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In-situ, Field Scale Evaluation of Surfactant-Enhanced DNAPL Recovery Using a Single-Well, "Push-Pull" Test

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EXECUTIVE SUMMARY

Nonaqueous phase liquids (NAPLs), which include a variety of common petroleum fuels and chlorinated solvents, are groundwater contaminants at many DOE sites. In the subsurface, a portion of the NAPL (called residual NAPL) may become trapped in the pore space by capillary forces. Conventional treatment technologies typically are ineffective in removing residual NAPL because the slow rate of dissolution and low aqueous solubility of many NAPLs limit their removal by extraction pumping. One approach for increasing the effectiveness of NAPL removal is to inject surface-active-agents (surfactants) to enhance NAPL solubilization. Surfactant-enhanced DNAPL recovery involves the use of injected surfactants to increase the solubility and/or mobility of DNAPL in the subsurface in order to reduce the time and cost required for site remediation. The successful design of a surfactant-enhanced DNAPL recovery system requires a quantitative understanding of the competing processes of DNAPL solubilization and mobilization, sorption, precipitation, as well as ion exchange, which affect the transport and phase behavior of injected surfactants. An innovative new site-characterization technology termed the single-well, "push-pull" test method was used for this study. This technology has been the recent subject of development at Oregon State University because it can be used in the field to determine a wide range of aquifer physical, chemical, and biological characteristics. A push-pull test consists of the controlled injection of a prepared test solution into a single monitoring well followed by the extraction of the test solution/groundwater mixture from the same well.

The overall goal of this project was to further develop the single-well, "push-pull" test method as a feasibility-assessment and site-characterization tool for studying the fundamental fate and transport behavior of injected surfactants and their ability to solubilize and mobilize DNAPLs in the subsurface. The specific objectives were:

(1) to develop a modified "push-pull" test for use in identifying and quantifying the effects of sorption, precipitation, and biodegradation on the fate and transport of injected surfactants,

(2) to use the developed test method to quantify the effects of these processes on the ability of injected surfactants to solubilize and mobilize residual phase trichloroethene (TCE), and

(3) to demonstrate the utility of the developed test method for performing site characterization and feasibility studies for surfactant-enhanced DNAPL recovery systems in the field.

The project was a collaborative research effort between the Departments of Civil Engineering and Environmental and Molecular Toxicology at Oregon State University (OSU). The project was interdisciplinary and designed to utilize the scientific skills, experimental systems, and analytical capabilities available in each department.

To address the three objectives, the research plan combined controlled intermediate-scale laboratory experiments in unique physical aquifer models with a parallel series of pilot-scale field experiments in existing monitoring wells at a TCE-contaminated field site. The physical models were constructed in the shape of a circular arc ('piece of pie') to represent the alternating diverging/converging radial flow field near a well during the injection and extraction phases of a push-pull test. Intermediate-scale, push-pull test experiments (as opposed to studies in small scale batch reactors or columns) were selected for this project because spatial and temporal information on surfactant sorption, precipitation, and ion exchange in the vicinity of a monitoring well can be obtained from data acquired during a push-pull test. Furthermore, data from push-pull tests can

be used to quantify the effects of these physio-chemical processes on surfactant composition, concentration, and activity because they allow for the calculation of accurate mass balances for all solutes in both aqueous and solid phases. To address Objectives 1 and 2, laboratory push-pull tests in the physical aquifer models were conducted using native aquifer sediment and groundwater collected from Lawrence Livermore National Laboratory Site 300, which is a TCE-contaminated field site located in California. To address Objective 3, a series of field push-pull tests were performed at that site using existing monitoring wells located in an uncontaminated portion of the aquifer. In addition, push-pull tests also were conducted at an uncontaminated site in Corvallis, OR.

The first sets of experiments were designed to evaluate the ability of the single-well, push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment *in-situ*. Loss of injected surfactants due to sorption onto aquifer solids was determined to be a function of surfactant structure. Our finding is consistent with others that show that surfactant selection is critical to the success of surfactant-enhanced remediation. Numerical transport simulations that used batch sorption isotherm data were unable to predict the surfactant behavior that was observed in both laboratory and field push-pull tests. This finding indicates that the single-well, push-pull test method can more accurately describe *in-situ* surfactant sorption and transport behavior than can conventional batch sorption isotherms.

Because the DOWFAX surfactant was conservatively transported in both laboratory and field push-pull tests, the second set of experiments was designed to determine the ability of the DOWFAX surfactant to enhance the solubilization of TCE. Experiments were conducted in a TCE-free sediment pack and in a sediment pack initially containing liquid TCE that had an initial saturation of 5 % of the total pore volume. Increases in TCE concentration were obtained upon the injection and extraction of DOWFAX solutions compared to injection/extractions performed without surfactant. The increase in TCE concentrations were consistent with TCE solubilization increases obtained in batch solubilization experiments. However, two subsequent surfactant injection/extractions with identical DOWFAX solutions yielded smaller maximum TCE concentrations and mass recoveries. The increased density of injected DOWFAX solutions due to TCE solubilization resulted in significant sinking of injected solutions and an accumulation of DOWFAX and TCE at greater depths in the sediment pack; however, no mobilization or sinking of *liquid* TCE was observed. The results indicate that push-pull tests can provide useful information on surfactant-enhanced solubilization of NAPLS in the subsurface.

