Progress Report to:

Environmental Management Sciences Program
U.S. Department of Energy

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

Submitted by:

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Motivation and Objectives

Surfactant enhanced DNAPL recovery involves the use of injected surfactants to increase the solubility and/or mobility of DNAPL in the subsurface 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, and sorption, precipitation, and microbial degradation of injected surfactant components. **An innovative new site-characterization technology, the single-well, "push-pull" test method,** is currently under development at Oregon State University and has been successfully 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 type, combination, and concentration of injected solutes is selected to investigate specific aquifer characteristics.

The overall goal of this project is to further develop the single-well, "push-pull" test method as a new 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 are:

(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,

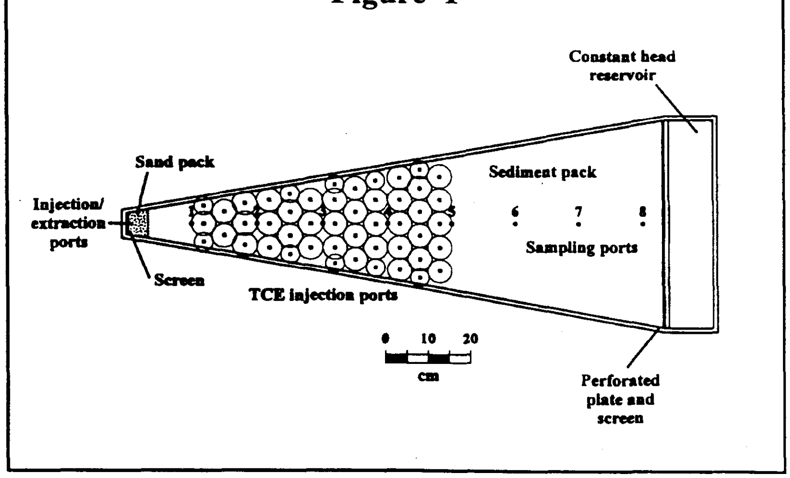
(2) to use the developed test method to quantify the effects of these processes on the ability of injected surfactants to solubilize and mobilize residual phase trichloroethylene, and

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

Progress

Laboratory and field push-pull tests have been performed using linear alkylbenzene sulfonate (LAS) and hexadecyl diphenyl oxide disulfonate (DPDS) surfactants. Laboratory push-pull tests were performed in unique intermediate-scale, physical aquifer models designed to simulate the alternating diverging/converging radial flow surrounding a well during a field test (shown in plan view in Fig. 1). The models were packed with **natural aquifer sediment** from the Building 834 (Site 3OO)operable unit at **Lawrence Livermore National Laboratory (LLNL).** Experiments were performed in clean sediment and sediment containing 5 vol. % residual DNAPL (trichloroethene or TCE).

Figure 1



The push-pull test method was completely successful in identifying, characterizing, and quantifying the sorption of injected surfactants to aquifer sediments. Example breakthrough curves for the extraction phase of two tests are representative of the results obtained. LAS displayed strong sorption and chromatographic separation of the four principal alkyl chain length homologs (C_{10}, C_{11}, C_{12}, C_{13}) but DPDS displayed essentially conservative transport when compared to a co-injected bromide tracer (Figs. 2,3). These results ate consistent with batch sorption data and with results of injection phase sampling (data not shown).

Figure 2

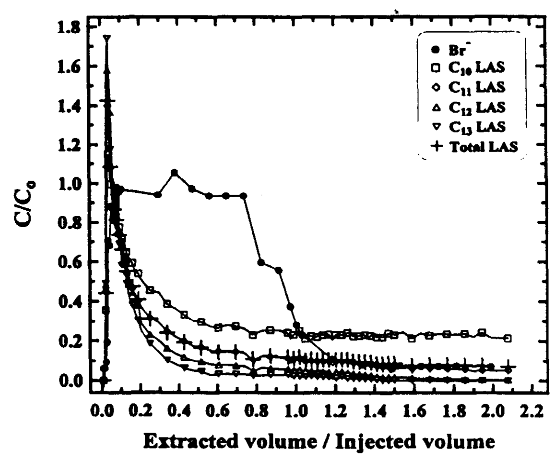
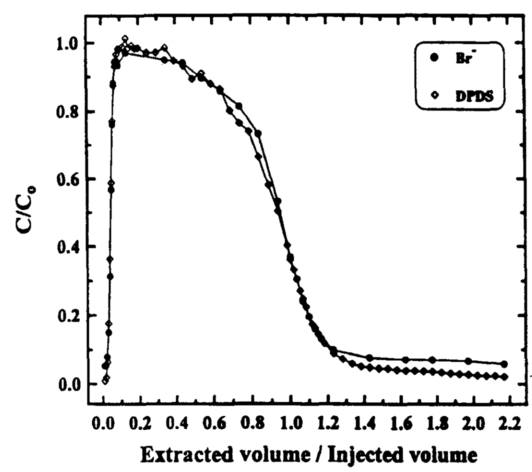
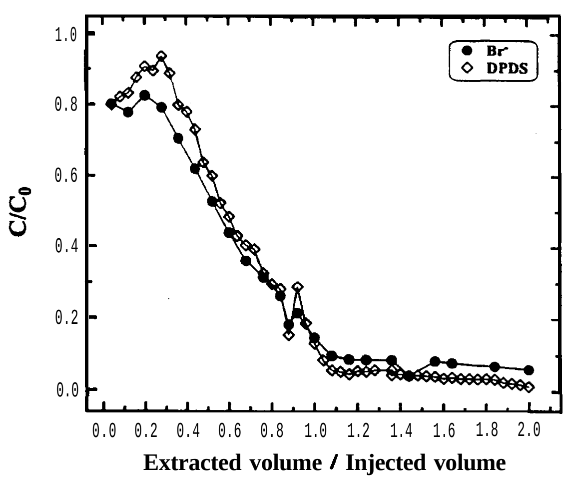


