

## Surfactant enhanced remediation of soil columns contaminated by residual tetrachloroethylene

Kurt D. Pennell<sup>a,\*</sup>, Minquan Jin<sup>b</sup>, Linda M. Abriola<sup>a</sup>, Gary A. Pope<sup>b</sup>

<sup>a</sup>*Department of Civil and Environmental Engineering, The University of Michigan, Ann Arbor, MI 48109, USA*

<sup>b</sup>*Department of Petroleum Engineering, University of Texas at Austin, Austin, TX 78712, USA*

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### Abstract

The ability of aqueous surfactant solutions to recover tetrachloroethylene (PCE) entrapped in Ottawa sand was evaluated in four column experiments. Residual PCE was emplaced by injecting <sup>14</sup>C-labeled PCE into water-saturated soil columns and displacing the free product with water. Miscible displacement experiments were conducted before and after PCE entrapment to determine the influence of residual PCE on column dispersivities. The first two column studies involved the injection of a 4% solution of polyoxyethylene (POE) (20) sorbitan monooleate, resulting in the removal of 90% and 97% of the residual PCE from 20-30- and 40-120-mesh Ottawa sand, respectively. Although micellar solubilization of PCE was the primary mode of recovery in these experiments, this process was shown to be rate-limited based on: (a) the disparity between initial steady-state concentrations of PCE in the column effluent and equilibrium values measured in batch experiments; and (b) the increase in effluent concentrations of PCE following periods of flow interruption. In the latter two experiments, surfactant solutions containing mixtures of sodium sulfosuccinates removed > 99% of the residual PCE from soil columns packed with 40-270-mesh Ottawa sand. Approximately 80% of the PCE was mobilized as a separate organic liquid after flushing with < 100 mL of these surfactant solutions. This study demonstrates the capacity of surfactant flushing to enhance the recovery of residual PCE from Ottawa sand and indicates that ultra-low interfacial tensions (< 0.001 dyn cm<sup>-1</sup>) are not required to achieve significant PCE mobilization when buoyancy forces are important. The potential for displacement of dense nonaqueous-phase liquids as a separate organic phase should, therefore, be evaluated during the selection of surfactant formulations for aquifer remediation.

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## 1. Introduction

The contamination of groundwater by organic solvents and other petroleum products has become a major environmental concern throughout the U.S.A. These compounds frequently enter the subsurface as a separate organic-phase or non-aqueous-phase liquid (NAPL). As the NAPL is transported downward due to gravitational and capillary forces, a portion of the organic liquid may be retained in soil pores as immobile globules or ganglia, due to interfacial forces. This residual organic liquid frequently represents a long-term source of aquifer contamination as it dissolves into groundwater or infiltrating rainwater.

It is widely recognized that pump-and-treat methods are neither an effective nor economical means of recovering residual NAPL's from contaminated aquifers. The inefficiency of this technique is attributed to the low aqueous solubility of most NAPL's and the relatively large interfacial tension between groundwater and NAPL's, which prevents the displacement of residual NAPL globules at realistic pumping velocities. The use of aqueous surfactant solutions in conventional pump-and-treat systems has been proposed as a means of enhancing the removal of NAPL's from contaminated aquifers. This approach capitalizes on the ability of surfactants to: (a) increase the apparent solubility of NAPL's; and (b) reduce the interfacial tension between the aqueous and organic phases sufficiently to induce mobilization of residual organic liquids.

Surfactant washing has been used to facilitate the removal of sorbed and deposited polychlorinated biphenyls (PCB's), polycyclic aromatic hydrocarbons (PAH's), and diesel fuel from soil materials (e.g., Gannon et al., 1989; Vigon and Rubin, 1989; Abdul and Gibson, 1991; Peters et al., 1992). The success of this technique can be attributed to the capacity of surfactants, at concentrations above the critical micelle concentration (CMC), to dramatically enhance the aqueous solubility of hydrophobic organic compounds (e.g., Saito and Shinoda, 1967; Kile and Chiou, 1989; Edwards et al., 1991; West, 1992). Almost 20 years ago it was recognized that surfactant-based technologies could be employed to enhance the recovery of NAPL's from subsurface environments (Schwille, 1975). However, subsequent laboratory and field tests of such technology achieved mixed results (e.g., TRI, 1985; Nash, 1987; Ziegenfuss, 1987). More recently, Ang and Abdul (1991) demonstrated that surfactant flushing could increase the removal of automatic transmission fluid from soil columns with initial organic saturations ranging from 34% to 41%. Surfactant flushing was also successfully employed by Pennell et al. (1993) to enhance the recovery of residual dodecane via micellar solubilization. To date, few studies have explored the use of surfactants for the recovery of dense NAPL's (DNAPL's). Fountain et al. (1991) identified several surfactant formulations that were capable of diminishing "pools" of tetrachloroethylene (PCE) in soil columns. These column studies, however, did not directly address the recovery of an entrapped DNAPL phase.

The purpose of the present work was to test the ability of several surfactants to recover a DNAPL, PCE, which was entrapped in soil columns at residual levels. Three surfactant formulations, a polyoxyethylene (POE) sorbitan monooleate and two mixtures of sodium sulfosuccinates were employed in the column studies. The

surfactants were selected for use based on their phase behavior and capacity to solubilize PCE, and to provide a range of interfacial tensions between the surfactant solution and PCE. The primary objectives of the research were to: (a) quantify the recovery of residual PCE from soil columns; and (b) to determine the proportion of PCE mobilized (displaced) as a separate organic phase vs. that solubilized in aqueous micellar solutions. In the application of surfactant enhanced remediation, the potential for inadvertent or uncontrolled mobilization of NAPL's is an issue of concern. This is particularly relevant to DNAPL's which, upon mobilization, would tend to migrate downward to less accessible zones within a formation. Therefore, data obtained from the soil column experiments are used to assess the onset and extent of PCE mobilization during surfactant flushing.

## 2. Experimental methods

### 2.1. Materials

The following surfactant formulations were utilized in the soil column experiments: POE (20) sorbitan monooleate, a 1:1 mixture of sodium diamyl sulfosuccinate and sodium dioctyl sulfosuccinate, and a 4:1 mixture of sodium dihexyl sulfosuccinate and sodium dioctyl sulfosuccinate. POE (20) sorbitan monooleate is a nonionic surfactant commonly used in food and pharmaceutical products and was supplied by the Witco Corp. Sodium diamyl, dihexyl and dioctyl sulfosuccinate are anionic surfactants and were obtained from American Cyanamid. All of the surfactants were used as received from the manufacturer, except for sodium dihexyl sulfosuccinate which was distilled to remove water and ethanol. PCE was employed as the nonaqueous-phase liquid, and is representative of the chlorinated solvents commonly reported as groundwater contaminants. PCE has a density of  $1.63 \text{ g cm}^{-3}$  and an aqueous solubility of  $\sim 200 \text{ mg L}^{-1}$  at  $25^\circ\text{C}$  (Gillham and Rao, 1990). Spectro-grade PCE was obtained from Fisher Scientific, while  $^{14}\text{C}$ -labeled PCE was purchased from Sigma Chemical. Tritiated water ( $^3\text{H}_2\text{O}$ ), a nonreactive tracer, was obtained from American Radio-labeled Chemicals. All aqueous solutions were prepared with deionized, distilled water that had passed through a Nanopure<sup>®</sup> purification system (Barnstead/Thermolyne Corp.) to remove organic contaminants. Ottawa sand, a nonporous silica sand, was used as the solid matrix for the column experiments. The 20–30- and 40–270-mesh size fractions were obtained from Fisher Scientific and U.S. Silica (F-95), respectively. Prior to use, the Ottawa sand was rinsed with 0.1 *N* HCl and Nanopure<sup>®</sup> water.

