water (mg/kg)*	Mass in Soil (mg/kg)*	Mass in NAPL (mg/kg)*	Conc. in Water (mg/L)	Sorbed in Soil (mg/kg)^	Conc. in NAPL (kg/L)	Mole Fraction in NAPL
c-DCE	4.89	0.4335	0.245	4.2115	3.3227	0.2858	0.0005	0.0005
PCE	0.28	0.0006	0.0014	0.2781	0.0043	0.0016	0	0.0000
TCE	12345	180.571	149.561	12014.9	1384.2	174.41	1.4594	0.9995
t-DCE	0.1	0.0059	0.0023	0.0918	0.0454	0.0027	0	0.0000

(mg/kg)* = mg per kg of soil sample (wet soil)

(mg/kg)^ = mg per kg of solid (dry soil)

Water Volume Frac. (L/L)	0.28219	Bulk Density (kg/L)	2.1632
NAPL Volume Frac. (L/L)	0.01781	NAPL Density (kg/L)	1.4599
Soil Volume Frac. (L/L)	0.7		
Porosity (Volume Frac.)	0.3	NAPL Saturation (%)	5.9364

Figure B-2. NAPANAL Output

APPENDIX C

CAPILLARY BARRIER CHARACTERIZATION METHODS

APPENDIX C

CAPILLARY BARRIER CHARACTERIZATION METHODS

There are a number of laboratory experimental methods, such as the centrifuge method and the pressure cell method, available to determine capillary entry pressure. These experimental approaches are described below and more detailed information can be found in Bear (1972).

- ☐ **Centrifuge Method-** With this method, a plug sample, a few centimeters in length, is taken from the soil core and then saturated with the wetting fluid (usually water). The sample is placed with its long axis horizontal in a centrifuge that has a diameter of a few centimeters. The centrifuge is run at a single, fixed angular velocity until the wetting fluid contained in the sample has reached equilibrium with the centrifugal force imposed by the rotation. During the centrifuge process, air phase displaces the wetting fluid from the soil core. The wetting-phase saturation along the axis of the sample can be measured using gamma radiation attenuation. The entry pressure and the drainage capillary pressure as a function of saturation is then obtained by calculating the forces acting on the fluids and the distribution of fluids along the axis of the sample during rotation.

- ☐ **Pressure Cell Method-** With this method, a soil core sample saturated with water is placed on one side of a semipermeable barrier in a confined chamber surrounded by DNAPL. In this context, the term semipermeable implies that during the experiment, the barrier permits the passage of the water, but not the DNAPL. The water phase is on the opposite side of the container so that its pressure can be controlled. The capillary pressure at the surface of the semipermeable barrier in contact with the sample is adjusted either by adjusting the water-phase pressure or by adjusting the DNAPL-phase pressure in the sample chamber. When the sample has reached an equilibrium saturation at the imposed pressure, its saturation is determined by measuring the amount of wetting fluid that was discharged or imbibed during the increment of capillary pressure imposed. To accurately reproduce in situ conditions during the experiment, soil cores should be oriented in the same direction as samples were originally positioned in the subsurface. The best infiltrating fluid for use in these experiments is DNAPL collected from the site. It should be noted that with a low permeability sample, the time required to reach equilibrium may be too large for this measurement to be practical.

APPENDIX D

SURFACTANT SCREENING WITH SOIL COLUMN EXPERIMENTS

APPENDIX D

SURFACTANT SCREENING WITH SOIL COLUMN EXPERIMENTS

D.1 SEAR Soil Column Experiments

Soil column experiments are conducted in order to screen surfactant formulations and to explore the influence of entrapment geometry and soil matrix properties on SEAR performance. Figure D-1 shows a typical soil column experimental setup. To the extent possible, these experiments should be conducted with site DNAPL, soil, and groundwater and performed at the average site groundwater temperature. Table D-1 summarizes the methods used for analysis of the soil column surfactant solution effluent. Soil column experimental methods are described in detail in Dwarakanath et al. (1999) and the steps involved are briefly discussed below:

1) **Soil Column Materials** - Soil columns should be made of stainless steel with stainless steel end pieces. Teflon® end pieces are less suitable than steel because they have the potential to desorb contaminants at the end of surfactant flooding (Dwarakanath, 1999). Column lengths should range between 15 and 40 cm with diameters between 2.2 and 4.8 cm. The aspect ratio, defined as the ratio of the length to the diameter of the soil columns, should be greater than three to minimize end effects due to the inlet and outlet end pieces.