A third set of experiments was conducted with an anionic surfactant, sodium dihexyl sulfosuccinate (Aerosol MA 80-I), that had attracted considerable attention from groups involved in surfactant-enhanced remediation due to it greater ability to enhance TCE solubility compared to that of DOWFAX. The sulfosuccinate surfactant was transported conservatively (e.g., no losses due to sorption) in sediment packs containing no TCE. Increasing concentrations of Ca^{2+} and Mg^{2+} were observed during these experiments and were the result of cation exchange between the injected surfactant solution and the aquifer sediment. In contrast, the transport of the sulfosuccinate surfactant was strongly retarded in a sediment pack containing 5 vol % residual TCE because cation exchange resulted in the partitioning (loss) of the sulfosuccinate surfactant into the residual TCE phase. Conservative sulfosuccinate transport was restored by pre-flushing the sediment with 130 mM NaCl; this step reduced the quantities of exchangeable Ca^{2+} and Mg^{2+} in the sediment pack. The results of this study emphasize the importance of cation exchange on the performance of surfactant-enhanced TCE solubilization and demonstrate the utility of the

push-pull test for predicting the potentially deleterious effects of cation exchange on surfactant phase behavior in the presence of residual TCE. As a follow-up to this set of experiments, we found that injecting and extracting a solution containing *only* NaCl can be used to predict cation exchange and its potential impact on an injected surfactant. In this approach, *no surfactant was added.* The behavior of the surfactant was evaluated *ex-situ* using samples obtained from a physical aquifer model sediment pack that had undergone ion exchange with the surfactant. Thus, a push-pull test conducted with a low concentration of salt potentially can be used as a low-risk, low-cost tool for predicting cation exchange and its affect on surfactant effectiveness.

The results from the intermediate-scale laboratory experiments conducted for this project indicate that the single-well, push-pull test method can provide quantitative information on the effectiveness of injected surfactants in enhancing DNAPL solubilization in natural aquifer sediments. Specifically, the results of this research demonstrate the ability of the single-well, push-pull test to characterize the behavior of multi-component surfactants in the presence of natural aquifer sediment under laboratory and *in-situ* field conditions. For this reason, the single-well push-pull test appears to be a useful method for obtaining site-specific information on the behavior of injected surfactants. The overall benefits of the push-pull test method also include the fact that it can be applied in existing monitoring wells without the need for sediment cores. Laboratory and field push-pull tests confirmed that quantitative information can be obtained using only extraction phase breakthrough curves, which eliminates the need for additional (expensive) monitoring wells. Because it often is difficult and expensive to obtain sediment cores, it is a distinct advantage to have a test method that can utilize existing wells. In addition, the push-pull test method can be used to perform small-scale pilot tests that closely approximate conditions occurring in the vicinity of injection wells that will be used in full-scale NAPL remediation systems. The intermediate-scale and cost-effectiveness of the push-pull test makes it an ideal tool for optimizing surfactant-enhanced remediation schemes and for minimizing risks prior to conducting full-scale demonstrations. This research bridges between the fundamental work done on surfactant phase behavior and solubilization and the immediate need for field-scale demonstrations of the surfactant-enhanced remediation. With the project completed, a field-ready technology is now at the disposal of other research and consulting groups, whose efforts are aimed at full field-scale implementation of surfactant-enhanced remediation.

RESEARCH OBJECTIVES

Dense nonaqueous phase liquids (DNAPLs) are common subsurface contaminants at U.S. Department of Energy sites. Once released, these liquids, which include the common solvents trichloroethene and carbon tetrachloride move vertically downward through unsaturated and saturated zone sediments, following complex flow paths influenced by the physiochemical properties of the DNAPL and the geologic materials at the site. As a DNAPL flows through a porous media, a fraction of the liquid is trapped in the pore space by capillary forces. This residual fraction is essentially immobile and can not generally be removed as a separate liquid phase (e.g. by pumping from wells). Residual DNAPL is an important environmental problem at DOE sites because it can provide a long-term source of contamination as the trapped liquid slowly dissolves, releasing DNAPL components to groundwater. Common DNAPL dissolution products include chlorinated aliphatic hydrocarbons, polyaromatic hydrocarbons (PAHs), and pentachlorobiphenyls (PCBs). Because dissolution rates are limited by the slow rates of diffusion of DNAPL components from the interior of the residual phase to the DNAPL-groundwater interface, and because the dissolution products do not typically undergo rapid biological or chemical degradation under natural conditions, remediating sites containing residual DNAPL can be extremely difficult using conventional treatment technologies (e.g., pump and treat). This is made more difficult by the low aqueous phase solubilities of DNAPL components and their strong tendency to sorb to aquifer solids.

Pump and treat is typically ineffective for remediating sites contaminated with nonaqueous phase liquids (NAPLs) because the slow rate of dissolution and low aqueous solubility of many NAPLs limit their removal by pumping. One approach for increasing the effectiveness of NAPL removal is to inject surface-active-agents (surfactants) to enhance NAPL aqueous solubility. Increased NAPL solubility in the presence of surfactant micelles results from the partitioning of NAPL molecules into the hydrophobic interior of surfactant micelles, which are aggregates of surfactant monomers that form spontaneously at a system-specific surfactant concentration called the critical micelle concentration (CMC). The use of surfactants to enhance the recovery of crude oil has been extensively investigated in laboratory and field studies (Bourrel and Schecter, 1988; Lake, 1989).