### 2.2. Soil column procedures

Soil column experiments were performed at the University of Michigan and the University of Texas at Austin to measure the capacity of 4% (w/w) solutions of POE (20) sorbitan monooleate and mixtures of sodium sulfosuccinates, respectively, to recover residual PCE from Ottawa sand. Similar experimental protocols, based on

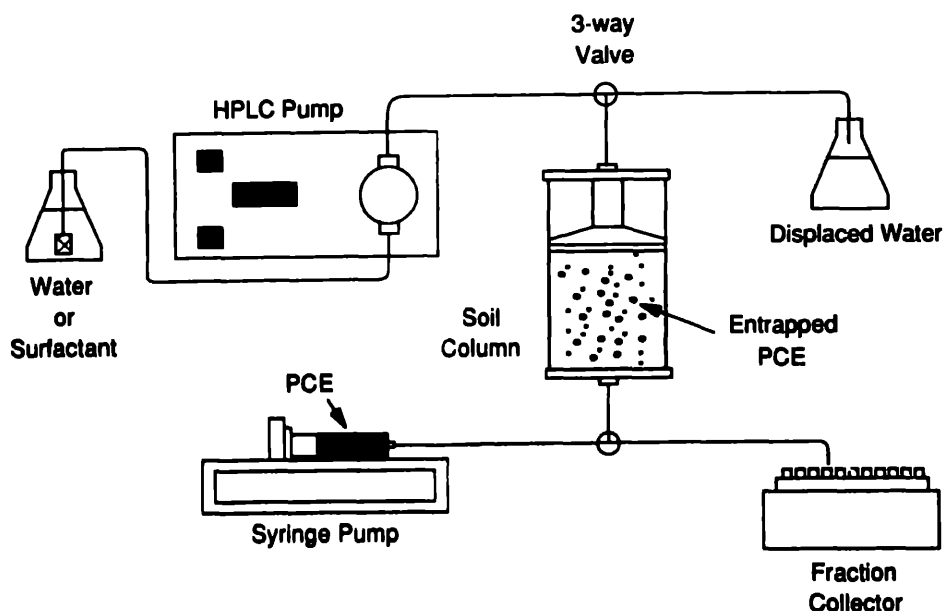


Fig. 1. Schematic diagram of soil column apparatus used for the surfactant flushing experiments.

procedures described by Pennell et al. (1993), were followed in both laboratories. The column apparatus consisted of a Kontes<sup>®</sup> preparative chromatography column made of borosilicate glass (4.8-cm i.d.) equipped with a single column adapter that allowed the bed length to be adjusted from 1 to 13 cm (Fig. 1). The soil columns were oriented in the vertical direction throughout each experiment. Column endplates were fitted with a 40-mesh polytetrafluoroethylene (PTFE) screen to enhance radial distribution at the column inlet and to reduce dispersion at the outlet. All connections to the columns were made with either stainless-steel or Teflon<sup>®</sup> tubing to minimize interactions with PCE.

The soil columns prepared at the University of Michigan were packed under vibration with either 20–30- or 40–120-mesh Ottawa sand. Soil columns containing 40–120-mesh sand were fitted with an additional Nylon<sup>®</sup> screen (70  $\mu\text{m}$ ) on the bottom endplate to hold the sand in place, but allow for the passage of PCE liquid. The top endplate was lined with Whatman<sup>®</sup> #42 filter paper to yield water-wetting conditions and inhibit the breakthrough of PCE. To saturate the column, 20 PV (pore volumes) of de-aired Nanopure<sup>®</sup> water were pumped through the bottom of the column using a Rainin<sup>®</sup> high-performance liquid chromatography (HPLC) pump. The weight of the column was measured before and after water saturation to determine the bulk density, porosity and pore volume of the soil column, and to ensure complete water saturation.

Residual saturations of PCE were established by injecting <sup>14</sup>C-labeled PCE through the bottom of water-saturated soil columns at a superficial or Darcy velocity of 1.0  $\text{cm h}^{-1}$  using a syringe pump (Harvard Apparatus<sup>®</sup>). The specific activity of PCE used in the column experiments was  $\sim 0.07 \mu\text{Ci mL}^{-1}$ . Since PCE has a greater density than water, the organic liquid was pumped in an upflow mode to achieve stable displacement of water from the soil column. When  $\sim 70\%$  of the pore volume

was occupied by PCE, the flow was reversed and water was again pumped through the top of the column. PCE was displaced from the column by pumping 2 PV of water through the column at a Darcy velocity of  $1 \text{ cm h}^{-1}$ , followed by an additional 10 PV of water at a Darcy velocity of  $15 \text{ cm h}^{-1}$ . The resulting PCE saturation ( $s_o$ ) was determined gravimetrically based on the difference in the density of water and PCE (Wilson et al., 1990). The process used to emplace residual PCE is often referred to as insular filling, in which the nonwetting phase (i.e. PCE) occupies the centers of larger pores, surrounded by the wetting phase (water).

A 4% solution of POE (20) sorbitan monooleate was then pumped through the column in a downflow mode at a Darcy velocity of  $1.65 \text{ cm h}^{-1}$  to remove the entrapped PCE. Column effluent was collected in glass vials that were sealed immediately after sampling. A 1-mL sample of the aqueous phase from each effluent fraction was transferred to vials containing 10 mL of Ecolume<sup>®</sup> scintillation cocktail (ICN Biomedicals). The activity of solubilized PCE in the effluent solution was assayed by standard liquid scintillation counting (LSC) procedures using a LKB Wallac<sup>®</sup> Model 1219 Rackbeta scintillation counter. Following the injection of surfactant solution, a small amount of PCE appeared in the column effluent solution as discrete droplets. The mobilized PCE was transferred to a graduated test tube to measure the cumulative volume of PCE recovered as a separate organic phase.

Soil columns prepared at the University of Texas at Austin were packed under vibration with 40–270-mesh Ottawa sand (F-95). Both endplates of the column were lined with 20- $\mu\text{m}$  filter paper. Prior to saturation, a suction was applied to one end of the column. An electrolyte solution containing  $500 \text{ mg L}^{-1} \text{ CaCl}_2$  was then allowed to enter the soil column until complete saturation was achieved. Water permeability measurements were performed by displacing the electrolyte solution through the column at several flow rates until a steady-state pressure drop was obtained using a Beckman<sup>®</sup> Model 100A pump. To emplace the organic phase,  $^{14}\text{C}$ -labeled PCE was pumped through the bottom of the column at a Darcy velocity of  $2 \text{ cm h}^{-1}$  until no  $\text{CaCl}_2$  solution was observed in the column effluent. The flow was then reversed and  $\text{CaCl}_2$  solution was injected at a Darcy velocity of  $2 \text{ cm h}^{-1}$  until PCE was no longer displaced from the column. A 4% solution of either 1:1 sodium diamyl/dioctyl sulfosuccinate or 4:1 sodium dihexyl/dioctyl sulfosuccinate was then introduced to the column at a Darcy velocity of  $0.5 \text{ cm h}^{-1}$ . Effluent fractions were collected using an automated ISIS<sup>®</sup> autosampler manufactured by ISCO. A 0.25-mL sample of the aqueous phase and, if present, the organic phase were transferred to vials containing 5.0 mL of scintillation cocktail (Beckman<sup>®</sup>). The activity of PCE in the samples was determined by standard LSC procedures using a Beckman<sup>®</sup> Model LS 9800 liquid scintillation counter.

Before and after PCE entrapment, miscible displacement experiments were conducted to measure the transport of a nonreactive tracer, tritiated water, in each soil column. After completely saturating the columns with water, a pulse of tritiated water, with a specific activity of  $\sim 0.015 \mu\text{Ci mL}^{-1}$  was displaced through each column at a Darcy velocity of  $3.0 \text{ cm h}^{-1}$ . The flow rate was verified by either weight or volume measurements of the column effluent. The activity of tritiated water in the effluent fractions was determined by standard LSC procedures as described previously. Following the

emplacement of PCE, a second pulse of tritiated water was displaced through the column to determine the effect of residual PCE on aqueous-phase dispersivity.