2) **Soil Column Packing** - The columns should be packed such that the larger cobbles are removed and the column diameter is greater than 10 times the size of the largest soil particle. If the soil column is packed "wet", the soil packing will cause loss of interstitial fluids and residual volatile contaminant, thus resaturation of soils with water and volatile contaminant may be necessary.

3) **Soil Column Water Flood** - Once the column is packed, it should be flooded with CO_2 to displace the air. Water saturation of the soil columns should be carried out with de-aired aquifer groundwater and a backpressure to solubilize any trapped CO_2. Water saturation of the column should begin from the bottom upward to ensure gravity-stable displacement and dissolution of CO_2.

4) **Soil Column Permeability Test** - Once a column is packed, its permeability should be measured by flowing water at different flowrates while concurrently measuring the pressure across the inlet and outlet.

5) **Soil Column DNAPL Entrapment** - In the case of columns packed with uncontaminated soils, DNAPL is emplaced in the column by flooding from the bottom upward and following it with a water flood from the top downward. This is done to ensure gravity-stable displacement of the water and DNAPL.

6) **Soil Column Tracer Test** - An initial partitioning tracer test should be conducted to determine the initial DNAPL saturation. In addition, the initial tracer can also determine the pore volume, and the dispersivity of the soil pack.

7) **Surfactant Flooding** - The surfactant solution is then applied to the column at a rate that would be representative of achievable flowrates in the field. The effluent concentrations of the contaminant are measured to assess SEAR performance.

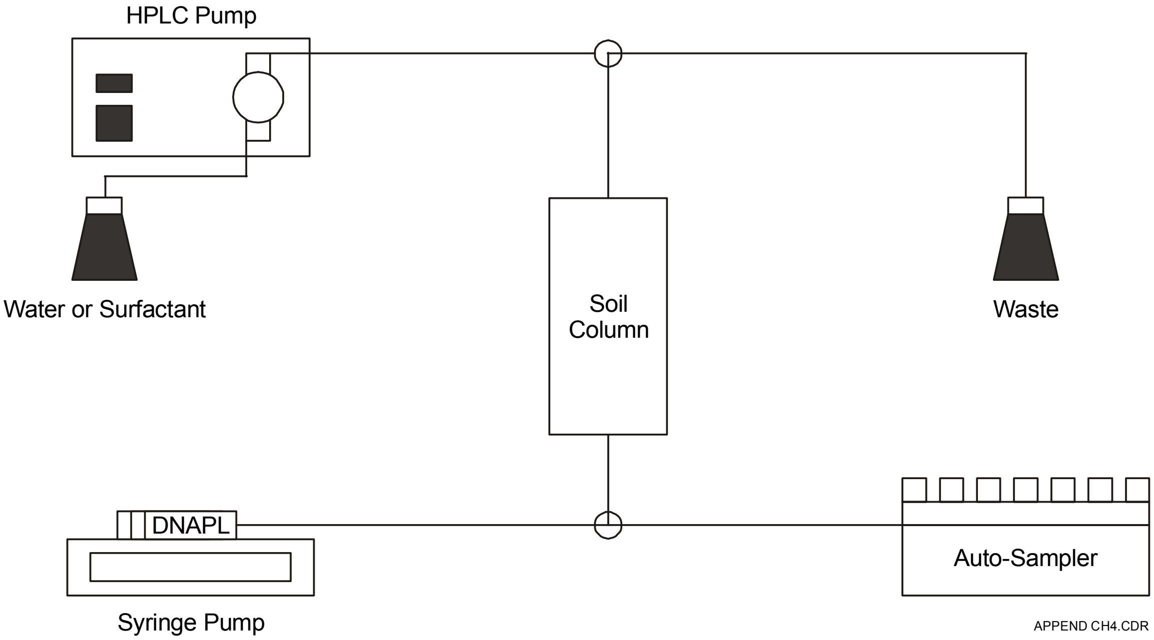


Figure D-1. Soil Column Experimental Setup

Table D-1. Analytical Methods for Soil Column Studies

Analyte	Method
Contaminant	EPA Method 8260 for VOCs, EPA Method 8270 for SVOCs, and/or EPA Method 8080 for pesticides and PCBs
Surfactant	Liquid chromatography
Calcium	EPA Method 200.7
Alcohol Tracers(a)	EPA Method 8015 modified

(a) Alcohol tracers: 1-propanol, *sec*-butanol, 1-hexanol, 1-heptanol, and 2-ethyl-1-hexanol.