A surfactant's CMC is known to be a function of a several variables including surfactant chemistry, temperature, ionic strength, and the type and concentration of organic contaminants present (Rosen, 1989). The effectiveness of a particular surfactant for enhancing NAPL solubility is typically evaluated in the laboratory using molar (MSR) or weight solubilization (WSR) ratios determined from batch solubilization isotherms (Edwards et al., 1991a; Rouse et al., 1993; Valsaraj and Thibodeaux, 1989). The magnitude of solubility enhancement can also be quantified using micelle-phase/aqueous-phase partition coefficients that describe the mole or weight fraction of NAPL dissolved in the two phases. For example, the molar micelle-phase/aqueous-phase partition coefficient, K_m is defined as

$$K_m = X_m/X_a \qquad [1]$$

where X_m and X_a are the NAPL mole fractions in the micellar and aqueous phases, respectively. X_m is calculated as $X_m = MSR/(1+MSR)$, and X_a is calculated as $X_a = (S^*_{CMC}\ V_w)$, where S^*_{CMC} is the solubility of the NAPL at the CMC and V_w is the molar volume of water (0.01805 L/mol) (Edwards et al., 1991a).

However, surfactant selection for this application currently is complicated by the need to balance the physiochemical properties of the surfactant that affect its transport in the aquifer with those

that affect its ability to solubilize residual NAPL (West and Harwell, 1992). Processes that affect surfactant transport and fate in the subsurface include advection, dispersion, sorption, precipitation, and ion exchange. These processes can decrease the concentration and therefore the solubilization or mobilization activity of an injected surfactant. In particular, the portion of injected surfactant that sorbs to aquifer sediments is unavailable for micelle formation and therefore will be ineffective in solubilizing residual NAPL (Kibbey and Hayes, 1987).

Many laboratory experiments have been conducted to examine the interactions among surfactant type, composition, and concentration and type and concentration of organic contaminants on enhanced solubility (Valsaraj and Thibodeaux 1989; Abdul et al. 1990; Edwards et al. 1991; West 1992; Rouse et al. 1993; Jafvert et al. 1994; Pennell et al. 1997). Typically, this information is obtained in small-scale batch experiments (Edwards et al., 1991a). Linear relationships between log K_m and log K_{ow} have been reported for a variety of anionic and nonionic surfactants and many chlorinated aliphatic compounds, polycyclic aromatic hydrocarbons, and chlorinated aromatic compounds (Edwards et al., 1991a; Jafvert et al., 1994; Valsaraj and Thibodeaux, 1989; West, 1992). Based on a field investigation of the ability of a diphenyl oxide disulfonate surfactant (DOWFAX 8390) to enhance the solubility of residual tetrachloroethene, Knox et al. (1997) concluded that laboratory solubilization experiments should be designed to replicate *in-situ* field conditions as closely as possible in order to provide usable results. Thus, the utility of batch solubilization experiments for predicting enhanced NAPL solubilization *in-situ* is not clear.

Chemical structure can be used to estimate the extent that a particular surfactant will sorb to aquifer sediments. For example, sorption of linear alkylbenzene sulfonates (LAS) increases with increasing alkyl chain length (Hand and Williams, 1987) while sorption of polyethoxylated surfactants increases with the number of ethoxy units (Podoll et al., 1987). Also, surfactants with two anionic head groups, such as alkyl diphenyl oxide disulfonates typically sorb less than surfactants with a single anionic head group, such as LAS (Rouse et al., 1993). However, sorption estimates based on chemical structure are largely qualitative and do not provide the quantitative and system-specific information on surfactant sorption required for remedial design. Surfactant effectiveness for enhancing NAPL solubility has been evaluated in the laboratory for a wide range of system-specific conditions including type and concentration of surfactants, electrolytes, cosolvents, temperature, major ion composition of site groundwater; mineral composition, organic matter content of aquifer sediments, and other factors (Edwards et al., 1991b; Rouse et al., 1993; Valsaraj and Thibodeaux, 1989). For example, anionic surfactant phase behavior and resulting NAPL solubility enhancement is strongly dependent on electrolyte concentration and composition (Baran et al., 1994a). At electrolyte concentrations below a critical value, anionic surfactants typically display Winsor Type I (oil-in-water microemulsion in equilibrium with excess oil) phase behavior and NAPL aqueous solubility increases with increasing electrolyte concentration. However, above a critical electrolyte concentration, the Type I system may convert to a Winsor Type III with the formation of a separate middle-phase microemulsion in equilibrium with excess aqueous and oil phases. At a second higher critical electrolyte concentration, the system may convert to a Winsor Type II system (water-in-oil microemulsion in equilibrium with an excess aqueous phase) in which surfactant partitions into the NAPL phase resulting in a negligible increase in aqueous NAPL solubility. Moreover, the critical electrolyte concentrations and the magnitude of NAPL solubility increasing with increasing electrolyte concentration will vary with the major cation composition of the electrolyte. For example, divalent cations are often more effective in increasing NAPL

aqueous solubility than monovalent cations. However, for divalent cations the critical electrolyte concentrations that cause a change from Type I to Type II or Type III behavior are smaller than those for monovalent cations. While less sensitive to solution-phase chemistry, the solubility of nonionic surfactants in NAPL phases also may be significant, thus reducing their ability to enhance NAPL solubility (Zimmerman et al., 1999).

