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Effect of cation exchange on surfactant-enhanced solubilization of trichloroethene

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Abstract

The objective of this study was to develop the single-well push–pull test as a diagnostic tool for assessing the potential for cation exchange to adversely affect the phase behavior of sodium dihexyl sulfosuccinate surfactant (Aerosol MA 80-I) and its solubilization of trichloroethene (TCE) in the subsurface. Laboratory push–pull tests were conducted on a model natural aquifer sediment collected from a TCE-contaminated field site and a test solution consisting of 36,800 mg/l (3.7 wt.%) sulfosuccinate, 100,000 mg/l (10 wt.%) isopropanol, and 3200 mg/l (0.32 wt.%) KBr. Laboratory experiments were designed to simulate conditions occurring during single-well, "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 1.000 g/cm^3. The sulfosuccinate surfactant was transported conservatively in sediment packs containing no TCE. However, increasing concentrations of Ca^{2+} and Mg^{2+} resulting from cation exchange caused the TCE solubilization potential of the injected surfactant to exceed values predicted from the solubilization isotherm. Sulfosuccinate surfactant transport was strongly retarded in sediment packs containing 5 vol.% residual TCE because cation exchange resulted in the formation of a Winsor Type II system, which resulted in the partitioning of the sulfosuccinate surfactant into the residual TCE phase. Conservative sulfosuccinate transport was observed in a separate sediment pack containing 5 vol.% residual TCE when a 130 meq/l Na^+ pre-flush was used to reduce quantities of Ca^{2+} and Mg^{2+} in the sediment pack prior to

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sulfosuccinate injection. 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.

Keywords: Surfactants; NAPL; Remediation; Single-well tests; Ion exchange

1. Introduction

One approach for remediating sites contaminated with nonaqueous phase liquids (NAPLs) is to inject surfactants to enhance NAPL aqueous solubility and thus, the efficiency of NAPL removal by extraction pumping (West and Harwell, 1992). Increased NAPL solubility results from the partitioning of NAPL molecules into the hydrophobic interior of surfactant micelles, which form above the surfactant's 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). More recently, laboratory and field studies have addressed surfactant-enhanced recovery of NAPL contaminants including alkanes, chlorinated solvents, and polycyclic aromatic hydrocarbons (Baran et al., 1994b; Edwards et al., 1994; Hernandez and Rowe, 1987; Kile and Chiou, 1989; Kile and Chiou, 1990; Pennell et al., 1997; Smith et al., 1991).

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, and cosolvents included in the injected surfactant mixture; temperature and major ion composition of site groundwater; mineral composition and organic matter content of aquifer sediments; and other factors (Edwards et al., 1991; 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 solubility increase 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 III or from Type III to Type II 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 in 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, and 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: $2Na^+(\text{micelles}) + Ca^{2+}(\text{sediment}) \Leftrightarrow Ca^{2+}(\text{micelles}) + 2Na^+(\text{sediment})$. 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 Type III system or Winsor Type II system, resulting in the partitioning of surfactant into the NAPL and 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.

The objective of this study was to develop the single-well, "push–pull" test as a diagnostic tool for assessing the potential for cation exchange to adversely affect the phase behavior of sodium dihexyl sulfosuccinate surfactant (Aerosol MA 80-I) and its solubilization of trichloroethene (TCE) DNAPL in the subsurface. A push–pull test consists of the injection of a tracer/surfactant test solution into a single monitoring well followed by the recovery of the test solution/groundwater mixture from the same location (Istok et al., 1997). The push–pull test was selected for this study because of its ability to provide quantitative in situ information on surfactant transport (Istok et al., 1999) and TCE solubilization (Field et al., 1999). However, it is recognized that the flow reversal that occurs during a push–pull test precludes its efficient use in full-scale surfactant-enhanced aquifer remediation. Aerosol MA 80-I was selected because it has been the subject of numerous laboratory and field studies (Dwarakanath, 1997; Kostarelos, 1998; Shook et al., 1997) and because it has a high TCE solubilization potential, low sorption, and food-grade surfactant status. Although the natural aquifer sediment used in these experiments was collected from a TCE-contaminated field site, an evaluation of the feasibility of surfactant-enhanced remediation at that site was not the goal of this study. For this reason, no attempt was made to conduct laboratory experiments under the same geochemical or hydrological conditions in the subsurface at this site. Instead, laboratory push–pull tests were performed with sediment packs prepared with and without TCE to obtain quantitative information on the effects of cation exchange on sulfosuccinate transport, phase behavior, and TCE solubilization potential that could occur during a field test. The effect of a NaCl pre-flush on reducing the quantity of exchangeable divalent cations in the same sediment and its implications on surfactant transport and TCE solubilization was also examined.

2. Experimental methods

2.1. Sediment

Sediment for laboratory experiments was collected from a TCE-contaminated field site at the Site 300 Building 834 operable unit at Lawrence Livermore National Laboratories (LLNL) in Livermore, CA (Carpenter et al., 1984). Uncontaminated sediment was collected in a single batch from a surface exposure of the aquifer, homogenized, sieved (<5 mm), and air-dried prior to use. The sieved sediment is classified as a sandy loam with 76.9% sand, 10.9% silt, 12.1% clay, a median grain diameter of 0.8 mm, a uniformity coefficient of 2.9, a particle density of 2.65 g/cm^3, an organic carbon content of 0.17 wt.%, a pH of 9, a cation exchange capacity of 19.8 meq/100 gm, and exchangeable cation capacities of 0.27 meq/100gm (Na^+), 0.23 meq/100 gm (K^+), 29.9 meq/100 gm (Ca^{2+}), and 8.8 meq/100 gm (Mg^{2+}), all determined using standard methods (Klute, 1986). The majority of the cation exchange capacity of the sediment is associated with the presence of small amounts of smectite clays (primarily montmorillonite) (Carpenter et al., 1984).