### 2.3. PCE solubility measurements

The apparent solubility of PCE in a 4% solution of POE (20) sorbitan monooleate was determined by the maximum additive concentration (MAC) method, in which the amount of excess organic liquid is minimized. The use of this technique was prompted by the formation of emulsions when the surfactant solution was mixed with PCE. Similar behavior has been reported for mixtures of PCE and aqueous solutions of nonionic surfactants (Fountain et al., 1991). Duplicate 25-mL Corex<sup>®</sup> centrifuge tubes were filled with 20 mL of surfactant solution and 0.5 mL of <sup>14</sup>C-labeled PCE. The centrifuge tubes were sealed with open-top screw caps and Teflon<sup>®</sup>-backed septa. The solutions were gently mixed on a reciprocating shaker for 72 h in a temperature control room maintained at 25 ± 0.1°C. Following equilibration, phase separation was achieved by centrifugation at 7500 rpm for 45 min. Duplicate 1-mL samples were taken from the aqueous phase using a gas-tight syringe and transferred to vials containing 10 mL of scintillation cocktail. The activity of PCE in the aqueous phase was determined by standard LSC procedures as described previously.

### 2.4. Interfacial tension measurements

The interfacial tension (IFT) between PCE and the 4% mixture of sodium diamyl and dioctyl sulfosuccinate was measured using a spinning drop tensiometer (Cayias et al., 1975). Prior to the actual IFT measurement, the surfactant solution was equilibrated with PCE. A small amount of the equilibrated surfactant solution was then contacted with PCE in the spinning drop tensiometer. The system was allowed to equilibrate for ~ 15 min before a reading was taken. Measurements of the IFT between PCE and a 4% solution of POE (20) sorbitan monooleate were obtained using an axisymmetric drop shape analysis (ADSA) technique (Desai et al., 1992). Prior to IFT measurements the 4% solution of POE (20) sorbitan monooleate was equilibrated with PCE using a PCE:surfactant solution ratio of 0.025. A drop of PCE was formed in the equilibrated surfactant solution using a Gilmont<sup>®</sup> micrometer syringe (Barnant Co.). An enlarged image of the drop was photographed and digitized to yield an IFT measurement based on the Laplace equation.

## 3. Results and discussion

### 3.1. Miscible displacement of tritiated water

Prior to surfactant flushing, miscible displacement experiments were conducted to assess the impact of entrapped PCE on the transport of a nonreactive tracer. Two representative breakthrough curves (BTC's) for tritiated water, measured before and after PCE entrapment, are shown in Fig. 2. The experimental data are expressed as

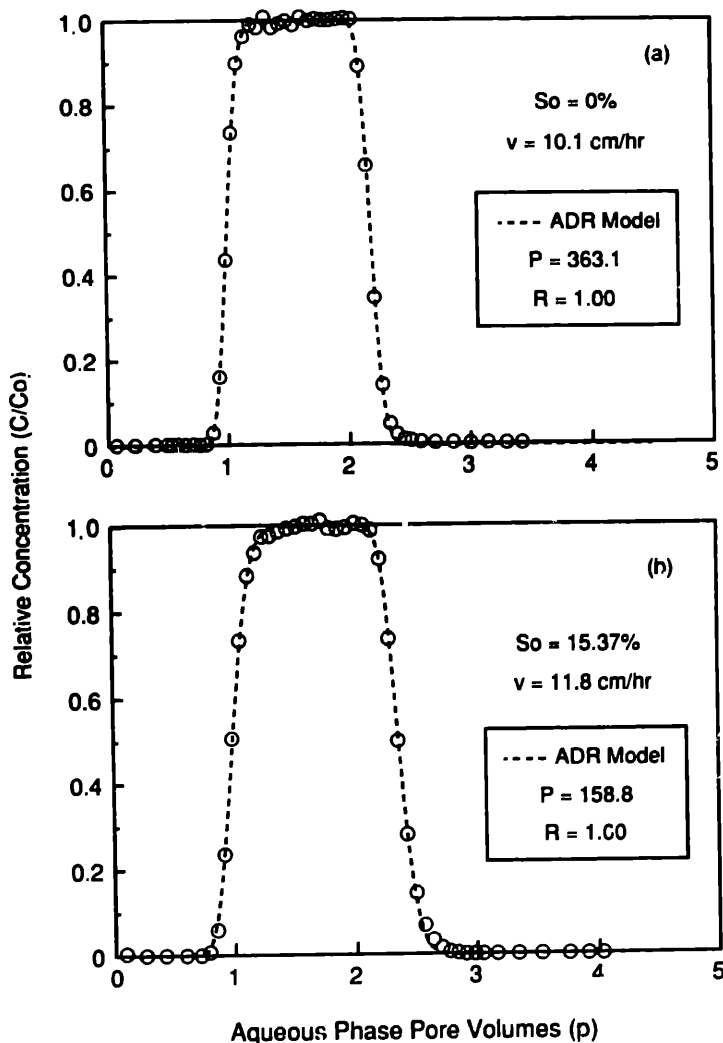


Fig. 2. Measured and fitted breakthrough curves for the displacement of tritiated water through 20-30-mesh Ottawa sand before (a) and after (b) PCE entrapment (column 1).

the relative concentration of tritiated water in each effluent fraction vs. the number of aqueous pore volumes displaced through the soil column. The results of each miscible displacement experiment were fit to an analytical solution of the one-dimensional advection-dispersion reaction (ADR) solute transport equation to assess the retardation and dispersion of tritiated water. Assuming conditions of homogeneity, local equilibrium, isotherm linearity and isotherm singularity, the one-dimensional ADR equation may be written in dimensionless form as:

$$R \frac{\partial C^*}{\partial p} = \frac{1}{P} \frac{\partial^2 C^*}{\partial X^2} - \frac{\partial C^*}{\partial X} \quad (1)$$

$$R = 1 + \frac{\rho_b K_p}{n s_w}; \quad C^* = \frac{C}{C_o}; \quad p = \frac{\nu t}{L}; \quad P = \frac{\nu L}{D}; \quad X = \frac{x}{L} \quad (2)$$

where  $R$  is the retardation factor;  $\rho_b$  is the soil bulk density;  $K_p$  is the partition coefficient;  $n$  is the porosity;  $s_w$  is the water saturation;  $C$  is the aqueous-phase solute

**Table 1**  
Summary of experimental conditions and physical properties of each soil column

Experimental parameter	University of Michigan		University of Texas at Austin	
	column 1	column 2	column 3	column 4
Surfactant solution	4% POE (20) sorbitan monooleate	4% POE (20) sorbitan monooleate	4% 1:1 sodium diamyl/dioctyl sulfosuccinate	4% 4:1 sodium dihexyl/dioctyl sulfosuccinate
Column packing	Ottawa sand, 20–30 mesh	Ottawa sand, 40–120 mesh	Ottawa sand, 40–270 mesh	Ottawa sand, 40–270 mesh
$L$ (cm)	10.58	10.42	11.80	12.20
$\rho_b$ (g cm <sup>-3</sup> )	1.76	1.68	1.70	1.70
$n$	0.335	0.365	0.360	0.364
$\alpha_l$ (cm)	0.029	0.018	0.225	0.072
$s_o$ (%)	15.37	13.50	25.00	17.66
$\alpha_o$ (cm)	0.066	0.034	0.730	0.141

concentration;  $C_o$  is the influent solute concentration;  $p$  is the aqueous-phase pore volume;  $v$  is the pore-water velocity;  $t$  is time;  $L$  is the column length;  $P$  is the Péclet number;  $D$  is the hydrodynamic dispersion coefficient; and  $x$  is distance.