8) **Post-Surfactant Water Flooding** - Water is injected to remove surfactant from the column

9) **Final Soil Column Permeability Test** - Using the same flowrates as in the previous step, the permeability of the column is measured to compare to conditions existing before surfactant treatment. Permeability reductions may be caused by the formation of gels/liquid crystals during surfactant flooding.

10) **Final Soil Column Partitioning Tracer Test** - This measures the final DNAPL saturation following surfactant treatment to determine the efficacy of the surfactant in removing contaminant.

During surfactant flooding, pressure gradients should be measured across the soil column to verify that the induced hydraulic gradient is not too high for the aquifer conditions of interest. In addition, the final water permeability of the soil after surfactant flooding should be close to its initial value. The induced hydraulic gradient during surfactant flooding is a function of the injected surfactant and microemulsion viscosity. In general, a slight increase in the induced hydraulic gradient is acceptable during surfactant flooding. Such an increase is usually proportional to the higher viscosity of the injected surfactant and microemulsion, compared to water under the ambient aquifer conditions. The gradient steadily increases until the breakthrough of the surfactant followed by a decline as illustrated in Figure D-2. In this experiment, the gradient increases from 0.27 to 0.34 at the beginning of surfactant injection due to the increased viscosity of the surfactant. A sudden increase from 0.35 to 0.45 is observed at 0.8 pore volumes, corresponding to the breakthrough of the mobilized DNAPL. The gradient then declines to a final gradient of 0.2 after postsurfactant water flooding. These gradients are acceptably low and indicate excellent behavior of the surfactant in the porous medium. An example of a column flood that generated a very unacceptable hydraulic gradient is shown in Figure D-3. The hydraulic gradient increased continuously during surfactant injection and eventually reached more than 38, at which time a water flood was started and it decreased rapidly. This is an indication of gel formation and plugging of the soil column. The quick decline of the hydraulic gradient at the start of water flooding suggests fingering and rapid breakthrough of water. Surfactants that exhibit such high gradients should be considered unacceptable for SEAR.

D.2 Other Soil Column Experiments

In addition to the experiments discussed above, it is necessary to measure the loss of surfactant that will occur as surfactant sorbs to site soils. These sorption experiments should be conducted with uncontaminated soil unless surfactant impurities are suspected and the SEAR test will be followed by a tracer test to quantify the residual DNAPL saturation. To detect whether surfactant impurities will cause sorption effects, clean Ottawa sands[2] are recommended for sorption experiments. This is due to the natural tendency of surfactant to sorb slightly to organic material. A nonsorbing tracer such as IPA or tritium should be used as a conservative tracer. The retardation factor of the surfactant with respect to the conservative tracer can be calculated from the surfactant effluent concentration data and the tracer test data to yield a distribution coefficient (K_d). Surfactants with low values of sorption (e.g., less than 0.3 mg/kg) are preferred for SEAR.

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[2] Ottawa sand is a silica sand from an aquifer in Ottawa, Illinois that is sold by U.S. Silica. It is a standard civil engineering testing material that can be purchased in a variety of grades and mesh sizes.