2.2. Surfactant formulation

The commercial surfactant product, Aerosol MA 80-I (Cytec Industries, West Paterson, New Jersey) consisted of 80 wt.% sodium dihexyl sulfosuccinate, 5 wt.% isopropanol, and 0.46 wt.% NaCl in water. Initial experiments were aimed at identifying an optimal surfactant test solution that would give high TCE solubilization yet remain neutrally buoyant (e.g., 1.000 g/cm^3) with Type I surfactant phase behavior. During full-scale aquifer remediation, neutrally buoyant conditions are desired to avoid the potential for downward migration of injected surfactant (Kostarelos, 1998; Pennell et al., 1996; Shook et al., 1997). To this end, experiments were conducted by adjusting isopropanol and electrolyte additions to the commercial surfactant (Aerosol MA 80-I) product. To facilitate the use of Br^- as a conservative tracer during laboratory push–pull tests and to avoid the potential dispersal of clay minerals in the sediment by the introduction of additional Na^+, we prepared surfactant formulations with KBr instead of the NaCl. Batch experiments were conducted by combining 2 ml of neat TCE with 6 ml of a 40,000 mg/l (4 wt.%) Aerosol MA 80-I solution containing between 0 and 100,000 mg/l (10 wt.%) isopropanol and between 0 and 9500 mg/l (0.95 wt.%) KBr at 22°C in 8 ml glass Teflon-lined-lid vials. The solutions were vigorously shaken and then allowed to equilibrate and settle overnight prior to analysis for sulfosuccinate and TCE.

2.3. TCE solubilization

Once the test solution that formed a Type I system and had a maximum TCE solubility with neutral buoyancy was identified, TCE solubilization isotherms were

prepared by combining between 0 and 6 ml of test solution with 2 ml of neat TCE and sufficient tap water to bring the total volume to 8 ml in glass Teflon-lined-lid vials. The number of liquid phases present in the vials was determined by visual inspection. Aliquots of the aqueous phase were analyzed to determine solution density and concentrations of sulfosuccinate and TCE. A similar procedure was used to determine the TCE solubilization potential of water samples collected during laboratory push–pull tests except that a 1.6 ml water sample was combined with between 200 and 400 μl of neat TCE in 2 ml vials.

2.4. Laboratory push–pull tests

Laboratory push–pull tests were performed in physical aquifer models (PAMs) constructed in a wedge-shape to simulate the radial flow field near an injection/extraction well during a field push–pull test (Fig. 1a). The PAMs were constructed of polypropylene with interior dimensions of 5 cm (width at narrow end), 50 cm (width at wide end), 125 cm (length), 20 cm (height), and a total internal volume of 0.069 m^3 (Fig. 1b). Air-dried sediment was packed into the PAMs to a uniform bulk density (1.35 g/cm^3) and total porosity (0.49) using the method of Istok et al. (1997). A screen and thin pack of washed silica sand were placed next to the injection/extraction ports to prevent sediment from entering tubing leading to the pump, and a perforated plate and

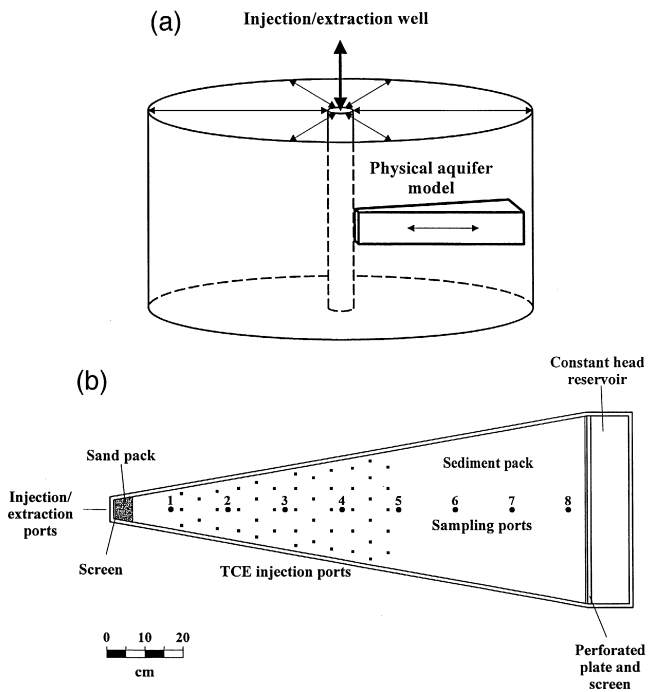

Fig. 1. Physical aquifer models used in laboratory push–pull tests: (a) model design; (b) plan view.

screen were placed at the PAM's wide end to prevent sediment from entering the constant head reservoir. The sediment pack was saturated with tap water and a lid containing eight sampling ports was installed.

Three push–pull tests were conducted with the optimized test solution, each in a separate sediment pack. In Test 1, the sediment pack contained no TCE. In Tests 2 and 3, the sediment packs contained a known initial quantity of liquid TCE, which was introduced by first draining water from a previously water-saturated sediment pack and then slowly injecting aliquots of neat TCE at alternating depths of 8 and 12 cm into 48 injection ports located in the model lid between sampling ports 1 and 5 (Fig. 1b). A total of 920 g of TCE was injected, which represents a volume of liquid TCE equivalent to ~5 vol.% of the total pore space of the sediment pack within the treated zone. After TCE injection, the sediment pack was again saturated with tap water. A push–pull tracer test (Br^- only) was performed prior to injecting surfactant (1) to remove small amounts of mobile TCE from the injection/extraction and sampling ports, (2) to attempt to entrap TCE within the pore space, and (3) to determine effective porosity of the sediment pack. Less than 40 ml of liquid TCE were removed from the sediment pack during these tests and the remaining TCE was assumed to be at the residual saturation for TCE in this sediment. In Test 3, the sediment pack was flushed with ~10 pore volumes of 130 mM NaCl (130 meq/l Na^+) prior to injecting surfactant in an attempt to reduce quantities of exchangeable divalent cations in the sediment pack.