As anticipated, values of the retardation factor ( $R$ ) obtained from all tritiated-water BTC's were close to 1, which indicates that no retention of tritiated water occurred before or after residual saturations of PCE were established. Soil column dispersion coefficients ( $D$ ), derived from the measured Péclet numbers, are expressed as dispersivities ( $\alpha$ ), where  $\alpha = D/v$  (Table 1). The values of  $\alpha$  obtained prior to PCE entrapment are typical of those reported for glass columns packed with quartz sands. Following the emplacement of residual PCE, the value of  $\alpha$  increased by a factor of 1.9–3.2. This increase in dispersivity in the presence of immobile PCE globules may be related to the enhancement of local velocity variations resulting from blockage of pore spaces and to the increased tortuosity of mobile water flow paths. The observed increase is consistent with dispersivity values obtained before and after the entrapment of residual dodecane in soil columns packed with 20–30-mesh Ottawa sand (Pennell et al., 1993). Taken in concert, these data indicate that the impact of residual NAPL's on aqueous-phase dispersion should be accounted for when modeling multiphase flow.

### 3.2. Surfactant flushing

Following the measurement of tritiated-water BTC's, an aqueous surfactant solution was pumped through each soil column to determine its ability to enhance the recovery of entrapped PCE (Table 1). The capacity of a 4% solution of POE (20) sorbitan monooleate to remove residual PCE from 20–30-mesh Ottawa sand was evaluated in the first column experiment (Fig. 3). The cumulative volume of PCE recovered in the aqueous phase (solubilization) and that displaced as a separate



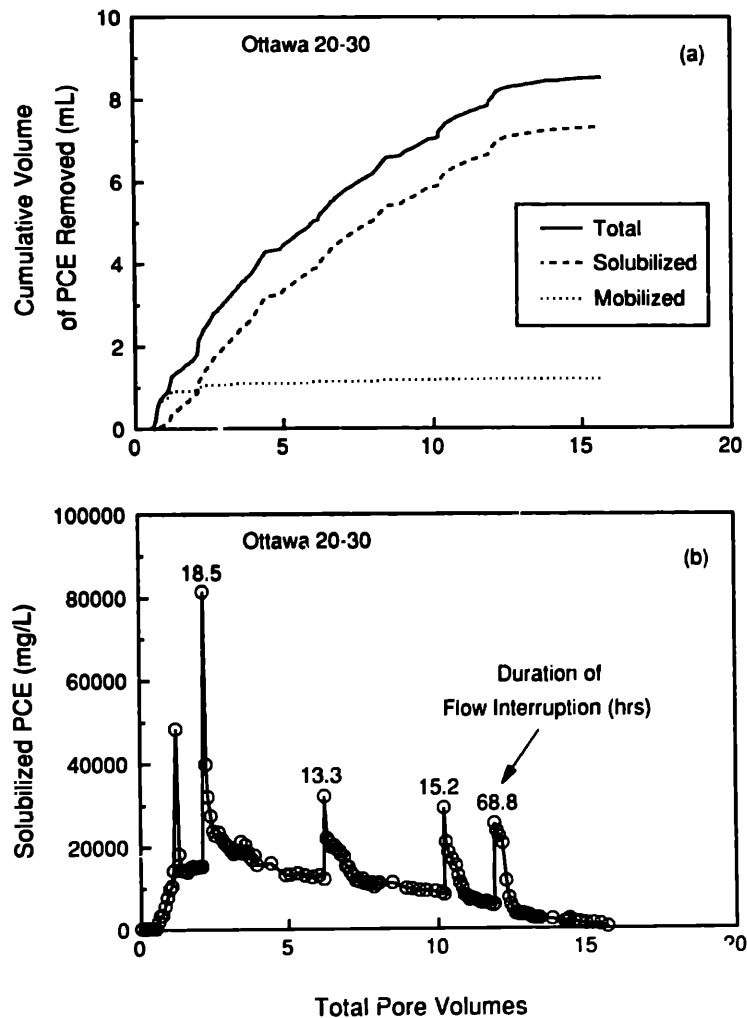


Fig. 3. Cumulative recovery of residual PCE (a) and aqueous-phase concentrations of PCE in the column effluent (b) following the injection of a 4% solution of POE (20) sorbitan monooleate into column 1.

organic phase (mobilization) are shown in Fig. 3a. Approximately 90% of the residual PCE was removed after flushing with 15.5 PV ( $\sim 1$  L) of surfactant solution. Further inspection of Fig. 3a reveals that PCE mobilization primarily occurred during the displacement of the first 1.0–1.5 PV of surfactant solution. These data suggest that the reduction in interfacial tension between PCE and the aqueous phase was achieved quite rapidly following the introduction of surfactant solution, which resulted in the mobilization of 13% of the residual PCE. However, PCE solubilization was the dominant recovery mechanism, accounting for the removal of 77% of the entrapped PCE from the soil column.

To further explore solubilization as a recovery process, the aqueous-phase concentration of PCE was plotted against the volume of surfactant solution displaced through the column (Fig. 3b). PCE appeared in the aqueous phase of the column effluent after flushing with  $\sim 1$  PV of surfactant solution. These data suggest that surfactant retardation had a minimal impact on the solubilization of residual PCE. This finding is consistent with data reported for the sorption of POE (20) sorbitan

monooleate by 20–30-mesh Ottawa sand (Pennell et al., 1993). Following the increase in effluent concentrations of PCE, a constant or steady-state value of  $\sim 15,000 \text{ mg L}^{-1}$  was attained. As more surfactant solution was displaced through the column, however, the concentration of PCE in the column effluent declined. This trend continued throughout the remainder of the experiment, which suggests that PCE solubilization was occurring under transient conditions. Similar reductions in the effluent concentration of NAPL's with time have been reported for dissolution experiments conducted in one-dimensional soil columns (Gellar and Hunt, 1993; Powers et al., 1994). As the NAPL saturation is reduced, either by dissolution or micellar solubilization, the surface area of organic liquid in contact with the aqueous phase will decrease. This may be due, in part, to the initial removal of small NAPL globules or droplets which possess relatively large specific surface areas. The remaining NAPL globules will tend to be larger in size, and thus, the interfacial area across which mass transfer can occur will be reduced as surfactant flushing progresses. The elevated spikes of PCE concentration in the column effluent correspond to periods of flow interruption. This experimental technique was employed to investigate rate-limited solubilization of PCE and will be discussed in the next section of the paper.

In the second column experiment, 40–120-mesh Ottawa sand was used as the packing material to explore the influence of grain size on the recovery of PCE by POE (20) sorbitan monooleate. After flushing with  $\sim 18.6 \text{ PV}$  ( $\sim 1.28 \text{ L}$ ) of surfactant solution,  $\sim 97\%$  of the PCE was removed from the column (Fig. 4a). The total recovery of PCE was almost entirely due to solubilization, with mobilization accounting for only 1.0% (0.15 mL) of the PCE recovered. Presumably the existence of smaller pores in this finer sand created larger capillary forces which acted to retain more organic under the same interfacial tension conditions. After the initial breakthrough of surfactant, the effluent concentration of PCE reached a steady-state value of  $\sim 23,000 \text{ mg L}^{-1}$  (Fig. 4b). This concentration was slightly higher than that observed for the 20–30-mesh Ottawa sand, suggesting that the rate of mass transfer was greater in the 40–120-mesh Ottawa sand. This may have been due to a wider size distribution of PCE globules present in the smaller size fraction of Ottawa sand. In experiments using a Wagner soil, Powers et al. (1992) reported that a larger percentage of small styrene globules formed in 50-mesh compared to 18-mesh material. Small globules would possess greater specific surface area than large globules, thereby enhancing mass transfer between the organic and aqueous phases.