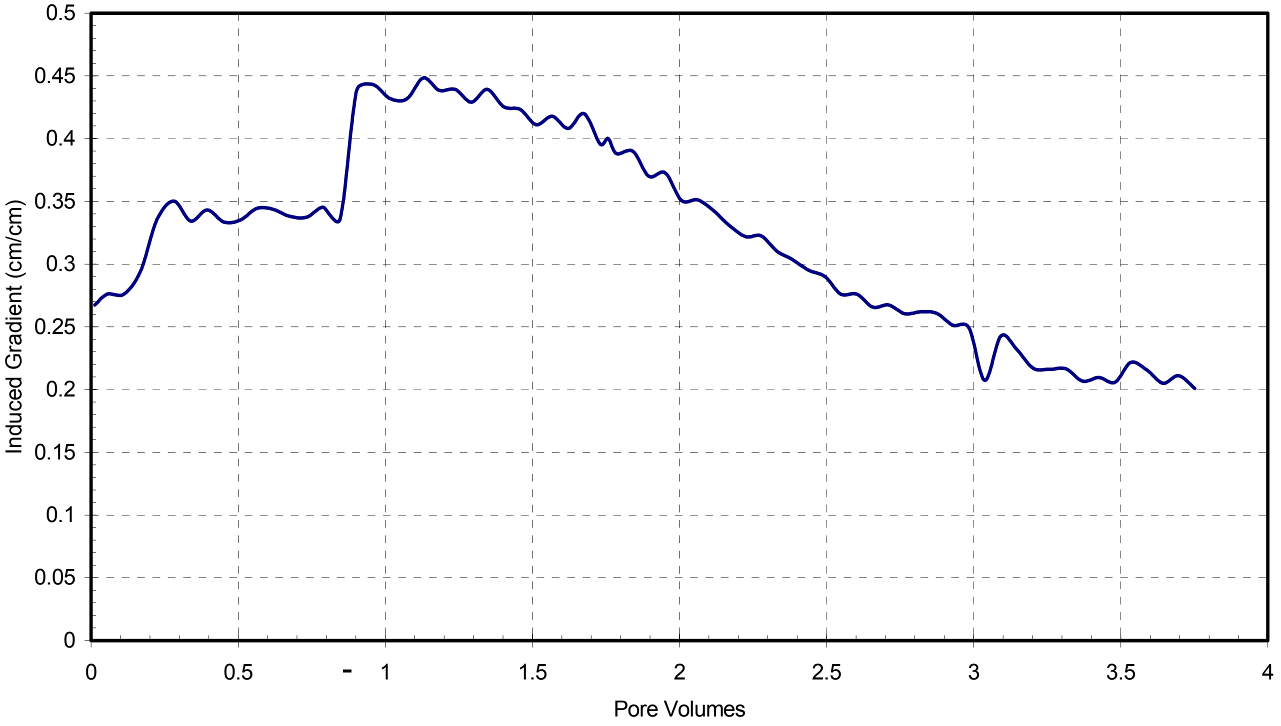

Figure D-2. Acceptable Gradients During Surfactant Flooding

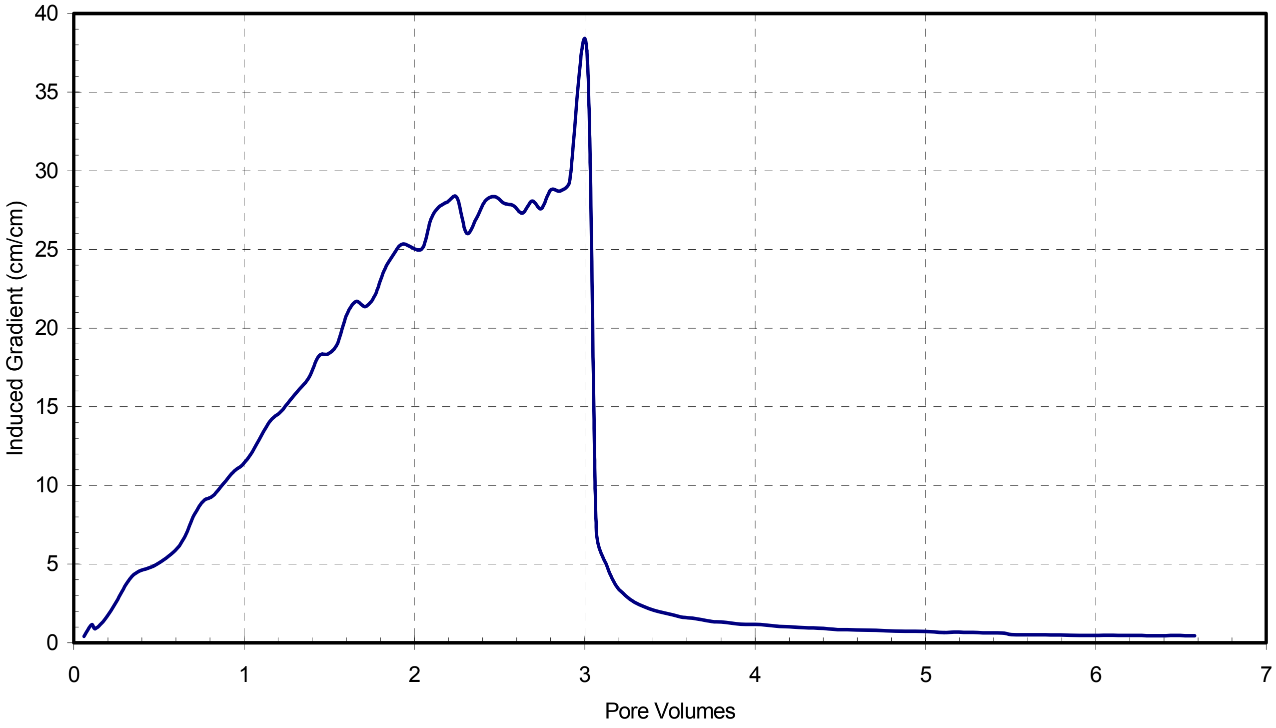

Figure D-3. Unacceptable Gradients During Surfactant Flooding