Push–pull tests were performed at 22 ± 1°C under confined conditions with a constant saturated thickness (20 cm). During the injection phase, flow was from the injection/extraction ports at the PAM's narrow end toward the constant head reservoir at the PAM's wide end; during the extraction, phase flow was reversed. The test solution composition was identical for all tests and consisted of the optimized surfactant formulation determined in batch solubilization experiments (described below). For each experiment, ~9 l of test solution was injected at ~15 ml/min; the extraction phase began within 30 min after the end of the injection phase and continued at ~15 ml/min until ~22 l had been extracted. Water samples were collected during the injection phase by inserting a stainless steel syringe needle (through a septum in the sampling port cap) into brass "well" screens that fully penetrated the sediment pack beneath each sampling port. Additional water samples were collected from the injection/extraction ports during the extraction phase.

2.5. Analytical methods

Bromide concentrations were determined using a Dionex Model DX-120 (Sunnyvale, CA) ion chromatograph equipped with electrical conductivity detector. Samples for Br^- analysis that contained sulfosuccinate were diluted 1:20 with deionized water and extracted prior to analysis by passage through a 0.5 g C_{18}-bonded phase silica cartridge (Varian, Harbor City, CA). Concentrations of sulfosuccinate and TCE were determined using a Waters Alliance Model 2690. Cations were analyzed by inductively coupled plasma atomic emission spectrometry using Standard Method 3120-B (Greenberg et al., 1992).

3. Results and discussion

3.1. Test solution formulation and TCE solubilization

The optimal test solution consisted of 36,800 mg/l (3.7 wt.%) sulfosuccinate, 100,000 mg/l (10 wt.% isopropanol), and 3200 mg/l (0.32 wt.%) KBr in tap water with an initial density of 0.990 g/cm^3. In the presence of excess liquid TCE, the solution gave a Winsor Type I system with an aqueous TCE concentration of 26,700 ± 1500 mg/l (RSD 5.6%) and a solution density of 1.000 g/cm^3. In batch solubilization experiments, the aqueous TCE concentration increased from 1500 to 26,700 mg/l as the sulfosuccinate concentration increased from 0 to 36,800 mg/l. Variable sulfosuccinate concentrations were achieved by diluting the optimal test solution with tap water (Fig. 2), which was selected to approximate the dilution of the test solution that occurs during a push–pull test upon mixing with the porewater of the PAM. The solubilization isotherm was fitted with the equation (concentration units are mg/l):

$$(\mathrm{TCE}) = 1319 \exp\left[8.13 \times 10^{-5} (\mathrm{Sulfosuccinate})\right] \quad (2)$$

Over this range in sulfosuccinate concentrations, the diluted test solution showed Winsor Type I phase behavior in the presence of excess TCE.

Because we are working with a natural sediment that contains exchangeable cations, we also evaluated the batch solubilization potential and phase behavior of solutions containing 36,700 mg/l (3.7 wt.%) sulfosuccinate, 100,000 mg/l (10 wt.%) isopropanol, and 148 meq/l Na^+ in the presence of added Ca^{2+} (data not shown). To simplify our discussion of the data, it is convenient to define the cation ratio (Ca^{2+} +

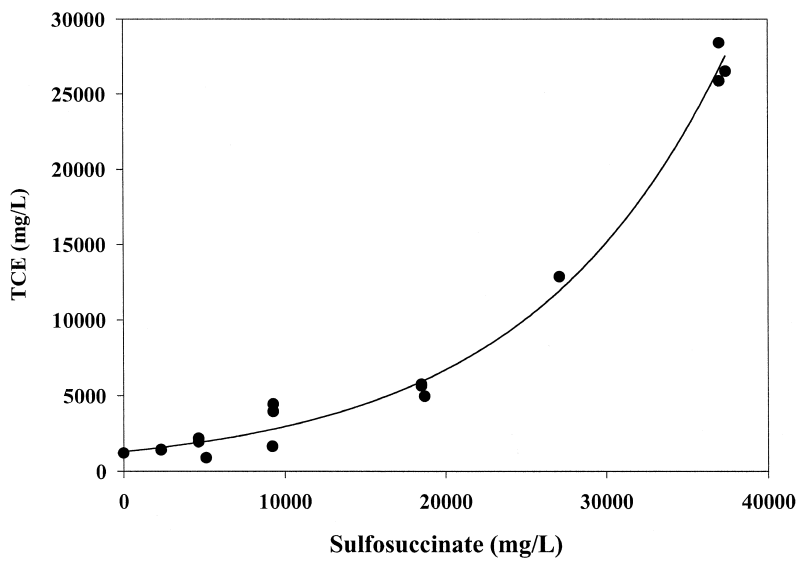

Fig. 2. Batch solubilization isotherm for TCE prepared by diluting the optimized test solution with tap water. Fitted line is given in Eq. (2).