In the third column experiment, the ability of a 1:1 mixture of sodium diamyl and sodium dioctyl sulfosuccinate to recover PCE from 40–270-mesh Ottawa sand was investigated (Table 1). Flushing with a 4% solution of this surfactant mixture resulted in the removal of  $\geq 99\%$  of the residual PCE (Fig. 5a). Mobilization of PCE was clearly the dominant recovery mechanism, accounting for 82% (15.85 mL) of the PCE removed. Due to the importance of mobilization in this experiment, the volume of PCE displaced as a separate organic phase was plotted vs. the total pore volumes of surfactant solution injected (Fig. 5b). Although the aqueous-phase pore volume of the soil column prior to surfactant flushing was 57.6 mL, measurable quantities of PCE liquid appeared in the effluent after only 40 mL of surfactant solution had entered the column. These data indicate that the mobilized PCE formed a bank of free

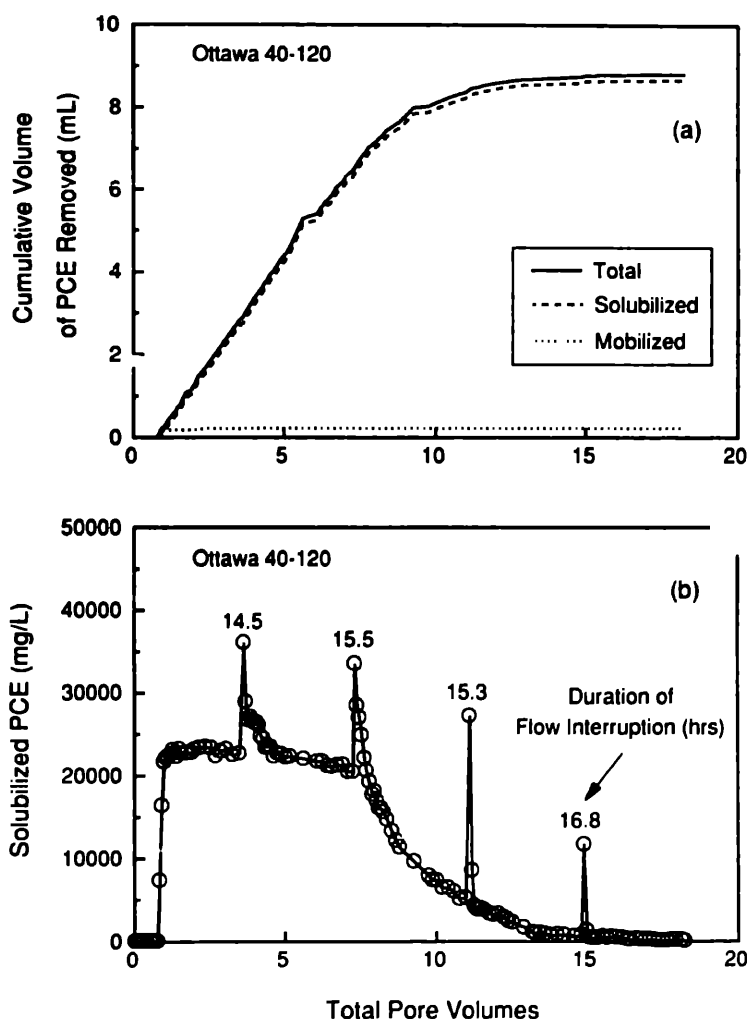


Fig. 4. Cumulative recovery of residual PCE (a) and aqueous-phase concentrations of PCE in the column effluent (b) following the injection of a 4% solution of POE (20) sorbitan monooleate into column 2.

product that was displaced from the column prior to surfactant breakthrough. Displacement of PCE as free product ceased after  $\sim 90$  mL of surfactant solution had passed through the soil column. In contrast, the solubilization of PCE was delayed slightly compared to the onset of mobilization, with an increase in effluent PCE concentrations occurring after 50 mL of surfactant solution had been injected. Elevated concentrations of PCE continued in the next 65 mL of column effluent. Thus,  $< 2$  PV of surfactant solution were required to achieve  $\geq 99\%$  recovery of residual PCE. This recovery rate is considerably greater than that obtained using a 4% solution of POE (20) sorbitan monooleate in a similar size fraction of Ottawa sand (column 2). These results demonstrate that rapid removal of residual PCE from a soil column can be achieved by surfactant flushing when mobilization is the dominant recovery mechanism.

In the fourth column experiment, the components of the 4% surfactant solution were modified slightly in an attempt to reduce the proportion of PCE mobilized as a separate organic phase by increasing the interfacial tension between the aqueous and organic phases (Table 2). The cumulative volume of PCE removed from the column

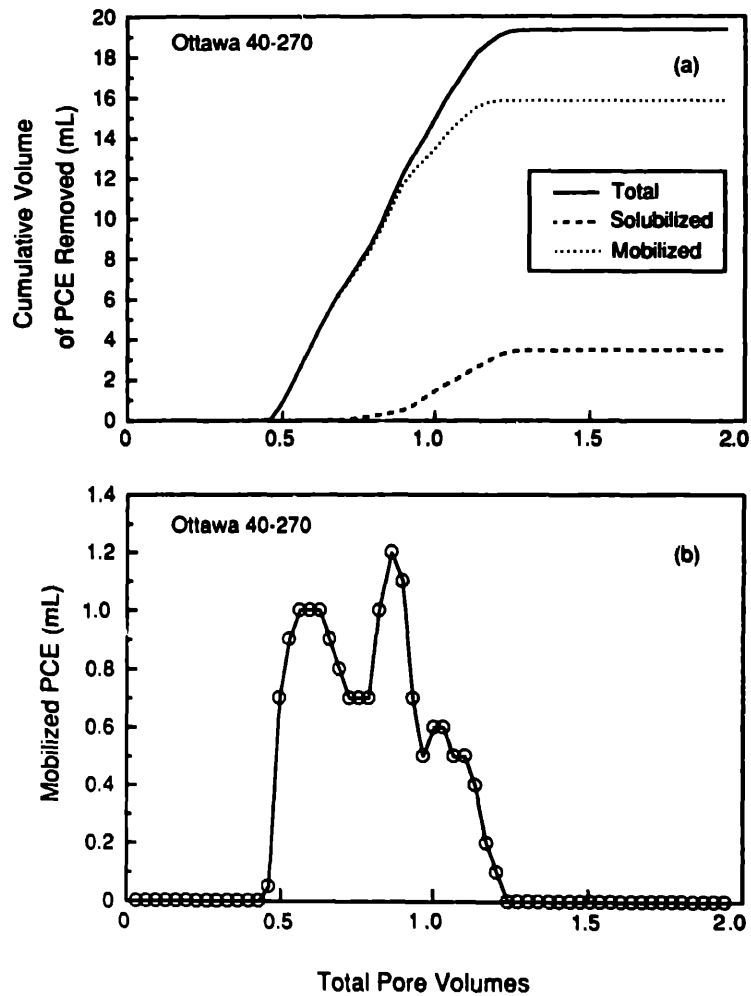


Fig. 5. Cumulative recovery of residual PCE (a) and volume of PCE displaced (b) from column 3 following the injection of a 4% solution of 1:1 sodium diamyl and sodium dioctyl sulfosuccinate.

Table 2  
Capillary and Bond numbers for each surfactant flushing experiment

Experiment	IFT ( $\text{dyn cm}^{-1}$ )	$k$ ( $\text{cm}^2$ )	$k_{rw}^a$	$N_B$	$N_{Ca}$	$N_B + N_{Ca}$
Column 1	5.0 <sup>b</sup>	$1.75 \cdot 10^{-7}$	0.50	$1.08 \cdot 10^{-5}$	$8.75 \cdot 10^{-7}$	$1.17 \cdot 10^{-5}$
Column 2	5.0 <sup>b</sup>	$5.97 \cdot 10^{-8c}$	0.50	$3.96 \cdot 10^{-6}$	$8.75 \cdot 10^{-7}$	$4.57 \cdot 10^{-6}$
Column 3	0.09 <sup>d</sup>	$2.74 \cdot 10^{-8}$	0.40	$7.52 \cdot 10^{-5}$	$1.47 \cdot 10^{-5}$	$8.99 \cdot 10^{-5}$
Column 4	0.58 <sup>d</sup>	$5.97 \cdot 10^{-8}$	0.45	$2.86 \cdot 10^{-5}$	$2.28 \cdot 10^{-6}$	$3.08 \cdot 10^{-5}$

<sup>a</sup>Estimated from Kueper (1989).