Because of the importance of electrolyte composition on anionic surfactant phase behavior and NAPL solubility enhancement, cation exchange between electrolytes in the injected surfactant mixture and those initially present in groundwater and on aquifer sediments is potentially an important process controlling the effectiveness of surfactant-enhanced NAPL recovery in the subsurface. For example, anionic surfactants may be selected to minimize surfactant sorption to aquifer solids. In commercial surfactant mixtures, the negative charge of surfactant molecules is typically balanced by Na^+. Thus, injected anionic surfactant micelles and their associated Na^+ counter ions can displace cations (e.g., Ca^{2+}) from aquifer sediment as illustrated by the exchange reaction:

$$2Na^+_{(micelles)} + Ca^{2+}_{(sediment)} \Leftrightarrow Ca^{2+}_{(micelles)} + 2Na^+_{(sediment)}$$

In the presence of NAPL, the increase in divalent cation concentrations resulting from cation exchange can lead to the conversion of the injected surfactant mixture to a Winsor Type II or Type III system, which can result in the partitioning of surfactant into the NAPL together with little increase in aqueous NAPL solubility (Baran et al., 1994b). Surfactant transport would also be greatly retarded in a Winsor Type II system (similar to the way that transport of a hydrophobic organic contaminant is retarded by partitioning of the contaminant between groundwater and sediment organic matter) making it more difficult to distribute surfactants throughout NAPL-contaminated portions of the aquifer.

Only a limited number of field studies have been performed to evaluate surfactant-enhanced solubilization of residual DNAPL. Experimental systems have included well-to-well tests with sheet-pile enclosures (Fountain et al., 1996; Fountain et al., 1995) and without sheet-pile enclosures (Smith et al., 1997) as well as vertical recirculation wells (Knox et al., 1997). Although these approaches provide useful pilot-scale information they are typically expensive and logistically complicated. Any of these mechanisms can also cause chromatographic separation of surfactant components, wherein the composition of the surfactant formulation, and hence, its ability to solubilize or mobilize residual DNAPL changes with transport distance and time from the injection well. For example, surfactant composition has been shown to vary during subsurface transport due to differential sorption of the individual surfactant components (Istok et al., 1999; Krueger et al., 1998). This findings indicate the potential for spatial variation in surfactant concentrations (e.g., the presence of micelles) and hence varying abilities of the surfactant to enhance the solubility of residual DNAPL. An additional complication can occur when injected surfactants are used to mobilize residual DNAPL. If surface tension is reduced sufficiently, buoyancy forces may cause mobilized DNAPL to sink into underlying sediments before it can be recovered by extraction wells. Clearly, the successful design of a surfactant-enhanced DNAPL recovery system requires a quantitative understanding of the competing processes of DNAPL solubilization and mobilization, sorption, precipitation, and ion exchange.

Traditionally, this information has been obtained in small-scale laboratory studies that utilize batch, column, and microcosm reactors. Although these methods are convenient, they have several disadvantages including the need for samples of subsurface material from the site, typically small and potentially unrepresentative volumes of such samples, the potential for

disturbance and contamination of subsurface material during core collection, and the difficulty in reproducing all relevant field conditions in an artificial laboratory environment.

In an attempt to overcome these limitations and those inherent in batch solubilization experiments, an *in-situ* site-characterization technology, called the "push-pull" test, is being developed for use in obtaining site-specific information on surfactant-enhanced solubilization of NAPL (Istok et al., 1997; Schroth et al., 1998). A push-pull test consists of the controlled injection of a prepared test solution into a single monitoring well followed by the recovery of the test solution/groundwater mixture from the same well (Istok et al., 1997). The test solution consists of water containing a tracer and one or more reactive solutes; the type, combination, and concentration of these solutes are selected to investigate specific aquifer characteristics. During the injection phase, the prepared test solution is injected ("pushed") into the saturated zone of an aquifer using an existing monitoring well; during the extraction phase, the test solution/groundwater mixture is extracted ("pulled") from the same location. Water samples collected during the extraction phase are analyzed to prepare breakthrough curves for each solute, which are then interpreted to obtain quantitative information on the transport and/or rate of transformation of injected solutes (Haggerty et al., 1998).