$Mg^{2+})/(Na^{+} + K^{+})$, where the concentrations of all species are in meq/l. The batch solubilization isotherm accurately described aqueous TCE solubilities when Ca^{2+} was added to achieve a cation ration of < 0.04 ($Ca^{2+} < 5.92$ meq/l). However, when Ca^{2+} was added to achieve cation ratios $0.04 <$ cation ratio < 0.48 (5.92 meq/l $< Ca^{2+} <$ 71.00 meq/l), the batch solubilization isotherm underestimated aqueous TCE solubilities. Finally, when Ca^{2+} was added to achieve a cation ratio > 0.48 ($Ca^{2+} > 71.00$ meq/l) the batch solubilization isotherm overestimated aqueous TCE solubilities. For example, an aqueous TCE concentration of 29,200 mg/l was obtained when the Ca^{2+} concentration was 18 meq/l (a cation ration of 0.12), compared to a TCE concentration of 20,400 mg/l obtained in the absence of Ca^{2+}. In contrast, an aqueous TCE concentration of only 2700 mg/l was obtained when the Ca^{2+} concentration was 71.00 meq/l (a cation ratio of 0.48). The reduction in aqueous TCE concentration for cation ratio > 0.48 is attributed to the partitioning of the divalent salts of sulfosuccinate out of the aqueous phase into either a middle-phase emulsion (Type III system) or into the TCE DNAPL phase (Type II system) (Baran et al., 1994a; Lake, 1989). Baran et al. (1994a,b) observed Winsor Type II behavior and a reduction in TCE solubility when Ca^{2+} was added to sulfosuccinate in the presence of TCE.

4. Laboratory push–pull Test 1 (sediment pack with no TCE)

4.1. Surfactant transport

Conservative transport of the injected surfactant test solution in sediment packs containing no TCE was indicated by the essentially identical shape of breakthrough curves for sulfosuccinate and Br^{-} during the injection phase of Test 1 (Fig. 3a). In Fig. 3, Br^{-} and sulfosuccinate concentrations are presented as breakthrough curves that display relative concentration (C/C_o) vs. time, where C is the Br^{-} or sulfosuccinate concentration in a water sample collected from the mid-depth of the sediment pack beneath a sampling port (Fig. 1b), and C_o is the concentration of the same solute in the injected test solution (3200 mg/l for Br^{-} and 36,800 mg/l for sulfosuccinate). At each sampling port, values of C/C_o for Br^{-} and sulfosuccinate increased fairly smoothly from zero to one with increasing time as the injected test solution penetrated further into the sediment pack. Sulfosuccinate and Br^{-} travel times, defined as the time required for C/C_o to reach 0.5, for each port were essentially identical to those predicted from the physical model geometry, pumping rate, and an effective sediment pack porosity equal to the total porosity (0.49).

Similar extraction phase breakthrough curves for sulfosuccinate and Br^{-} also were consistent with conservative sulfosuccinate transport during Test 1 (Fig. 4a). In Fig. 4, elapsed time during the extraction phase is displayed as the dimensionless ratio: (volume extracted)/(volume injected), abbreviated hereafter as V_{ext}/V_{inj}. Breakthrough curves displayed an initial plateau with $C/C_o \approx 1$ followed by a gradual decline in C/C_o from one to zero as tap water entering the physical model from the constant head reservoir displaced injected test solution from the sediment pack. Mass balance calculations indicated that almost complete recoveries ($> 96\%$) of injected Br^{-} and sulfosuccinate were achieved during the extraction phase of Test 1. Conservative sulfosuccinate

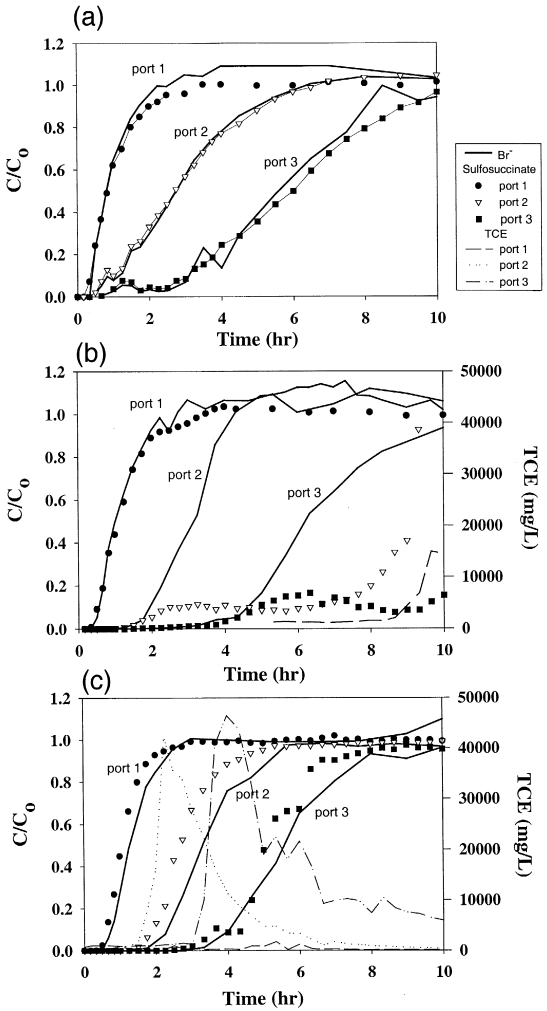

Fig. 3. Selected injection-phase breakthrough curves for Br^- and sulfosuccinate for push–pull tests conducted with (a) no TCE present (Test 1), (b) 5% initial TCE saturation (Test 2), and (c) 5% initial TCE saturation in sediment pack pre-flushed with 130 meq/l Na^+ (Test 3).

transport is attributed to the high sulfosuccinate concentration in the injected test solution and the weak affinity of the anionic surfactant for the LLNL sediment; sorption sites (if present) were essentially instantaneously saturated with sulfosuccinate without causing any apparent retardation in sulfosuccinate transport relative to Br.