<sup>b</sup>Measured with ADSA apparatus.

<sup>c</sup>Estimated from column 4.

<sup>d</sup>Measured with spinning drop tensiometer.

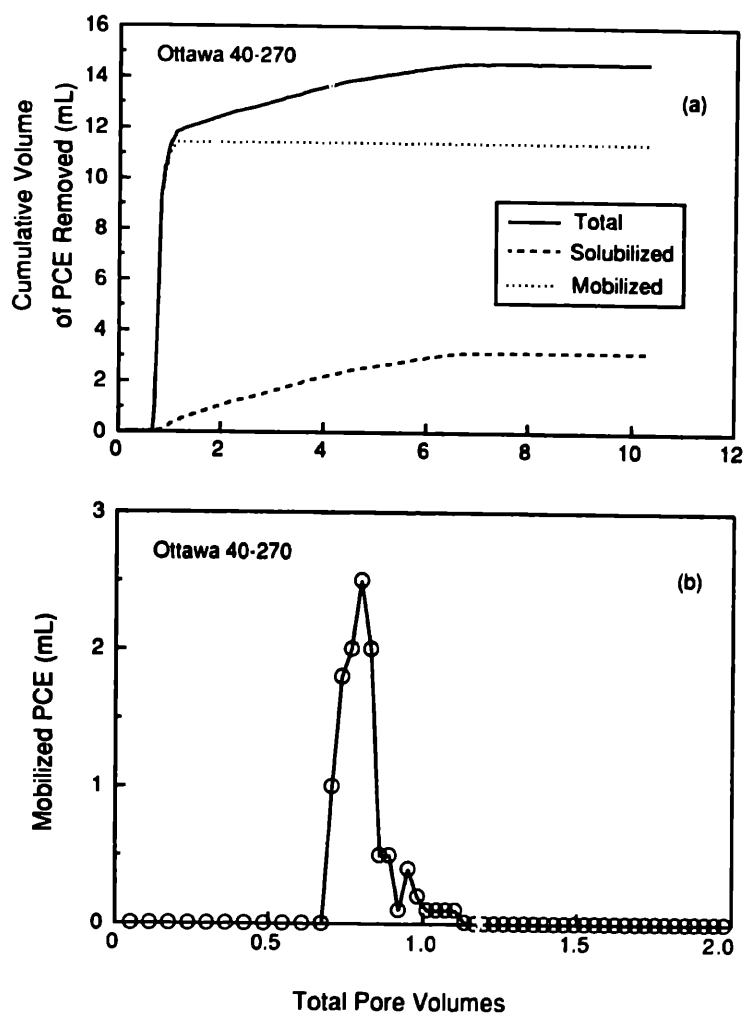


Fig. 6. Cumulative recovery of residual PCE (a) and volume of PCE displaced (b) from column 4 following the injection of a 4% solution of 4:1 sodium dihexyl and sodium dioctyl sulfosuccinate.

after flushing with 1000 mL of a 4:1 mixture of sodium dihexyl and sodium dioctyl sulfosuccinate is shown in Fig. 6a. Mobilized PCE appeared in the column effluent after 55 mL of surfactant solution had entered the column. Over the next 40 mL of surfactant flushing, 11.41 mL of residual PCE were displaced from the column as a separate organic phase (Fig. 6b). During one sampling period, the entire effluent fraction (2.5 mL) consisted of PCE liquid. The timing and extent of PCE mobilization were similar to that reported for column 3, indicating that the change in surfactant formulation had little impact on the elution of PCE as a separate phase. Increased aqueous-phase concentrations of PCE due to solubilization corresponded closely to the mobilization of PCE (Fig. 6a). Measurable amounts of solubilized PCE were detected in the aqueous phase until ~ 660 mL of surfactant solution had passed through the column. Thus, ~ 5 times more surfactant solution was required to achieve the same recovery of PCE ( $\geq 99\%$ ) observed in column 3. This difference was due to the prolonged period of PCE solubilization, rather than to a significant difference in the displacement of PCE as a separate liquid.

### 3.3. Rate-limited solubilization of PCE

In this section evidence of rate-limited PCE solubilization is presented and experimental results are compared to similar data published for NAPL dissolution into water. Potential models of the micellar solubilization process are explained and discussed from a mechanistic perspective. Recall that the aqueous-phase concentrations of PCE reached steady-state values of  $\sim 15,000$  and  $\sim 23,000$  mg L<sup>-1</sup> after injecting 4% solutions of POE (20) sorbitan monooleate. Although these values represent a sizable enhancement in PCE solubility, the effluent concentrations were still considerably less than the equilibrium solubility of PCE determined in batch experiments (38,500 mg L<sup>-1</sup>). These data indicate that PCE solubilization did not reach equilibrium at the applied Darcy velocity of 1.65 cm h<sup>-1</sup>. To verify the existence of rate-limited solubilization, a flow interruption technique was employed during the remainder of these column experiments.

The flow interruption procedure involved the displacement of surfactant solution at a constant flow rate, stoppage of flow for a specified period of time, and recommencement of flow at the initial flow rate. In these experiments flow was interrupted for periods ranging from 13 to 70 h (Figs. 3b and 4b). The elevated concentrations of PCE in the column effluent correspond to the volume of surfactant solution residing within the column during the period of flow interruption. The increased PCE concentration in the interrupted solution is indicative of rate-limited, rather than instantaneous, solubilization of PCE. Flow interruption allows for greater contact time between the surfactant solution and residual PCE, thereby increasing the solubilization of PCE. Rate-limited solubilization has also been observed during surfactant flushing of soil columns containing residual dodecane (Pennell et al., 1993). In that work, Pennell et al. (1993) showed that the effluent concentration of dodecane approached the equilibrium solubility as the duration of flow interruption was increased to 100 h. In addition, effluent concentrations of dodecane were found to decrease as the pore-water velocity was increased. A similar trend, decreasing mass transfer with increasing velocity, was observed by Powers et al. (1992) for the aqueous-phase dissolution of styrene and trichloroethylene (TCE) under steady-state conditions. It should be noted, however, that the divergence from equilibrium observed for the solubilization of PCE and dodecane in the surfactant studies was 2 and 7 times greater, respectively, than that reported for styrene dissolution at comparable flow velocities. The greater rate of PCE solubilization compared to dodecane solubilization is consistent with data of Carroll (1981), who reported that the solubilization rate increased as the polarity of the organic liquid increased. Results of these studies suggest that rate-limited mass transfer between the organic and aqueous phases is more prevalent during micellar solubilization of NAPL's than during dissolution of NAPL's into water.

Two mechanistic models, consisting of several coupled processes, have been proposed to describe the solubilization of organic liquids in surfactant solutions. In the first model, the organic liquid dissolves into the aqueous phase, is adsorbed at the micelle-water interface, and is then incorporated within the surfactant micelle (e.g., Volkov, 1979; Baumgardt and Kahlweit, 1980). The second model involves diffusion

of surfactant micelles to the organic–water interface, dissociation of the micelles into monomers which are adsorbed at the interface, and subsequent reformation of micelles containing the organic liquid (e.g., Chan et al., 1976; Carroll, 1981; Bolsman et al., 1988). The results of the column studies reported above, unfortunately, do not support the selection of either conceptual model or permit the assessment of the relative contribution of each specific process proposed in the models. It can be noted, however, that the observed rate of NAPL solubilization was several times less than that reported for NAPL dissolution in relatively short columns (Powers et al., 1992). Thus, one can infer that dissolution into the aqueous phase would not have been a rate-limiting process under steady-state conditions. Furthermore, the symmetrical shape and sharpness of the tritiated-water BTC's suggest that, under flowing conditions, regions of immobile water had no measurable impact on transport in the aqueous phase. Thus, one would not expect the rate of solubilization to be limited by physical nonequilibrium between regions of mobile and immobile water. Regardless of the specific mechanisms, the results of these studies demonstrate the potential impact of rate-limited solubilization on the recovery of entrapped NAPL's during surfactant flushing.