Figure 3



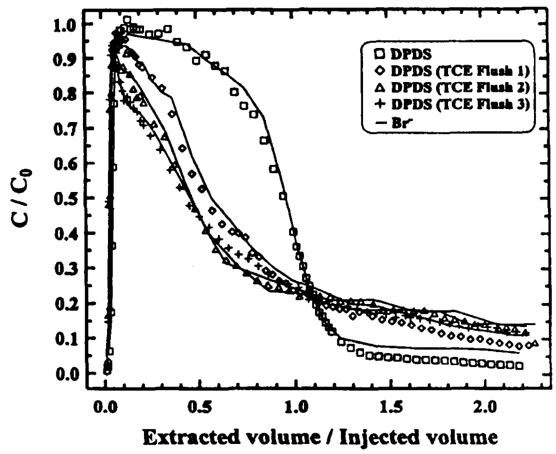
Similar results were obtained in a series of field push-pull tests. An example of the breakthrough curves obtained during the extraction phase of push-pull tests conducted at Site 300 illustrates that, in this aquifer, DPDS transport is conservative (Fig. 4). Additional push-pull tests are being conducted at the site to screen other potentially useful surfactants for use in surfactant enhanced DNAPL recovery at this site.

Figure 4



Additional laboratory push-pull tests have been conducted to evaluate the ability of the method to quantify enhanced TCE solubility in the presence of DPDS. Sediment packs were prepared with 5 vol. % residual TCE by injecting TCE into ports installed in the model lid (Fig. 1). Then a series of push-pull tests were conducted with a 4 wt % DPDS solution. DPDS transport in the presence of residual TCE was conservative for all tests (Fig. 5). The curve labeled "DPDS" is for the sediment pack with no residual TCE; the three additional curves are for repeated push-pull tests ("Flush l", "Flush 2", and "Flush 3"). **In each case, DPDS and bromide breakthrough curves are identical indicating conservative transport of DPDS.** TCE breakthrough curves clearly illustrate the ability of the push-pull test method to rapidly evaluate the ability of DPDS to enhance TCE solubility (Fig. 6). In Figure 6, the curve labeled "water flush" shows the TCE concentrations obtained during a push-pull test conducted with only water and bromide tracer (no DPDS). Maximum aqueous TCE concentrations of ~ 500 mg/L were obtained from the TCE contaminated sediment pack.

Figure 5



However, in the presence of DPDS, **maximum** TCE **concentrations increased to ~** 3200 **mg/L,** which is consistent with the results of batch solubilization experiments conducted with these materials. In subsequent DPDS push-pull tests, maximum TCE concentrations decreased as additional TCE was removed from the sediment pack ("Flush 2, 3 in Figure 6). The results are plotted as mass recoveries in Fig. 7 and clearly show how the use of DPDS initially increased the mass of TCE removed during the test and how the recovered TCE mass decreased in subsequent tests. **These data are being used to evaluate the economic viability of using surfactant enhanced** TCE **recovery at LLNL Site 300.**

Figure 6

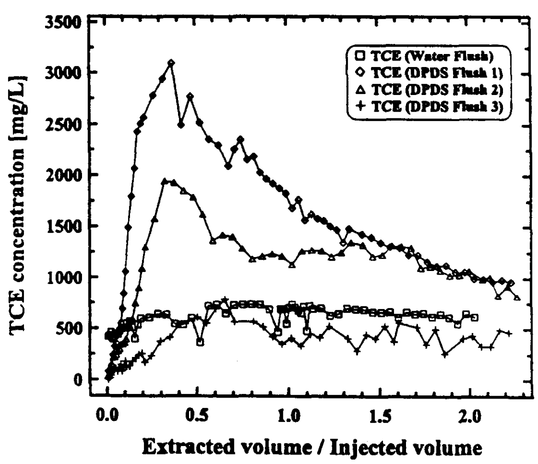
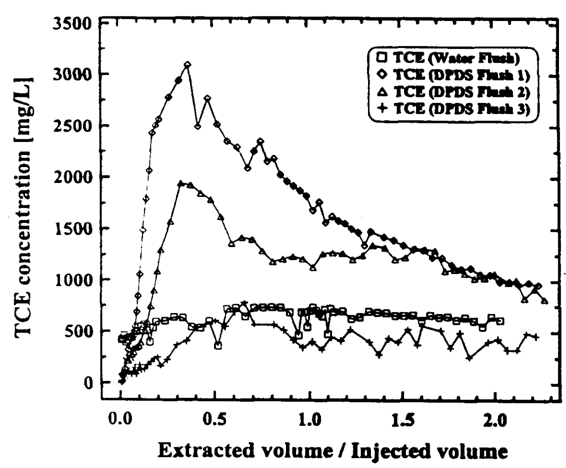


Figure 7



Future plans

Numerical models are being used to develop simplified procedures for interpreting push-pull test breakthrough curves to obtain sorption parameters for injected surfactants (linear and Langmuir-type isotherms) and to obtain solubilization potential for TCE. Additional field push-pull tests are planned for this month at LLNL with DPDS and at least one other surfactant. Additional laboratory and field push-pull tests will be conducted this year using middle-phase, and neutral buoyant surfactant formulations. The push-pull test methodology is also being extended for use in quantifying biodegradation of injected surfactants by indigenous microorganisms as well as the effect of injected surfactant on the metabolic activity of indigenous microorganisms.