4.2. TCE solubilization potential and surfactant phase behavior

Prior to Test 1, cation concentrations in samples from all ports were approximately uniform at 0.45 ± 0.04 meq/l for $(Na^+ + K^+)$ and 2.10 ± 0.18 meq/l for $(Ca^{2+} +$

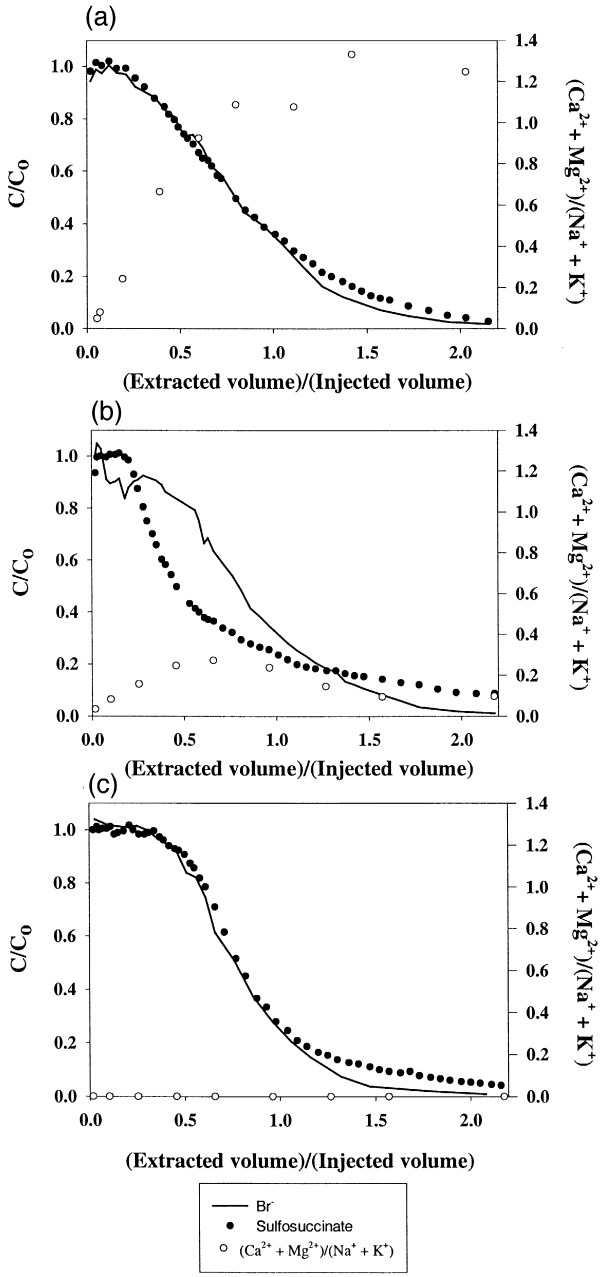

Fig. 4. Extraction phase breakthrough curves for Br^- and sulfosuccinate with (a) no TCE present (Test 1), (b) 5% initial TCE saturation (Test 2), and (c) 5% initial TCE saturation in sediment pack pre-flushed with 130 meq/l Na^+ (Test 3).

Mg^{2+}). Combined concentrations for cations of the same charge are reported here due to the similar effects that monovalent and divalent cations have on TCE solubilization potential and surfactant phase behavior. Cation concentrations in all ports increased during the injection phase of Test 1 (Table 1) (recall that the concentrations of $(Na^+ + K^+)$ and $(Ca^{2+} + Mg^{2+})$ in the optimized test solution were 126.7 and 0 meq/l, respectively with a cation ratio = 0. For example, at port 1 concentrations of $(Na^+ + K^+)$ and $(Ca^{2+} + Mg^{2+})$ increased during the injection phase from 0.45 to 89.4 meq/l and from 2.20 to 36.8 meq/l, respectively. Monovalent cation concentrations also increased at ports 2 and 3 but reached smaller maximum concentrations than at port 1 because these ports are located farther from the injection/extraction ports. Values of the cation ratio also increased in each port during the injection phase (Table 1). Increases in $(Na^+ + K^+)$ concentrations are attributed to the presence of these cations in the injected test solution while increases in $(Ca^{2+} + Mg^{2+})$ concentrations are attributed to the release of exchangeable Ca^{2+} and Mg^{2+} from the sediment. In Test 1, a total of 221.2 meq Ca^{2+} and Mg^{2+} was recovered, which is 2.3% of the total exchangeable Ca^{2+} and Mg^{2+} in the portion of the sediment pack ($\sim$ 24.4 kg) interrogated by the injected test solution.

The TCE solubilization potential of selected injection phase samples was determined by combining the sample with excess liquid TCE and measuring the aqueous TCE concentration after equilibration. Sulfosuccinate concentrations in ports 1–3 at the end of the injection phase were equal to the sulfosuccinate concentration in the injected test solution (36,800 mg/l) (Fig. 3a) and for this sulfosuccinate concentration the TCE solubilization potential predicted from the batch solubilization isotherm was 26,700 mg/l. However, the TCE solubilization potential for a sample from port 1 at the end of the injection phase was much larger (67,000 mg/l), while the solubilization potential for samples from ports 2 and 3 were much smaller (< 1700 mg/l) than predicted from the solubilization isotherm (Table 1).

Differences in TCE solubilization potential for samples from ports 1–3, despite their similar sulfosuccinate concentrations, are attributed to changes in cation composition that occurred as the injected test solution came into contact with the sediment pack The presence of divalent cations (cation ratio = 0.41) for the sample from port 1 resulted in a measured TCE solubilization potential that exceeded the solubilization potential predicted by the solubilization isotherm (Table 1). This is consistent with the results of batch solubilization experiments performed by adding divalent cations to the surfactant test solution as described in the previous section. The low measured TCE solubilization potentials for samples collected at the end of the injection phase from ports 2 and 3 are attributed to the large concentrations of divalent cations (cation ratio = 2.05 and 10.92, respectively) in these samples, which caused the conversion of the surfactant system to a non-Winsor Type I system upon the addition of liquid TCE (Table 1).