### 3.4. Mobilization of PCE

The results of the column experiments demonstrate that surfactants have the capacity to simultaneously enhance the aqueous solubility of PCE and to mobilize residual PCE as a separate organic phase. The relative importance of these processes is clearly dependent upon the surfactant formulation selected for remediation. The sodium sulfosuccinate mixtures tested here were found to promote the mobilization of residual PCE, while POE (20) sorbitan monooleate acted primarily to solubilize PCE. In order for a NAPL to be mobilized during surfactant flushing, the reduction in interfacial tension between the aqueous and organic phases must be sufficient to overcome the capillary forces which act to retain organic liquids within a porous medium. The capillary number ( $N_{Ca}$ ) and Bond number ( $N_B$ ) are dimensionless groups which can be used to evaluate the effect of viscous and buoyancy forces, respectively, on the residual saturation of organic liquids (Ng et al., 1978; Morrow and Songkran, 1981; Taber, 1981; Wilson and Conrad, 1984). These dimensionless numbers can be defined as follows:

$$N_{Ca} = \frac{k k_{rw} \rho_w g \Delta \phi}{\sigma_{ow} \Delta x} = \frac{\mu_w q}{\sigma_{ow}} \quad (3)$$

$$N_B = \frac{\Delta \rho g k k_{rw}}{\sigma_{ow}} \quad (4)$$

where  $k$  is the intrinsic permeability;  $k_{rw}$  is the relative permeability to water;  $\rho_w$  is the density of water;  $g$  is the acceleration due to gravity;  $\phi$  is the piezometric head;  $x$  is distance;  $\sigma_{ow}$  is the interfacial tension between the organic and aqueous phases;  $\mu_w$  is

the viscosity of water;  $q$  is the Darcy velocity; and  $\Delta\rho$  is the difference in fluid densities. Since the column experiments were conducted in a vertical orientation, with displacement of the PCE in the direction of the buoyancy force, the effects of the Bond number and capillary number are additive (Morrow and Songkran, 1981). In order to superpose these dimensionless groups, the capillary and Bond numbers should be expressed in a consistent form. Therefore, the Bond number (Eq. 4) was written in terms of the effective permeability,  $k_e = kk_{rw}$ .

The interfacial tension between the 4% solution of POE (20) sorbitan monooleate and PCE was found to be  $\sim 5.0 \text{ dyn cm}^{-1}$  (Table 2). This value falls within the range of interfacial tensions reported by Fountain et al. (1991) for PCE and 5% solutions of several ethoxylated nonionic surfactants. In contrast, the interfacial tensions between PCE and 4% solutions of sodium diamyl/dioctyl and dihexyl/dioctyl sulfosuccinate were 0.09 and 0.57  $\text{dyn cm}^{-1}$ , respectively. The low interfacial tensions between PCE and the sulfosuccinate mixtures, relative to POE (20) sorbitan monooleate, are typical of anionic surfactants used in enhanced oil recovery. The measured interfacial tensions were used in the calculation of capillary and Bond numbers (Table 2).

In each column experiment, the Bond number was larger than the capillary number, which indicates that gravity had a greater impact than viscous forces on PCE mobilization. When applied to vertical displacement in the direction of the buoyancy force, the Bond and capillary numbers were combined to evaluate the potential for NAPL mobilization. In column 1  $\sim 20\%$  of the residual PCE was mobilized, which suggests that the value of  $N_B + N_{Ca}$  ( $1.17 \cdot 10^{-5}$ ) exceeded the critical value by a small amount. In contrast,  $< 1\%$  of the residual PCE was displaced as a separate phase from 40–120-mesh Ottawa sand (column 2). Thus, the sum of the Bond and capillary numbers in this experiment ( $4.57 \cdot 10^{-6}$ ) was at or near the critical value required for PCE mobilization. These data are similar to the findings of Morrow and Songkran (1981), who reported that the residual saturation of Soltrol-130<sup>(®)</sup> in 80–100-mesh glass beads remained relatively constant until the value of  $N_B + N_{Ca}$  exceeded  $\sim 2 \cdot 10^{-5}$ . For columns 3 and 4,  $\sim 80\%$  of residual PCE was displaced after flushing with each sodium sulfosuccinate mixture. The high degree of PCE mobilization observed in these experiments suggests that the values of  $N_B + N_{Ca}$  ( $8.99 \cdot 10^{-5}$  and  $3.08 \cdot 10^{-5}$ ) were considerably greater than the critical value for 40–270-mesh Ottawa sand. The critical value of  $N_B + N_{Ca}$  will be influenced by properties of the porous medium, and thus, differences in onset and extent of PCE mobilization observed herein may be related to the particular size fraction of Ottawa sand and column packing of each experiment.

#### 4. Conclusions

The potential utility of surfactant flushing as a remediation strategy was investigated in soil columns containing PCE at residual saturation. The presence of entrapped PCE was shown to increase dispersivity by a factor of 1.9–3.2. Similar effects have been noted for soil columns containing entrapped dodecane (Pennell



et al., 1993), and indicate that residual NAPL's have a significant impact on local velocity variations and the tortuosity of aqueous-phase flow paths. This effect could be incorporated when modeling multiphase flow by using dispersivity values which account for the presence of residual organic liquids in the domain.

Flushing with < 1.5 L of surfactant solution was found to recover from 90% to  $\geq 99\%$  of the residual PCE entrapped in soil columns packed with Ottawa sand. The removal of similar quantities of PCE by water flushing would have required 70–150 L of water, assuming that the equilibrium solubility of PCE was maintained throughout the experiment. Flushing with  $\sim 15$  and  $\sim 18$  PV of 4% POE (20) sorbitan monooleate resulted in the recovery of 90% and 97% of the residual PCE from columns 1 and 2, respectively. This surfactant solution acted primarily as a solubilization agent, particularly in the case of 40–120-mesh Ottawa sand. However, rate-limited, rather than instantaneous, solubilization was evident in both experiments as indicated by: (a) the disparity between the initial steady-state concentration of PCE in the column effluent and the equilibrium solubility measured in batch experiments; and (b) the increase in PCE effluent concentrations following flow interruption. These data are consistent with results obtained from dodecane column studies (Pennell et al., 1993), and demonstrate that rate-limited solubilization may influence the recovery of dense, as well as light, NAPL's.

The most efficient recovery of PCE was achieved by flushing with mixtures of sodium sulfosuccinates. Approximately 80% of the PCE was displaced from the columns as a separate liquid after flushing with <2 PV of these surfactant solutions. These data demonstrate that ultra-low interfacial tensions ( $< 0.001$  dyn  $\text{cm}^{-1}$ ) commonly employed in enhanced oil recovery are not required to mobilize significant quantities of residual PCE. Based on the calculated Bond number, the mobilization of PCE was primarily attributed to the difference in density between water and PCE ( $0.63$  g  $\text{mL}^{-1}$ ). The Bond number was used to quantify the effect of gravitational or buoyancy forces on the displacement of residual PCE. The use of this expression, in conjunction with the capillary number, provides a means of evaluating the effect of both buoyancy and viscous forces on the residual saturation of organic liquids. Based on the capillary number alone, one would have expected little, if any, displacement of PCE from the soil columns.