Field trial results indicate that the push-pull test has many potential advantages over existing methods for aquifer characterization and feasibility assessment that make it particularly well suited for use in evaluating the effectiveness of surfactant-enhanced DNAPL recovery technologies. The composition of the injected test solution can be designed to investigate a wide range of aquifer characteristics including physical (e.g., effective porosity and dispersivity), chemical (e.g., sorption, ion exchange, and oxidation-reduction reactions), and microbial processes (e.g., primary substrate utilization or cometabolism). Because a push-pull test is performed in a single well, the time required to complete a test is much shorter than methods that require injected test solutions to flow from an injection well to downgradient monitoring wells (i.e., natural gradient test methods). Also, because the test does not require the collection of new core material, the method can utilize the large number of existing monitoring wells available at most sites, further reducing site characterization costs. Push-pull tests can be designed to investigate a much larger volume of aquifer material (tens to hundreds of liters) and can therefore potentially provide more representative information about subsurface conditions than laboratory studies performed on typically much smaller core samples. A series of replicate push-pull tests can be performed in a single well to quantify the fate and transport behavior of injected solutes at that location. Alternatively, a series of identical push-pull tests can be performed in several wells at a site to quantify site-scale variability in these processes. An important additional advantage of the push-pull test method is the ability to obtain quantitative mass balances for all injected/extracted surfactants and solubilized and/or mobilized DNAPL components so that the effectiveness of specific surfactant formulations can be rigorously evaluated.

The overall goal of this project is to further develop the single-well, “push-pull” test method as a site characterization and feasibility assessment tool for studying the fundamental fate and transport behavior of injected surfactants and their ability to solubilize and mobilize DNAPLs in the subsurface. The specific objectives were:

1. to develop a modified “push-pull” test for use in identifying and quantifying the effects of sorption, precipitation, and biodegradation on the fate and transport of injected surfactants,
2. to use the developed test method to quantify the effects of these processes on the ability of injected surfactants to solubilize and mobilize residual phase trichloroethene (TCE), and

3. to demonstrate the utility of the developed test method for performing site characterization and feasibility studies for surfactant-enhanced DNAPL recovery systems in the field.

To address the three objectives, the research plan combines controlled intermediate-scale laboratory experiments in unique physical aquifer models with a parallel series of pilot-scale field experiments in existing monitoring wells at selected trichloroethene (TCE) contaminated field sites.

METHODS AND RESULTS

Sorption to aquifer sediments can limit the effectiveness of surfactants injected to solubilize residual nonaqueous phase liquid contaminants in the subsurface. The first set of experiments was conducted to evaluate the ability of the single-well, push-pull test to characterize sorption of LAS and DOWFAX surfactants to natural aquifer sediment *in-situ*. The results demonstrated the ability of the push-pull test to characterize sorption of linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactants to natural aquifer sediment under laboratory and *in-situ* field conditions. Increased retardation and chromatographic separation of the LAS surfactant components (i.e., homologs) relative to Br^- observed during laboratory push-pull tests could not be accurately described by numerical transport simulations based on fitted sorption isotherms obtained from batch sorption experiments. Better agreement was obtained between simulated and observed breakthrough curves for DOWFAX; however, simulations predicted slight retardation for DOWFAX that was not observed in either laboratory or field push-pull tests. We attribute these differences to the inability of batch sorption isotherms to accurately represent *in-situ* conditions. In particular, simulations based on batch sorption isotherms produced for a commercial surfactant mixture can not accurately describe surfactant transport when the composition of the surfactant mixture changes (e.g. due to chromatographic separation) during transport. Moreover, equilibrium sorption isotherms produced in batch experiments cannot describe the kinetically-limited sorption of a surfactant, which can potentially occur during transport in the highly non-uniform pore water velocity field around an injection well.

Generally close agreement was observed for extraction phase breakthrough curves for LAS and DOWFAX in laboratory and field push-pull tests. Retardation and chromatographic separation of LAS homologs observed in breakthrough curves and mass recovery plots from laboratory push-pull tests were clearly visible in breakthrough curves and mass recovery plots for field push-pull tests conducted *in-situ*. Based on the results of this study, the single-well, push-pull test appears to be a useful method for obtaining site-specific information on the sorption behavior of injected surfactants (or other solutes). The method can be applied in existing monitoring wells without the need for sediment cores and appears to provide results that are more representative of *in-situ* conditions than laboratory batch sorption experiments. It should also be noted that the laboratory and field push-pull tests confirmed that information on sorption characteristics of an injected solute can be obtained from only the extraction phase breakthrough curve from a *singl*e well; no additional monitoring wells are needed to facilitate data interpretation. The method should be particularly useful for selecting and evaluating surfactants as part of a feasibility assessment. In addition, the method can be used to perform small-scale pilot tests because the test conditions closely approximate those occurring in the vicinity of injection wells that will be used in full-scale surfactant-enhanced NAPL recovery systems. The method also provides a simple and rapid method for characterizing the *in-situ* transport behavior of any solute without the need for sediment cores.

The second set of experiments was conducted to evaluate the ability of the push-pull test to characterize enhanced solubilization of trichloroethene (TCE) by a hexadecyl diphenyl oxide disulfonate (DOWFAX) surfactant. The results of intermediate-scale laboratory experiments indicate that the single-well, push-pull test method can provide quantitative information on the effectiveness of injected surfactants in enhancing liquid TCE solubilization in natural aquifer sediments. Push-pull test extraction phase breakthrough curves were used (1) to examine surfactant transport behavior relative to that of a coinjected tracer (e.g., Br^-); (2) to determine the recovery efficiency of the injected surfactant, and (3) to quantify the increase in aqueous TCE solubility due to injected surfactant.