For Test 1, the value of the cation ratio, increased from 0 to 1.30 during the extraction phase (Fig. 4a). For the sample collected at $V_{ext}/V_{inj} = 0.06$, which had a cation ratio of 0.04, the measured TCE solubilization potential was essentially identical to that predicted by the batch solubilization isotherm (Table 2). Measured TCE solubilization potentials for extraction phase samples were larger than those predicted from the batch solubilization isotherm for $V_{ext}/V_{inj} = 0.4$ (Table 2). The percent of the

Table 1
Sulfosuccinate and TCE concentrations, measured and predicted TCE solubilization potentials, and cation concentrations and ratios for injection phase samples from ports 1–3 collected at the end of the injection phase ($t = 9$ h) of laboratory push–pull tests

Test	Port	Sulfosuccinate (mg/l)	TCE (mg/l)	Measured TCE solubilization potential (mg/l)	Predicted TCE solubilization potential (mg/l)	$(Na^+ + K^+)$ (meq/l)	$(Ca^{2+} + Mg^{2+})$ (meq/l)	$(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$
1	1	36,800	–	67,220	26,700	89.4	36.8	0.41
1	2	36,800	–	1655	26,700	45.8	94.0	2.05
1	3	36,800	–	1559	26,700	9.6	104.8	10.92
2	1	36,800	84	41,309	26,700	89.3	41.8	0.47
2	2	14,720	13,578[a]	NA	4365	45.6	90.0	1.97
2	3	4784	3420	NA	1946	11.3	104.8	9.27
3	1	36,800	101	23,665	26,700	130.7	0.6	0.01
3	2	36,800	396	25,313	26,700	123.4	2.4	0.02
3	3	36,800	5945	28,600	26,700	112.3	11.6	0.10

NA = not analyzed; ND = not detected.
[a] Multiple fluid phases present in sample.

Table 2
Sulfosuccinate and TCE concentrations, measured and predicted TCE solubilization potentials, and cation concentrations and ratios for extraction phase samples from the injection/extraction ports

Test	V_{ext} / V_{inj}	Sulfosuccinate (mg/l) (% remaining)	TCE (mg/l)	Measured TCE Solubilization potential (mg/l)	Predicted TCE solubilization potential (mg/l)	$Na^+ + K^+$ (meq/l)	$Ca^{2+} + Mg^{2+}$ (meq/l)	$(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$
1	0.0	37,000 (92)	–	27,252	26,708	112.8	4.4	0.04
1	0.4	31,000 (81)	–	31,339	16,398	72.3	24.2	0.33
1	0.8	16,600 (43)	–	1647	5085	38.8	20.8	0.54
2	0.06	36,700 (97)	200	26,428	26,065	133.9	7.8	0.06
2	0.4	21,400 (98)	1485	14,096	7513	64.5	3.8	0.06
2	0.8	11,800 (88)	940	3604	3443	33.1	3.8	0.11
3	0.06	36,800 (100)	407	22,956	26,700	127.6	ND	0
3	0.4	25,800 (99)	7000	16,792	10,775	123.7	ND	0
3	0.8	18,800 (101)	5500	10,792	6081	118.3	ND	0

ND = not detected.

sulfosuccinate initially present in the sample that remained in the aqueous phase after liquid TCE addition was determined. For example, only 81% of the sulfosuccinate initially present in the sample collected at $V_{ext}/V_{inj} = 0.4$ remained in the aqueous phase after the addition of TCE (Table 2); 19% of the sulfosuccinate has partitioned into the liquid TCE added to the sample. Despite the loss of sulfosuccinate to the TCE phase, the measured TCE solubilization potential for this sample was larger than predicted from the solubilization isotherm because the cation ratio was > 0.04 and < 0.48.

The measured TCE solubilization potentials for extraction phase samples were smaller than those predicted from the batch solubilization isotherm for $V_{ext}/V_{inj} > 0.6$ (Table 2). For example, the measured TCE solubilization potential for a sample collected at $V_{ext}/V_{inj} = 0.8$ was only 1647 mg/l compared to the value of 5085 mg/l predicted for this sulfosuccinate concentration from the solubilization isotherm (Eq. 2). Moreover, only 43% of the sulfosuccinate initially present in this sample remained in the aqueous phase after the addition of TCE. The low solubilization potential combined with the loss of 57% of the surfactant in the liquid TCE added to the sample with a cation ration > 0.48 is consistent with non-Winsor Type I behavior. Although no TCE was present in the sediment pack during Test 1, these results predict that cation exchange would have resulted in the loss of injected sulfosuccinate if residual TCE had been present and this prediction was confirmed by the results of Test 2.

5. Laboratory push–pull Test 2 (sediment pack with TCE)

5.1. Surfactant transport

Conservative transport of injected sulfosuccinate was observed during the injection phase at port 1. However, sulfosuccinate transport at ports 2 and 3 was strongly retarded relative to the Br^- tracer (Fig. 3b). Relative concentrations for sulfosuccinate were much smaller than those for Br^- during the injection phase and reached maximum values less than 0.4. Retardation of the injected sulfosuccinate was also apparent in extraction phase breakthrough curves (Fig. 4b). Relative concentrations for sulfosuccinate were smaller than those for Br^- in the region $0.3 < V_{ext}/V_{inj} < 1.3$ and slightly higher than those for Br^- in the breakthrough curve for $V_{ext}/V_{inj} > 1.3$ (Fig. 4b). In addition, mass balance calculations indicated a smaller recovery of injected sulfosuccinate (73%) than of Br^- (81%) at the end of the extraction phase.