Although mobilization was shown to be an effective means of removing residual PCE from Ottawa sand, the implications of this process should be considered during the evaluation of surfactant enhanced remediation schemes. Of particular concern is the potential for migration of the mobilized DNAPL downward through an aquifer formation. The downward migration of dyed PCE in horizontal column studies has been observed in our laboratories after introducing aqueous surfactant solutions. In the field, such mobilization could extend the area of NAPL contamination into fine-textured or previously uncontaminated materials, thereby complicating aquifer remediation. Thus, further investigation of the interplay between viscous, buoyancy and capillary forces and the subsequent mobilization of residual NAPL's will be required to design effective surfactant remediation strategies. In such remediation efforts, selection of the appropriate surfactant and NAPL removal mechanisms will be governed by the properties of the organic liquid and site specific geology.

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## References

- Abdul, A.S. and Gibson, T.L., 1991. Laboratory studies of surfactant-enhanced washing of polychlorinated biphenyl from sandy material. *Environ. Sci. Technol.*, 25: 665–671.
- Ang, C.C. and Abdul, A.S., 1991. Aqueous surfactant flushing of residual oil contamination from sandy soil. *Ground Water Monitor. Rev.*, 121–127.
- Baumgardt, K. and Kahlweit, M., 1980. On the kinetics of dissolution of naphthalene particles in aqueous micellar solutions. *Tenside Deterg.*, 17: 135–139.
- Bolsman, T.A.B.M., Veltmaat, F.T.G. and van Os, N.M., 1988. The effect of surfactant structure on the rate of oil solubilization into aqueous surfactant solutions. *J. Am. Oil Chem. Soc.*, 65: 280–283.
- Carroll, B.J., 1981. The kinetics of solubilization of nonpolar oils by nonionic surfactant solutions. *J. Colloid Interface Sci.* 79: 126–135.
- Cayias, J.L., Schecter, R.S. and Wade, W.H., 1975. The measurement of low interfacial tension via the spinning drop technique. In: K.L. Mittal (Editor), *Adsorption at Interfaces*. Am. Chem. Soc., Symp. Ser., 8: 234–247.
- Chan, A.F., Evans, D.F. and Cussler, E.L., 1976. Explaining solubilization kinetics. *AIChE (Am. Inst. Chem. Eng.) J.*, 22: 1006–1012.
- Desai, F.N., Demond A.H. and Hayes, K.F., 1992. Influence of surfactant sorption on capillary pressure-saturation relationships. In: D.A. Sabatini and R.C. Knox (Editors). *Transport and Remediation of Subsurface Contaminants*. Am. Chem. Soc., Symp. Ser., 491: 133–148.
- Edwards, D.A., Luthy, R.G. and Liu, Z., 1991. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions. *Environ. Sci. Technol.*, 25: 127–133.
- Fountain, J.C., Klimek, A., Beirkirch, M.G. and Middleton, T.M., 1991. The use of surfactants for in situ extraction of organic pollutants from a contaminated aquifer. *J. Hazardous Mater.*, 28: 295–311.
- Gannon, O.K., Bibring, P., Raney, K., Ward, A., Wilson, J., Underwood, J.L. and Debelak, K.A., 1989. Soil clean up by in-situ surfactant flushing. III. Laboratory results. *Sep. Sci. Technol.*, 24: 1073–1094.
- Gellar, J.T. and Hunt, J.R., 1993. Mass transfer from nonaqueous phase liquids in water-saturated porous media. *Water Resour. Res.*, 29: 833–845.
- Gillham, R.W. and Rao, P.S.C., 1990. Transport, distribution, and fate of volatile organic compounds in groundwater. In: N.M. Ram, F.C. Russel and K.P. Contor (Editors), *Significance and Treatment of Volatile Organic Compounds in Water Supplies*. Lewis, Chelsea, MI, pp. 141–181.
- Kile, D.E. and Chiou, C.T., 1989. Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration. *Environ. Sci. Technol.*, 23: 832–838.
- Kueper, B.H., 1989. The behaviour of dense, non-aqueous phase liquid contaminants in heterogeneous porous media. Ph.D. Dissertation, University of Waterloo, Waterloo, Ont., 172 pp.
- Morrow, N.R. and Songkran, B., 1981. Effect of viscous and buoyancy forces on nonwetting phase trapping in porous media. In: D.O. Shah (Editor), *Surface Phenomenon in Enhanced Oil Recovery*. Plenum, New York, NY, pp. 387–411.

- Nash, J.H., 1987. Field studies of in-situ washing. U.S. Environ. Prot. Agency, Cincinnati, OH, EPA/600/2-87/110, 56 pp.
- Ng, K.M., Davis, H.T. and Scriven, L.E., 1978. Visualization of blob mechanics in flow through porous media. *Chem. Eng. Sci.*, 33: 1009–1017.
- Pennell, K.D., Abriola, L.M. and Weber, Jr., W.J., 1993. Surfactant enhanced solubilization of residual dodecane in soil columns, I. Experimental investigation. *Environ. Sci. Technol.*, 27: 2332–2340.
- Peters, R.W., Montemagno, C.D., Shem, L. and Lewis, B., 1992. Surfactant screening of diesel-contaminated soil. *Hazard. Waste-Hazard. Mater.*, 9: 113–138.
- Powers, S.E., Abriola, L.M. and Weber, Jr., W.J., 1994. An experimental investigation of nonaqueous phase liquid dissolution in saturated subsurface systems: Steady state mass transfer rates. *Water Resour. Res.*, 28: 2691–2705.
- Powers, S.E., Abriola, L.M. and Weber, Jr., W.J., 1994. An experimental investigation of NAPL dissolution in saturated subsurface systems: Transient mass transfer rates. *Water Resour. Res.*, 30: 321–332.
- Saito, H. and Shinoda, K., 1967. The solubilization of hydrocarbons in aqueous solutions of nonionic surfactants. *J. Colloid Interface Sci.*, 24: 10–15.
- Schulle, F., 1975. Groundwater pollution by mineral oil products. In: *Proceedings of the Moscow Groundwater Pollution Symposium*. IAHS–AISH (Int. Assoc. Hydrogeol. Sci.–Assoc. Int. Sci. Hydrogéol.), Publ. No. 103, pp. 226–240.
- Taber, J.J., 1981. Research on enhanced oil recovery: Past, present and future. In: D.O. Shah (Editor), *Surface Phenomenon in Enhanced Oil Recovery*. Plenum, New York, NY, pp. 13–52.
- TRI (Texas Research Institute, Inc.), 1985. Test results of surfactant enhanced gasoline recovery in a large-scale model aquifer. *Am. Pet. Inst.*, Washington, DC, Publ. No. 4390, 59 pp.
- Vigon, B.W. and Rubin, A.J., 1989. Practical considerations in the surfactant-aided mobilization of contaminants in aquifers. *J. Water Pollut. Control Fed.*, 61: 1233–1240.
- Volkov, V.A., 1979. Kinetics of solubilization. *Colloid J. USSR*, 36: 200–205.
- West, C.C., 1992. Surfactant-enhanced solubilization of tetrachloroethylene and degradation products in pump and treat remediation. In: D.A. Sabatini and R.C. Knox (Editors), *Transport and Remediation of Subsurface Contaminants*. Am. Chem. Soc., Symp. Ser., 491: 149–158.
- Wilson, J.L. and Conrad, S.H., 1984. Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? In: *Proceedings of NWWA Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water*. Natl. Well Water Assoc., Dublin, OH, pp. 274–298.
- Wilson, J.L., Conrad, S.H., Mason, W.R., Peplinski, W. and Hagan, E., 1990. Laboratory investigations of residual liquid organics from spills, leaks and disposal of hazardous wastes in groundwater. U.S. Environ. Prot. Agency, Ada, OK, EPA/600/6-90/004, 267 pp.
- Ziegenfuss, P.S., 1987. The potential use of surfactant and cosolvent soil washing as adjuvant for in-situ aquifer restoration. M.Sc. Thesis, Rice University, Houston, TX, 78 pp.