Batch solubilization experiments indicated a linear relationship between TCE solubility and DOWFAX concentration characterized by weight- and molar-solubilization ratios of 0.26 and 1.25, respectively. Laboratory push-pull tests were performed in wedge-shaped physical aquifer models to simulate the alternating radially divergent/convergent flow field in the vicinity of an injection/extraction well. Experiments were conducted in a TCE-free sediment pack and in a sediment pack initially containing liquid TCE with an initial saturation of ~ 5 % of the total pore volume. In an experiment conducted in the absence of DOWFAX, maximum TCE concentrations during the extraction phase were ~ 0.6 g/L. In contrast, in an experiment conducted with 13.5 g/L active DOWFAX, TCE concentrations during the extraction phase increased to ~ 3.2 g/L and TCE mass recovery increased by a factor of ~ 3. Two additional experiments conducted with DOWFAX in the same sediment pack yielded smaller maximum TCE concentrations and mass recoveries. The increased density of injected DOWFAX solutions due to TCE solubilization resulted in significant sinking of injected solutions and an accumulation of DOWFAX and TCE at greater depths in the sediment pack; however, no mobilization or sinking of liquid TCE was observed. This type of sinking can be alleviated by reducing the density of the injected surfactant solution, which was the subject of the next set of experiments.

A third set of experiments was conducted to evaluate the influence of cation exchange on the solubilization of residual trichloroethene (TCE) by the surfactant sodium dihexyl sulfosuccinate (Aerosol MA 80-I). Laboratory transport experiments were conducted using natural aquifer sediment collected or obtained from a TCE-contaminated field site. The test solution consisted of 36,800 mg/L sulfosuccinate surfactant, 100,000 mg/L isopropanol, and 3,200 mg/L KBr. Laboratory experiments were designed to simulate conditions occurring during field push-pull tests. In batch experiments conducted in the presence of excess TCE, the test solution gave a Winsor Type I system with an enhanced aqueous TCE solubility of 26,700 mg/L and a solution density of 1.0000 g/cm^3. The sulfosuccinate surfactant was transported conservatively in sediment packs containing no TCE; however, increased concentrations of Ca^{2+} and Mg^{2+} were observed due to cation exchange between the injected sulfosuccinate surfactant and the aquifer sediments. Sulfosuccinate surfactant transport was strongly retarded in sediment packs containing 5 vol % residual TCE because cation exchange in the presence of liquid TCE resulted in the formation of a Winsor Type II system, which resulted in the partitioning of the sulfosuccinate surfactant into the stationary (residual) TCE phase. Conservative sulfosuccinate transport was observed in a separate sediment pack containing 5 vol % residual TCE when a 130 mM NaCl pre-flush was used to reduce quantities of Ca^{2+} and Mg^{2+} in the sediment pack prior to sulfosuccinate injection. The results of this study emphasize the potentially detrimental effects of cation exchange on surfactant performance and enhanced TCE solubilization and demonstrate the

utility of the push-pull test for predicting the potential for cation exchange to affect surfactant phase behavior in the presence of residual TCE.

In the final set of experiments conducted for this project, we examined the ability of a modified push-pull test method for predicting cation exchange and the effects it will have on surfactant performance *without* the addition of surfactants to the subsurface. Our approach consisted of injecting a simple salt solution to displace divalent cations from the sediment, which simulated what would occur if a surfactant and its attendant salt were injected. Three physica aquifer models were packed with clean silica sand and two natural sediments. Injected test solutions contained 30 mM KBr to simulate the amount of salt typically added to the anionic surfactant Aerosol MA 80-I to promote Winsor Type I phase behavior and optimal TCE solubility. Porewater samples were collected from the sediment pack and analyzed for Na^+, K^+, Ca^{2+}, Mg^{2+}, and Br^-. In addition, the collected samples were combined with surfactant (Aerosol MA 80-I) and liquid TCE outside the sedimnent pack and were analyzed for aqueous phase surfactant and TCE concentrations. Samples collected during experiments conducted in clean silica sand, which had minimal cation exchange capacity, had low divalent/monovalent cation ratios and gave aqueous phase TCE concentrations essentially identical to those predicted from batch solubilization isotherms. In contrast, samples collected during experiments conducted in both natural sediments (which had similar cation exchange capacities of approximately 20 meq/100 gm) had divalent/monovalent cation ratios large enough to cause aqueous phase TCE concentrations to exceed those predicted from the batch isotherm. In previous work with these sediments and surfactant, the occurrence of TCE solubilization potentials larger than those predicted by the batch isotherm corresponded with the formation of Winsor Type II behavior and the partitioning of injected surfactant into the residual TCE phase. Thus, a push-pull test conducted with a low concentration of salt can be used as a low risk, low cost tool for predicting the deleterious effects of cation exchange on surfactant effectiveness.