5.2. TCE solubilization and surfactant phase behavior

During Test 2 aqueous TCE concentrations in samples collected from port 1 were very small and reached a maximum value of 84 mg/l at the end of the injection phase (Table 1), which is consistent with the composition of pore water passing through the TCE-free portion of the sediment pack between the injection/extraction ports and port 1. The TCE solubilization potential for the sample from port 1 collected at the end of the injection phase (41,309 mg/l), which had an initial sulfosuccinate concentration of 36,800 mg/l, was greater than the value predicted from the batch solubilization

isotherm (26,700 mg/l) and this is attributed to the increase in concentrations of $Ca^{2+} + Mg^{2+}$ resulting from cation exchange (Table 1). For this sample, the cation ratio was 0.47, which was close to the critical value of 0.48 identified in batch solubilization experiments that corresponded to a phase change.

Interestingly, samples from port 2 collected from $3 < t < 9$ h were initially milky in appearance and partially separated into an aqueous phase and a denser nonaqueous phase after settling, which indicates that these samples initially contained an unstable macroemulsion of aqueous and TCE phases. The maximum aqueous TCE concentration in port 2, which is within the portion of the sediment pack that contained residual TCE, was 13,578 mg/l (Table 1). This value is substantially larger than predicted from the solubilization isotherm (4365 mg/l) despite the high cation ratio (1.97) for this sample, which is much larger than the critical value of 0.48 that produced non-Winsor Type I behavior in batch solubilization experiments. We hypothesize that measured aqueous TCE concentrations in port 2 may have included the contribution of liquid TCE entrained into water samples collected from the sediment pack, and are thus a sampling artifact.

The aqueous TCE concentration in the sample collected from port 3 at the end of the injection phase was also higher than predicted from the solubilization isotherm (Table 1). Samples from port 3 were milky in appearance, indicating non-ideal phase behavior. Note that the cation ratio of 9.27 was much larger than the critical value of 0.48 that produced non-Winsor Type I phase behavior in batch solubilization experiments. Note also that monovalent and divalent cation concentrations and values of the cation ratio at the end of the injection phase for all ports were similar for Tests 2 and 1, indicating that the presence of residual TCE apparently did not significantly reduce the availability of exchangeable divalent cations in the sediment pack.

Extraction phase samples were clear in appearance and did not separate into multiple phases after settling. However, the total TCE recovery for Test 2 was 19.0 g or 2.1% of

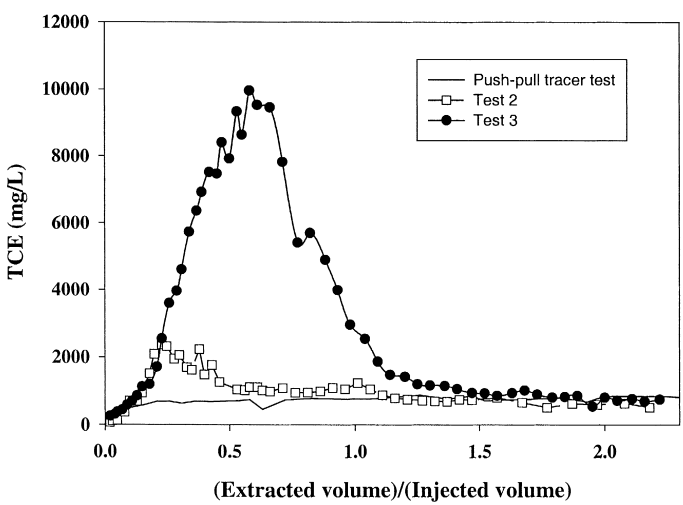

Fig. 5. Measured TCE concentrations during the extraction phase of push–pull tracer test and Tests 2 and 3.

the initial TCE mass emplaced, which was comparable to that of the push-–pull tracer test conducted without surfactant (Fig. 5). The TCE concentrations in extraction phase samples were substantially smaller than either the measured or predicted TCE solubilization potentials (Table 2). For example, the TCE concentration in a sample collected at $V_{ext}/V_{inj} = 0.4$ was only 1485 mg/l, compared to the predicted TCE solubilization potential (7513 mg/l) and much smaller than the measured TCE solubilization potential (14,096 mg/l). From these data we conclude that the extraction phase samples had the ability to solubilize TCE since the cation ratios were significantly less than 0.48. Cation ratios would have been higher (similar to Test 1), had divalent cations not partitioned into the residual TCE phase along with the sulfosuccinate. In Test 2, a total of 60.8 meq Ca^{2+} and Mg^{2+} was recovered, which is 0.6% of the total exchangeable Ca^{2+} and Mg^{2+} in the portion of the sediment pack ($\sim$ 24.4 kg) interrogated by the injected test solution. The reduction in mass of divalent cations between Test 1 (221.6 meq) when no TCE was present and Test 2 (60.8 meq) when TCE was present is consistent with partitioning (e.g., loss) of divalent cations into the TCE-DNAPL phase. Therefore, we hypothesize that the lack of significant TCE solubilization enhancement in Test 2 is due to (1) a loss of 8% of injected surfactant to the residual TCE phase and (2) retarded sulfosuccinate transport that reduced the degree of contact between the injected test solution and residual TCE.

6. Laboratory push–pull Test 3 (sediment pack with TCE and NaCL pre-flush)

6.1. Surfactant transport

Injection phase breakthrough curves for Br^- in Test 3 were similar to those for Tests 1 and 2 indicating that the hydraulic properties of the sediment packs in all tests were similar (Fig. 3c). However, in Test 3 sulfosuccinate breakthrough curves arrived at ports 1–3 prior to the arrival of the Br^- tracer (Fig. 3c). We attribute this behavior to mobilization of residual TCE by the injected surfactant as described in the next section. In contrast to the injection phase, extraction-phase breakthrough curves for sulfosuccinate and Br^- were nearly identical (Fig. 4c). Mass balance calculations indicated a slightly larger recovery of injected sulfosuccinate (91%) than Br^- (86%) at the end of the extraction phase.