RELEVANCE, IMPACT AND TECHNOLOGY TRANSFER

The results from the intermediate-scale laboratory experiments conducted for this project indicate that the single-well, push-pull test method can provide quantitative information on the effectiveness of injected surfactants in enhancing liquid TCE solubilization in natural aquifer sediments. Push-pull test extraction phase breakthrough curves can be used (1) to examine surfactant transport behavior relative to that of a coinjected tracer; (2) to determine the recovery efficiency of an injected surfactant, and (3) to quantify the increase in aqueous TCE solubility due to injected surfactant. Specifically, the results of this research demonstrate the ability of the single-well, push-pull test to characterize sorption of multi-component surfactants to natural aquifer sediment under laboratory and *in-situ* field conditions. For example, numerical simulations based on batch sorption isotherm data could not accurately describe surfactant transport when the composition of the surfactant mixture changed (e.g. due to chromatographic separation) during transport. In addition, equilibrium sorption isotherms produced in batch experiments cannot describe the kinetically-limited sorption of a surfactant that potentially occurs during transport in the highly nonuniform pore water velocity field around an injection well. For these reasons, the single-well, push-pull test appears to be a useful method for obtaining site-specific information on the behavior of injected surfactants. Our results demonstrate the utility of the push-pull test for predicting the deleterious effects of cation exchange on surfactant-enhanced DNAPL solubilization. Alternatives, such as pre-flushing, were

explored to minimize cation exchange. However, reduced interfacial tensions resulted in mobilization of residual TCE and the formation of an "oil bank", which may be undesirable under field conditions.

The method can be applied in existing monitoring wells without the need for sediment cores and appears to provide results that are more representative of *in-situ* conditions than laboratory batch sorption experiments. It should also be noted that the laboratory and field push-pull tests confirmed that data obtained on sorption characteristics of an injected solute can be obtained from only the extraction phase breakthrough curves, without the need for observations at additional monitoring wells. The method should be particularly useful for selecting and evaluating surfactants as part of a feasibility assessment. In addition, the method can be used to perform small-scale pilot tests because the test conditions closely approximate those occurring in the vicinity of injection wells that will be used in full-scale surfactant-enhanced DNAPL recovery systems. The method also provides a simple and rapid method for characterizing the *in-situ* transport behavior of any solute without the need for sediment cores. Because it often is difficult and expensive to obtain sediment cores, it is a distinct advantage to have a test method that can utilize existing wells. Therefore, the push-pull test can reduce the costs and risks associated with surfactant-enhanced remediation. The intermediate-scale nature of the push-pull test is useful for identifying problems before going to the full-scale demonstration phase. Alternatives to injecting surfactants, such as injecting only salt solutions, offers additional reductions in risk associated with injecting chemicals at an actual DOE site. Our work on cation exchange has highlighted a potential problem for surfactant-enhanced remediation technology that had previously received little attention. However, this problem was previously recognized by investigators within the field of enhanced-oil recovery.

This research bridges between the fundamental work done on surfactant phase behavior and solubilization and the immediate need for field-scale demonstrations of the surfactant-enhanced remediation. Intermediate-scale technology was identified as a priority in order to minimize the risks associated with the technology and to improve the likelihood of success prior to conducting full-scale remediation projects. With the project completed, a field-ready technology is now at the disposal of groups, including collaborators, whose efforts are aimed at full field-scale implementation of surfactant-enhanced remediation. Under "Transitions", we list two independent groups that have expressed an interest in the technology developed as a result of this research.

The principal hurdle to implementing this technology on a wider scale is the availability of field tests sites within the DOE complex. Additional funds also are needed to expand the concept that simple salt injections can be performed to predict the potential for cation exchange and its impact on surfactant phase behavior and NAPL solubilization.

PROJECT PRODUCTIVITY

We achieved our stated project goals; however, we would like to have had more opportunities to conduct field experiments at DOE sites.

PERSONNEL SUPPORTED

Dr. Jonathan Istok, Department of Civil, Construction, and Environmental Engineering-Principal Investigator

Dr. Jennifer Field, Department of Environmental and Molecular Toxicology, Oregon State- Co-Principal Investigator

Dr. Martin Schroth, Faculty Research Assistant, Department of Civil, Construction, and Environmental Engineering- assisted in modeling field and laboratory physical aquifer model experiments

Dr. Ralph Reed, Research Associate, Department of Environmental and Molecular – conducted surfactant and TCE analyses

Mark Humphrey, Research Assistant, Department of Civil, Construction, and Environmental Engineering- assisted in field and laboratory experiments and conducted inorganic chemical analysis

Tom Sawyer, Research Assistant, Department of Environmental and Molecular Toxicology- analytical methods development, assisted in laboratory and field experiments, and conducted surfactant and TCE analysis

PUBLICATIONS

Field, J.A., Humphrey, M.D., Reed, R.R. and J.D. Istok. 199X. A Single-Well Test for Predicting Effects of Cation Exchange on Surfactant Phase Behavior and TCE Solubilization Potential. In preparation for submission to the journal Ground Water.

Field, J.A., T.E. Sawyer, M.H. Schroth, and J.D. Istok. 199X. Effect of Cation Exchange on Surfactant Enhanced Solubilization of Trichloroethene. Submitted to Journal of Contaminant Hydrology

Schroth, M.H., J.D. Istok, and R. Haggerty. 199X. *In-situ* Evaluation of Solute Retardation Using Single-Well Push-Pull Tests". Submitted to Journal of Hydrology.

Field, J.A., J.D. Istok, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey. 1999. Laboratory Investigation of Surfactant-Enhanced TCE Solubilization Using Single-Well, "Push-Pull" Tests. Ground Water, 37, 581-588.

Istok, J.D., J.A. Field, M.H. Schroth, T.E. Sawyer, and M.D. Humphrey. 1999. Laboratory and Field Investigation of Surfactant Sorption Using Single-Well, "Push-Pull" Tests. Ground Water, 37, 589-598.

Field, J.A. and J.D. Istok. 1998. Comment on Estimation of Nonaqueous Phase Liquid-Water Interfacial Areas in Porous Media Following Mobilization by Chemical Flooding. Environmental Science and Technology, Vol. 32, No. 2, pp. 3836-3837.

INTERACTIONS

The principal and co-principal investigators of this EMSP project attended the EMSP workshops during the grant period. Our research benefited significantly from interactions with other PIs at these workshops. For example, the surfactants selected for our research were a direct extension of our conversations with other EMSP investigators. Our research group traveled to Austin, TX in order to present a seminar to Dr.Gary Pope, who is also an EMSP investigator and the Department of Petroleum Engineering on the push-pull test and its use for investigating surfactant-enhanced DNAPL recovery. While in Austin, Dr. Field presented a seminar on the environmental fate of surfactants to Vista Chemical Co., a producer of linear alkylbenzenesulfonates, which is a class of surfactants used for this research project. Lastly, both oral and poster presentations were made

during the project period to disseminate the findings of our EMSP research project. These presentations include:

Oral presentations:

Swiss Federal Institute for Environmental Science and Technology "Surfactant-enhanced dense nonaqueous phase recovery: characterizing surfactant behavior with single-well push-pull tests", Dübendorf, Switzerland, April 1999.

Istok, J.D., J.A. Field, M.D. Humphrey, K.M. Radakovich, T.E. Sawyer, and M.H. Schroth. Evaluation of Surfactant-Enhanced DNAPL Recovery Using Single-Well "Push-Pull" Tests." Fall Meeting of the American Geophysical Union, San Francisco, California, Dec. 8-12, 1997.

Poster presentations:

Field, J.A., J.D.Istok, M.D. Humphrey, T.E. Sawyer, M.H. Scroth. Impact of ion exchange on anionic surfactant-enhanced trichloroethene solubilization. San Francisco, CA, American Geophysical Union. Dec. 7-10, 1998.

Humphrey, M.D., J.A. Field, J.D. Istok, M.J. Kelley, K.M. Radakovich, T.E. Sawyer, and M.H. Schroth. Intermediate-Scale Physical Aquifer Models: An Investigative Tool for Contaminant Behavior Processes. Fall Meeting of the American Geophysical Union, San Francisco, California, Dec. 8-12, 1997.

Sawyer, T.E., J.A. Field, M.D. Humphrey, J.D. Istok, and M.H. Schroth. Quantifying Surfactant Sorption/Desorption Behavior in Natural Aquifer Sediments Using Push-Pull Tests in Physical Aquifer Models. Fall Meeting of the American Geophysical Union, San Francisco, California, Dec. 8-12, 1997.

Schroth, M.H., J.A. Field, R. Haggerty, M.D. Humphrey, J.D. Istok, M.J. Kelley, K.M. Radakovich, and T.E. Sawyer. *In-situ* Estimation of Solute Retardation in Aquifers Using Single-Well "Push-Pull" Tests. Fall Meeting of the American Geophysical Union, San Francisco, California, Dec. 8-12, 1997.

TRANSITIONS

Knowledge gained from this project potentially will be used by SURBEC-ART Environmental LLC in Norman, OK, which is a private consulting firm that specializes in surfactant-enhanced DNAPL recovery systems. Dr. Mark Hasagawa from SURBEC-ART Environmental is interested in implementing the push-pull technology as a field-scale test system in some of their surfactant-based remediation projects. Dr. Varadarajan Dwarakanath of Duke Engineering Systems and Services in Austin, TX also has indicated interest in implementing an analytical method that was developed specifically for this project, which simultaneously determines surfactants and TCE using high performance liquid chromatography. Throughout this project, we have engaged Dr. Gary Pope of the Department of Petroleum engineering at the University of Texas at Austin, who is a recognized leader in the subject of surfactant-enhanced oil (and DNAPL) recovery, in a series of discussions from which our project has benefited significantly.

PATENTS

No patents resulted from this research.

FUTURE WORK

The subject of our manuscript in preparation (see Publications) discusses the potential for conducting field-scale experiments to determine the potential for cation exchange and any deleterious effects that it may have upon surfactant phase behavior and efficacy for enhancing DNAPL solubility. We are interested in exploring the possibility of conducting push-pull tests in the field in support of the hypothesis that low risk, salt-only, push-pull tests can be used to predict surfactant performance *in-situ*. While laboratory experiments demonstrate the utility of this approach, field-scale tests are necessary to demonstrate this concept at the field scale.

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FEEDBACK

As principal investigators on this EMSP project, we feel that the project was managed quite well starting with a timely review and rapid decision process. The EMSP workshops were timely and informative due to the high rate of EMSP investigator attendance. However, it was not entirely clear how the various research projects and their potential for field implementation were communicated to the managers of DOE sites.

APPENDICES

None.