6.2. TCE solubilization and surfactant phase behavior

Aqueous TCE concentrations in samples collected from port 1 were small (Fig. 3c), which is consistent with the composition of pore water passing through the TCE-free portion of the sediment pack between the injection/extraction ports and port 1. However, aqueous TCE concentrations in ports 2 and 3 increased rapidly and reached maximum values between 40,000 and 50,000 mg/l (Fig. 3c). The maximum TCE concentrations corresponded with low sulfosuccinate concentrations. For example, at port 2 the maximum TCE concentration of 42,399 mg/l coincided with a sulfosuccinate concentration of only 7740 mg/l, which should only have yielded a TCE concentration of 2470 mg/l. In addition, solute concentrations increased in ports 2 and 3 in the

order: TCE, sulfosuccinate, and Br^- and we attribute this behavior to the formation of an "oil bank" and Type III surfactant phase behavior.

The formation of "oil banks" has been reported in the enhanced oil recovery literature (Lake, 1989; Pope and Baviere, 1991). In an "oil bank", an injected surfactant sufficiently reduces water–NAPL interfacial tensions such that residual NAPL is mobilized, resulting in the simultaneous transport of multiple fluid phases within the pore space. The potential for residual TCE mobilization in Test 3 is supported by calculated total trapping numbers. The total trapping number is defined as the ratio of the combined viscous and buoyancy forces, which cause NAPL movement, to the capillary forces that retain NAPL in the pore space (Pennell et al., 1996). Computed total trapping numbers for our system are $> 10^{-5}$ between the injection/extraction ports and port 3, which is within the range required to mobilize TCE (Pennell et al., 1996). Oil bank formation creates higher TCE saturations than the initial residual saturation and accounts for the breakthrough of TCE prior to that of sulfosuccinate and Br^- (Fig. 3c). The occurrence of Type III surfactant phase behavior in Test 3 is indicated by the breakthrough of sulfosuccinate prior to Br^- for ports 1–3 (Fig. 3c). In a Type III system, the preferential partitioning of surfactant from the aqueous phase into the separate, middle-phase microemulsion resulted in an apparent increase in surfactant concentration relative to Br^- (Dwarakanath, 1997). Additional evidence for Type III behavior was the visual observation of multiple fluid phases in samples collected from ports 1–3 during this test.

Monovalent cations achieved higher concentrations in port 1–3 during the injection phases of Test 3 than in Tests 1 and 2 with a correspondingly smaller increase in divalent cations (Table 1). Cation concentrations remained nearly constant during extraction phase of Test 3 (Table 2) and were similar to the cation composition of the NaCl pre-flush solution, which was 132 ± 7.1 meq/l for $Na^+ + K^+$and 0 meq/l for $Ca^{2+} + Mg^{2+}$. For Test 3, the cation ratios were 0 and indicated that the quantities of exchangeable Ca^{2+} and Mg^{2+} in the sediment pack had been significantly reduced by the NaCl pre-flush. As a consequence, 100% of the sulfosuccinate initially present in water samples from ports 1–3 and in extraction phase samples remained in the aqueous phase after liquid TCE addition and TCE solubilization potentials were similar to those predicted from the batch solubilization isotherm (Tables 1 and 2).

Aqueous TCE concentrations during the extraction phase were substantially larger than observed during Test 2 (Fig. 5) and this is attributed to the absence of divalent cations (cation ratio = 0) in these samples (Table 2). The total mass of TCE recovered during Test 3 was 56.7 g or 6% of the total mass of TCE emplaced. It is likely that TCE mass recovery would have been larger had residual TCE not been mobilized; sediment samples obtained by excavating the sediment pack at the end of the test indicated that liquid TCE had been displaced beyond port 5, where it would not be recovered during the extraction phase. Interestingly, sediment analyses indicated that liquid TCE was not displaced downward into the sediment pack but remained approximately at the initial emplacement depth. TCE concentrations also would have been increased if residual TCE had been emplaced uniformly throughout the entire depth of the sediment pack (instead of within the center of the pack) so that a higher degree of contact between injected surfactant and residual TCE could have occurred.

7. Conclusions

The results of Test 1 indicate that, in the absence of residual TCE, the optimized surfactant test solution was transported conservatively in LLNL sediment. However, the cation composition of the injected test solution changed during transport due to cation exchange. For samples that had values of the cation ratio: $(Ca^{2+} + Mg^{2+})/(Na^{+} + K^{+}) < 0.48$, TCE solubilization potentials, measured by adding excess TCE to the sample, were larger than predicted from the batch solubilization isotherm. However, for samples with cation ratio > 0.48, TCE solubilization potentials decreased below values predicted from the solubilization isotherm due to the partitioning of sulfosuccinate into the TCE–DNAPL phase. For this reason, batch solubilization isotherms constructed using only Na^{+} or K^{+} may not be appropriate for predicting TCE solubilization potentials or surfactant phase behavior when surfactants are injected into sediments with significant quantities of exchangeable cations (especially Ca^{2+} and Mg^{2+}).

The results of Test 2 confirmed the effects of cation exchange on surfactant transport, phase behavior, and TCE solubilization in the presence of residual TCE. Increasing concentrations of Ca^{2+} and Mg^{2+} resulted in the partitioning of sulfosuccinate into the residual TCE DNAPL phase and smaller aqueous TCE concentrations than predicted from the solubilization isotherm. Our results demonstrate the utility of the push–pull test for predicting such deleterious effects. The results of Test 3 indicated that quantities of exchangeable Ca^{2+} and Mg^{2+} could be substantially reduced by a 130 meq/l NaCl pre-flush, restoring conservative sulfosuccinate transport, Winsor Type I phase behavior, and increased aqueous TCE concentrations. However, reduced interfacial tensions resulted in mobilization of residual TCE and the formation of an “oil bank”, which may be undesirable under field conditions.

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